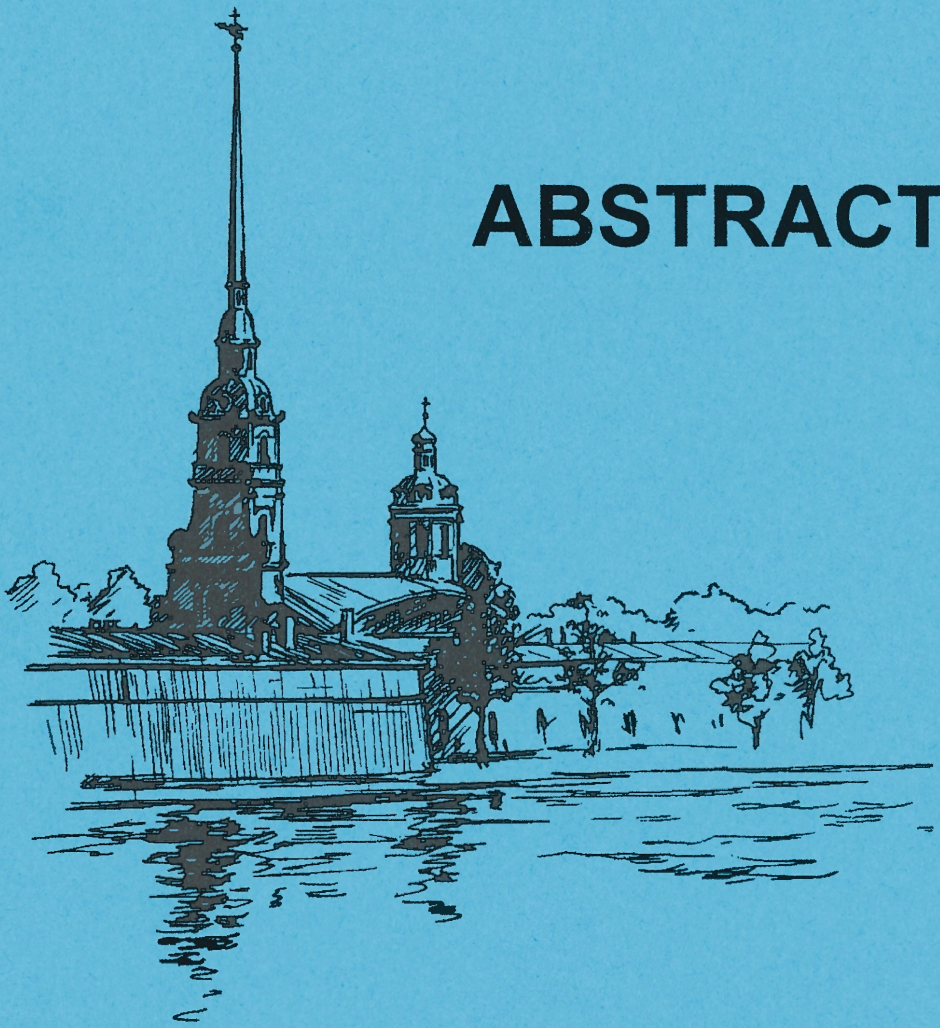
USPC-3

THIRD INTERNATIONAL CONFERENCE ON UNSTEADY-STATE PROCESSES IN CATALYSIS

30 June - 3 July, 1998 St. Petersburg, Russia



ABSTRACTS

Matros Technologies, St. Louis, USA
Boreskov Institute of Catalysis, Novosibirsk, Russia
Monsanto Enviro-Chem System, St. Louis, USA
DuPont, Wilmington, USA

THE THIRD INTERNATIONAL CONFERENCE ON UNSTEADY-STATE PROCESSES IN CATALYSIS

30 June - 3 July, 1998 St. Petersburg, Russia

ABSTRACTS

Novosibirsk, Russia, 1998

ORGANIZING COMMITTEE

Chairman	Yu. Sh. Matros	*Matros Technologies, St. Louis, USA*
Co-Chairman	A. S. Noskov	*Boreskov Institute of Catalysis, Novosibirsk, Russia*
Advisory Board	B. S. Balzhinimaev	*Boreskov Institute of Catalysis, Novosibirsk, Russia*
	A. G. Bazanov	*RSC "Applied Chemistry", St. Petersburg, Russia*
	G. A. Bunimovich	*Matros Technologies, St. Louis, USA*
	A. T. Bell	*University of California, Berkeley, USA*
	B. Delmon	*Catholic University, Louvain-la-Neuve, Belgium*
	G. F. Froment	*Gent University, Belgium*
	J. E. Kilkenny	*Monsanto Enviro-Chem. Systems, St. Louis, USA*
	J. J. Lerou	*DuPont, Orange, TX, USA*
	V. V. Lunin	*Moscow State University, Russia*
	D. Luss	*University of Houston, USA*
	P. L. Silveston	*University of Waterloo, Canada*
	K. R. Westerterp	*University of Twente, The Netherlands*
	V. A. Chumachenko	*Katalizator Company, Novosibirsk, Russia*
Executive Organizing Committee	A. G. Corey	*Monsanto Enviro-Chem. Systems, St. Louis, USA*
	S. P. Kildyashev	*Boreskov Institute of Catalysis, Novosibirsk, Russia*
	A. N. Zagoruiko	*Boreskov Institute of Catalysis, Novosibirsk, Russia*
	N.G. Zubritskaya	*RSC "Applied Chemistry", St. Petersburg, Russia*
Secretary	V. O. Strots	*Matros Technologies, St. Louis, USA*
Secretary	T. Zamulina	*Boreskov Institute of Catalysis, Novosibirsk, Russia*

Sponsors Monsanto Enviro-Chem Systems, ABB Lummus Global,
Dow Chemical, Matros Technologies, Monsanto

Co-sponsored by American Institute of Chemical Engineering
Canadian Society for Chemical Engineering
The Society of Chemical Engineers, Japan

The Organizers express their gratitude to **sponsors of the conference** for their generosity

PLENARY LECTURES

DYNAMIC APPROACHES TO HETEROGENEOUS CATALYSIS

B.S. Bal'zhinimaev

Boreskov Institute of Catalysis, 630090, Novosibirsk, Russia

Tel: (3832) 35 57 70, Fax: (3832) 35 57 66, e-mail: iccct@catalysis.nsk.su

The lecture concerns the use of dynamic approach for solving a key problem of heterogeneous catalysis related to interrelationship between the chemical (reaction mechanism) and physical (catalyst state) components of catalytic system consisting of reaction medium and catalyst. The approach lies in studying the spectrum of relaxation times for various physical-chemical processes including the «true catalysis» step «excited» by a stepwise disturbing of the catalytic system from the steady state. In order to reveal the «chemical» component from the transient response spectrum we use isotope-dynamic method (SSITKA), when at the constant composition of gas phase and adsorbed layer we study the dynamics of isotope label transfer from reactants to reaction products through sequence of surface transformation. In this case side physical-chemical processes, determining the catalyst state, are not «excited». Thus regarding the character of isotope responses, caused mainly by the surface reaction peculiarities, we may understand reaction mechanism. Specially designed software allows us not only to reveal the most likely reaction mechanism, but also to estimate the concentration of intermediate species and reaction rate constants. Combining SSITKA with transient response technique and spectroscopy methods, we may draw definite conclusions about the origin of side (with regard to catalysis) processes and about their influence on reaction rate.

The lecture exemplifies various cases of the approach use. In particular, SO_2 oxidation on vanadium catalysts, ethylene epoxidation on silver catalysts, selective NO_x reduction by methane on zeolite, etc.

PL-2

INDUSTRIAL APPLICATIONS OF UNSTEADY-STATE PROCESSES IN HETEROGENEOUS CATALYTIC REACTORS

G.A.Bunimovich, V.O.Strots, Yu.Sh.Matros

Matros Technologies, Inc., St. Louis, MO, USA

The objective of this lecture is to discuss theoretical and practical results related to forced unsteady-state operation (FUSO) in heterogeneous catalytic reactors. The attention will be focused on potential and actualized commercialized applications of FUSO.

In its first part, the lecture will discuss recent progress in the development of mechanistic kinetic models applicable for the design of reactors operated at unsteady-state conditions. Then we will review theoretical and experimental studies of methods used to organize forced unsteady-state operations. These methods include inlet composition and temperature cycling, catalyst circulation in fluidized beds, simulation of catalyst movement and periodic flow reversal in fixed bed.

A number of important potential applications of forced unsteady-state operation will be discussed. One well known example is the reactor with circulating fluidized bed for partial oxidation processes based on the concept of redox mechanism. These reactors have long been studied, but no commercial units have been built to date. Another, more recent example is small scale reactors for automotive exhaust purification installed after the engines with air-to-fuel ratio modulating.

Reverse flow reactor, probably, is the only one known example of FUSO that has enjoyed substantial commercial success. Discussion of recent advances in the design of commercial flow reversal reactors for VOC control, SO_2 oxidation and NOx reduction as well as new application for automotive exhaust treatment will be presented in the third part of the lecture.

PL-3

Periodic Flow Reversal in Chemical (Reaction) Engineering

Gerhart Eigenberger

Universität Stuttgart, Germany

Tel.: (0711) 641-2230
Fax: (0711) 641-2242
email eigenberger@icvt.uni-stuttgart.de

Periodic flow reversal is an efficient method to store heat or adsorb mass reversibly in a fixed bed. Starting with the well known examples of periodic flow reversal of catalytic fixed-bed reactors with weakly exothermic reactions, the concept is extended to the coupling of exo- and endothermic reactions. Concepts with mixed feed, or with an unsymmetric or symmetric operation mode will be discussed. For the example of styrene synthesis via ethyl benzene dehydrogenation experimental and simulation results are presented which show the superiority of the symmetric operation mode.

Similar to the regenerative storage and recovery of heat, treated above, mass can be stored regeneratively in fixed-beds via adsorption. Different applications including temperature- and pressure swing adsorption will be briefly reviewed and discussed with respect to reaction engineering applications.

The last example considers the somewhat overlooked concept of thermal compression where an oscillating fixed-bed regenerator in combination with an exothermic gas phase reaction is used to compress a gas flow with high thermal efficiency.

All the examples discussed require efficient numerical methods for their dynamic simulation and for the analysis of their periodic steady state. Therefore brief reference will be given to recent advances in this field.

ORAL PRESENTATIONS

Section 1.

Dynamic Processes on Catalyst Surface

OP-1-1

THE DYNAMICS OF SURFACE PROCESSES UNDER NON-STEADY STATE CONDITIONS

Alexis T. Bell

Department of Chemical Engineering
University of California
Berkeley, CA 94720-1462, USA

The behavior of catalytic reactors during non-steady state operation is intrinsically connected to the dynamics of chemical processes occurring on the surface of the catalyst. Many factors have been found to influence the rate coefficients for these processes. These include the effects of surface heterogeneity, the effects of surface coverage on the activation barrier and preexponential factors, and the effects of surface reconstruction. For bifunctional catalysts, changes in reaction conditions can influence the distribution between catalyst functionalities. This talk will illustrate each of these effects, discuss their relative importance, and examine the extent to which they must be taken into account for purposes of developing chemical reaction engineering models of reactors operating under non-steady-state conditions.

OP-1-2

Monte-Carlo Methods for Simulating Catalytic Reactions on Oxides. Example of the Oxidative Dehydrogenation of Propane over VMgO Catalysts

Yves BOUDEVILLE [a,b,*], Max KOLB [a,b], Amalia PANTAZIDIS [a,d],
Claude MIRODATOS [a], Vladimir ELOKHIN [c].

a) Institut de Recherches sur la Catalyse, CNRS
2, Avenue Albert EINSTEIN, F-69626 VILLEURBANNE Cédex France.

b) Ecole Normale Supérieure, ENS/Lyon. Laboratoire de Chimie Théorique
46, Allée d'Italie ; F69364 LYON Cédex 07 France

c) Boreskov Institute of Catalysis,
Pr. Ak. Lavrentyeva, 5 ; 630090 NOVOSIBIRSK Russia

Monte-Carlo methods are involved in the description of non-linear dynamic effects in catalytic heterogeneous or homo-heterogeneous reactions. The simplest modelling uses the Ziff, Gulari Barshad Monte-Carlo method with one reaction A(surf) + B(surf) $\xrightarrow{Pt[100]}$ AB(gas) [Ziff et al., 1986]. The Ziff scheme is a pure mathematical one (everything that can happen happens, it is a « boolean law »; if two things can happen, each as half for probability etc.) but the main features of surface adsorption of reactants, desorption of products, reaction are treated with a surprisingly good success, since the mathematical topology of the chemical process is taken into account. This permits the investigation of two kinetic phase transitions by using the partial pressures ratio of reagents as a macroscopic variable on the microscopic atomic surface. Other more sophisticated models [Boudeville et al., 1993] include Arrhenius laws and chemical engineering constants to describe diffusion- or reaction-controlled regimes in the catalytic reactor. At this level of modelling, temperature dependant non-linear effects can be investigated. The last level of complexity can be described in terms of the chemical graph of reactions : not only one catalytic reaction, but several ones; not only reactions on the catalyst but also reactions in the gas phase.

The "realism" of the reactor description was improved by using a catalytic reaction compiler linked to a Monte-Carlo program that simulates the whole hetero-homogeneous catalytic reactor. This approach was tested for the case of the oxidative coupling of methane [Boudeville, unpublished]. This model demonstrated the necessity of layered catalyst to increase the selectivity in ethane for more than 20 %. This model uses a sub-set of 17 reaction/diffusion equations with a catalysis data bank of 19 species.

Two types of catalytic mechanisms were investigated: the Langmuir-Hinshelwood and Eley-Rideal for CO oxidation or CH_4 oxidative coupling reactions, respectively.

The present paper reports our present efforts to model the Mars-van Krevelen mechanism which applies for most oxidation reactions. It requires to take into account the oxygen motion in the bulk oxide lattice by a kind of solid-on-solid model used by Resnyanskii et al. [Resnyanskii et al., 1996, 1997] for surface corrugation under catalytic conditions. The oxidative dehydrogenation of propane over VMgO catalysts was chosen as a model reaction, since numerous and detailed mechanistic and kinetic data are available [Kung et al., 1997 ; Pantazidis et al., 1996]. In this respect, a Monte-Carlo model was constructed to describe the process of propane dehydrogenation over a V containing overlayer supported on MgO platelets. This describes correctly the actual VMgO catalyst [Pantazidis et al., 1996].

A first approach of the bare surface mechanism, without oxygen lattice motion, was carried out with a system of 11 elementary steps occurring on the catalyst surface only, which implied the knowledge of 11 kinetic constants. The Monte-Carlo simulation was made on a 225 x 225 grid of atoms representing the bare surface, adsorbed species and catalytic reaction products.

$C_3H_8 + [O_\#] \xrightarrow{k_1} C_3H_6 + H_2O + [\#]$ (# means chemical species linked to surface)
$O_2 + 2\,[\#] \xrightarrow{k_2} 2\,[O_\#]$ ([#] means empty surface site for Monte-Carlo)
$O_2 + 2\,[\#] \xrightarrow{k_3} 2\,[O^{\circ}_\#]$ ($[O^{\circ}_\#]$ peroxidised oxygen surface forms)
$C_3H_8 + [O^{\circ}_\#] + 6\,(O_\#|O^{\circ}_\#) \xrightarrow{k_4} 3\,CO + 4\,H_2O + 7\,[\#]$ $(O_\#|O^{\circ}_\#)$ means any oxygen form.
$C_3H_8 + [O^{\circ}_\#] + 9\,(O_\#|O^{\circ}_\#) \xrightarrow{k_5} 3\,CO_2 + 4\,H_2O + 10\,[\#]$ (degradation reactions).
$[O_\#]_{i,j} + [\#]_{k,l\sim i,j} \xrightarrow{m_6} [\#]_{i,j} + [O_\#]_{k,l}$ (k,l~i,j means site{k,l} neighbour of site{i,j})
$[O^{\circ}_\#]_{i,j} + [\#]_{k,l} \xrightarrow{m_7} [\#]_{i,j} + [O^{\circ}_\#]_{k,l}$ (oxygen species surface migrations).

A subset of considered reaction/diffusion surface processes (where the k_i's are known for the related reactions and the 2 mobility constants m_6 and m_7 are assumed of the same magnitude as k_1 and k_4, respectively). For the whole 11 elementary steps, all k_i are equated to unity.

This procedure was based on two main assumptions:

i) the selectivity arises from the dynamic competition between the selective route leading to propene and the non selective one leading to CO and CO_2,

ii) an island of a selected number of surface atoms is necessary to accommodate the catalytic reaction. This is deduced from mechanistic studies suggesting that at least two VO_4^{3+} tetrahedral units are required for dehydrogenating the propane molecule [Pantazidis et al., 1996].

This level of modelling allows us to incorporate these experimental requirements in the Monte-Carlo dynamic model. This is a use of the real time pattern recognition model to see if the colliding molecule can undergo reaction with adsorbed species on the catalytic site. It is mainly used for the route of product degradation in the catalytic process (here, reactions k_4 and k_5).

Further data still in progress may be provided with a more advanced model which, if we obtain all the kinetic parameters, can discriminate between the possible adsorption sites for alkanes.

References

Boudeville Y., Wolf E.E., Surface Sci. 297 (1993) L127.
Kung H.H., Kung M.C., Appl. Catal. A **157** (1997) 105.
Pantazidis A., Mirodatos C., *Heterogeneous Hydrocarbon Oxidation*, Warren B. and Oyama S.T. (Ed.), ACS Symposium Series **638** (1996) 207.
Pantazidis A., and Mirodatos C., 11th International Congress on Catalysis, J.W. Hightower, W.N. Delglass, E. Iglesia, and A.T. Bell (Eds.), Studies in Surface Science and Catalysis, **101** (1996) 1029.
Resnyanskii E.D., Latkin E.I., Myshlyavtsev A.V., Elokhin, V.I. Chem. Phys. Lett., 248 (1996) 136.
Resnyanskii E.D., Myshlyavtsev A.V., Elokhin, V.I., Bal'zhinimaev B.S., Chem. Phys. Lett., 264 (1997) 174.
Ziff R.M., Gulari E., Barshad Y., Phys. Rev. Lett., 56 (1986) 2553.

OP-1-3

Dynamic Behaviour of Mixed V-Sb Oxide Catalysts in Oxidative Dehydrogenation of Ethane

V.Yu. Bychkov, Z.T. Fattakhova, M.Yu. Sinev, Yu.P. Tulenin, V.P. Vislovskii*

Semenov Institute of Chemical Physics, Russian Academy of Sciences
4 Kosygin str., Moscow 117334, Russia
Phone: (+7 095) 939 7547; fax: (+7 095) 938 2156; E-mail: sinev@center.chph.ras.ru

*Institute of Inorganic and Physical Chemistry, Azerbaijan Academy of Sciences
29 Husein Javid Avenue 370143, Baku, Azerbaijan
Phone: (+994 12) 931 153; fax: (+994 12) 931 153; E-mail: akhmedly@iname.com

Oxidative dehydrogenation (ODH) of light paraffins attracts the attention as a potential alternative process for olefins production. Mixed V-Sb oxide based systems enable to produce olefins from paraffins with high efficiency both in continuos catalytic and cyclic redox regimes. In the present work, studying an ethane ODH as a model reaction, we have focused on the following aspects of its mechanism:

- dynamics of the formation of active species during the preparation of mixed oxides and in the course of ODH reaction;
- participation of lattice oxygen in ODH reaction;
- factors determining the differences between oxides behaviour in continuos and cyclic redox regimes of operation.

Three different groups of V-Sb oxide systems were studied: (a) bulk mixed oxides; (b) oxides of the same composition deposited on different oxide supports (Al_2O_3, SiO_2); (c) mechanical mixtures of bulk oxides with oxide supports. Oxides of the group (b) supported on alumina are the most efficient in the continuos catalytic regime. Group (a) systems of the same composition have low activity and very poor olefin selectivity. In the group (b) systems we observed an increase of activity and selectivity in the course of catalytic reaction. This effect is much more pronounced in the case of alumina-based systems due to the spreading of an active component over the support surface [1]. In silica-based systems this spreading is less probable due to a low chemical affinity.

"Activity vs. selectivity" correlation for the systems which belong to different groups, but have the same chemical composition is substantially different in the case of cyclic redox mode. Group (b) systems have much higher activity due to a highly developed surface of active component, but their selectivity with respect to ethylene formation is relatively low (see Fig. 1). Group (c) sample aged in the reaction mixture has

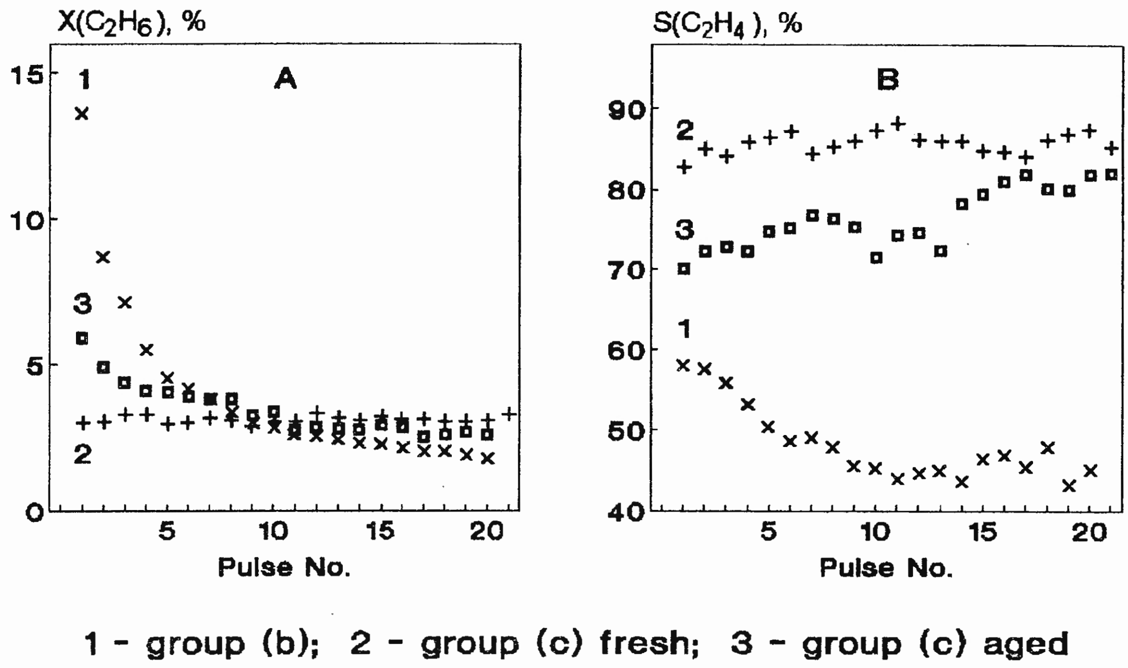


Fig. 1. Ethane conversion (A) and ethylene selectivity (B) as functions of pulse number over 30% $V_{0.44}Sb_{0.56}/Al_2O_3$ samples (550 °C, gas mixture - 10% C_2H_6/He).

an intermediate activity and selectivity. I.e. in the redox mode of operation, the higher the activity, the lower the selectivity. These differences in the regularities of ODH reaction in catalytic and cyclic redox regimes are analyzed in the terms of heterogeneous-homogeneous mechanism of the process under study.

The comparison of the samples having different active phase compositions, as well as the analysis of the heat of reduction indicate that ethane ODH proceeds mostly at a sacrifice of oxygen bound with vanadium atoms. The highest degree of reduction we have reached corresponded to $V^{5+} \rightarrow V^{3+}$ transformation.

A high degree of lattice oxygen utilization along with a high ethylene selectivity in cyclic redox regime make this mode of operation preferable in comparison with traditional catalytic ODH of ethane.

Reference.

1. Y. Cai, C.-B. Wang, and I. E. Wachs. Studies Surf. Sci. Catal., v.110, Eds. R. K. Grasselli, S. T. Oyama, A. M. Gaffney, and J. E. Lyons, Proc. 3rd World Congress on Oxidation Catalysis, San-Diego, CA, U.S.A., 21-26 Sept. 1997, Elsevier, 1997, p. 255.

Modeling reduction of oxide catalysts with CO

R. Doepper, H. Randall, F. Kollmer, A. Renken*

Institute of Chemical Engineering, EPFL, CH-1015 Lausanne, Switzerland

phone: +41-21-693 31 81; fax: +41-21-693 31 90; email: albert.renken@epfl.ch

The oxidation of CO has been investigated on Fe oxide and a Cu/Co oxide spinel supported on SiO_2, in the mainframe of the NO reduction by CO on oxide catalysts. Both catalyst show a redox behavior, i.e. they are oxidized by NO (and/or N_2O) and reduced by CO.

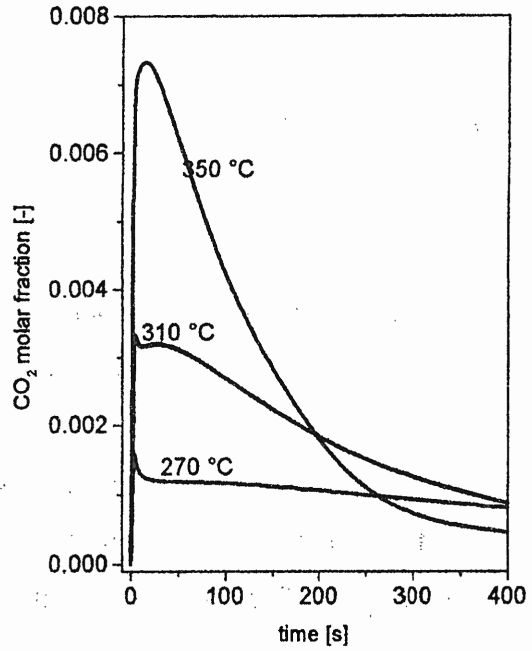


Fig 1a: Response to a CO concentration step on an oxidized iron oxide catalyst. Conditions: CO molar fraction 0.017, flow rate 100 ml(NTP)/min.

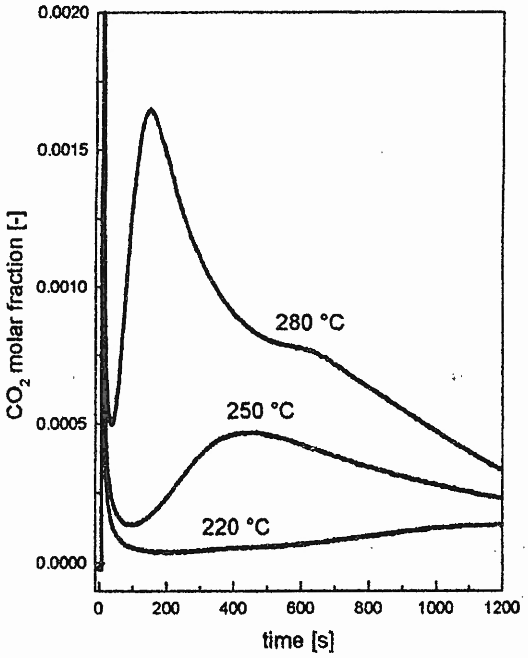


Fig 1b: Response to a CO concentration step on an oxidized Cu/Co oxide catalyst. Conditions: CO molar fraction 0.01, flow rate 200 ml(NTP)/min.

Figure 1 gives the responses of CO_2 to a CO concentration step over oxidized catalysts at different temperatures. At the lower temperatures, the response of CO_2 shows an instantaneous maximum, followed by a second broader maximum. With increasing temperature, the second maximum shifts to shorter times, and the ratio between the second and the first maximum increases. The rate of reduction of the catalyst, i.e. the molar fraction of CO_2 formed, increases drastically with temperature. After a few hundred seconds, the reaction rate falls to very low values, but CO_2 is still observed for over an hour.

The appearance of two maxima in the CO_2 responses indicates that CO oxidation takes place in two stages. The first step can be described by an Eley-Rideal reaction between gas phase CO and surface oxygen, since the first maximum is instantaneous. The appearance of the second maximum can be explained by the reaction of CO at another type of surface sites, which are not present in sufficient amount at the beginning of the experiment, and which are produced during the first Eley-Rideal step. Furthermore, the carbon-balance defect encountered during the transients implies that the second reduction process of the catalyst must include a CO adsorption step. Finally, the tailing of the CO and CO_2 responses is due to the limitation of the reduction of the catalyst by subsurface oxygen diffusion.

On the basis of the qualitative analysis of the transient responses of oxidized catalysts to concentration steps of CO, the following three-step mechanism is proposed for CO oxidation (Fig 2).

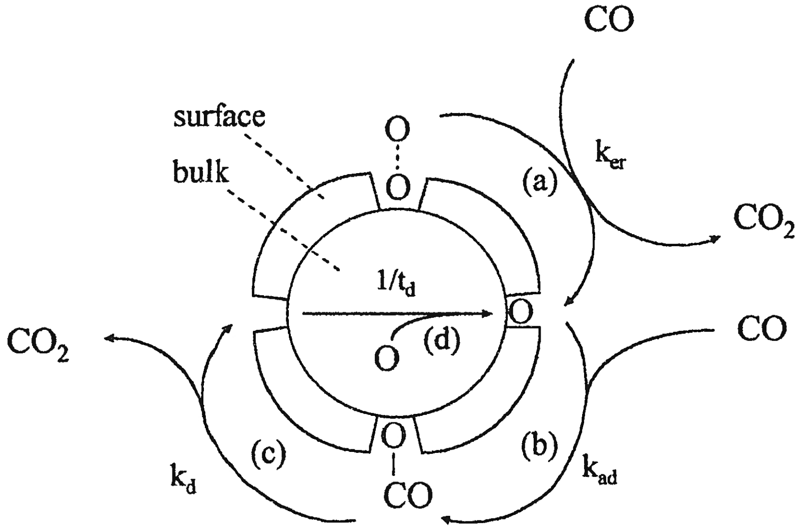


Fig 2: Schematic representation of the reduction of an oxide crystallite by CO. (a) Eley-Rideal reaction, (b) CO adsorption, (c) CO reactive desorption, (d) subsurface oxygen diffusion. t_d: characteristic diffusion time.

This mechanism can potentially be extrapolated to other oxide catalysts and similar reactions. It implies a very reactive oxygen species on the surface which is not present at steady-state It can therefore be taken advantage of this species by periodically reoxidizing the catalyst, in order to maintain the activity in a higher state. An increase of the performance has been shown possible theoretically, based on this mechanism, and has been measured in the order of 30 % for the reduction of N_2O by CO on an iron oxide catalyst.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the funding from the Swiss National Science Foundation

OP-1-5

OXIDATIVE DEHYDROGENATION OF PROPANE ON V_2O_5/TiO_2 CATALYSTS UNDER TRANSIENT CONDITIONS

F. GENSER and S. PIETRZYK

Laboratoire de Génie Chimique et d'Automatique, Ecole Nationale Supérieure de Chimie de Lille - Ecole Centrale de Lille, BP 48, Bd. Langevin, 59651 Villeneuve d'Ascq Cedex, France

The oxidative dehydrogenation of propane to propene has been studied under transient conditions on V_2O_5/TiO_2 catalysts, with or without added potassium, in the vicinity of 650 K. The purpose of this work is to study the behaviour of the catalysts in the conditions of a circulating bed reactor and to establish an adequate model of this behaviour based on a mechanism of the reaction.

To simulate the use of a circulating bed reactor, a fixed bed of catalyst was fed alternatively by mixtures of oxygen and inert, propane and inert, and inert alone (helium). The product gas was analysed on-line using a quadripole mass spectrometer, which makes possible very rapid analysis of the reaction mixture [fig.1]. The results for the V_2O_5/TiO_2 catalyst have been compared with those obtained previously on a $NiMoO_4$ catalyst [2, 3].

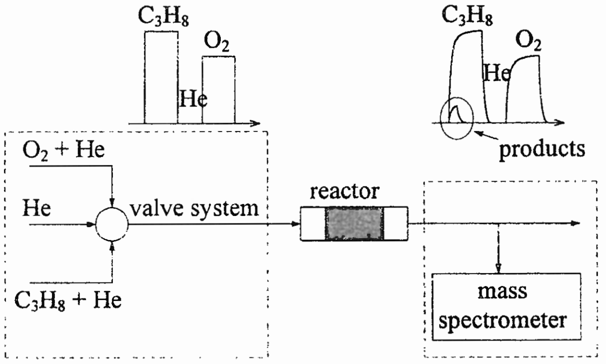


Fig. 1: principle of the experimental apparatus

The catalysts were those described in [1], prepared by impregnation of a commercial anatase support (48 m^2/g) with V compounds (5 monolayers) and K compounds (K/V=0.1).

Under steady-state conditions, the catalysts with added K have been found much less active but considerably more selective in propene formation than the catalysts without added K [1].

Under transient conditions, the products formed during the propane oxidation step (reaction step) are the same as under steady-state conditions: C_3H_6, CO, CO_2 and H_2O. The partial pressures of products were higher on the catalyst without K, and their evolution differed markedly from those obtained on K-doped catalyst. The differences of average selectivities were less pronounced that under steady-state conditions.

During the catalyst reoxidation (regeneration) step, the formed gases include carbon oxides and water, indicating the formation of a carbonaceous residue on the catalyst surface, containing hydrogen and carbon with a ratio H/C about 2. This behaviour is rather different from that observed with $NiMoO_4$ catalyst where only small amounts of carbon oxides and no water have been observed during the regeneration step. This can be attributed, at least partially, to much higher reaction temperatures in the case of molybdate [3].

Concerning the reaction steps, to express the difference in the evolutions of partial pressures of products with time, some plausible reaction mechanisms have been tried. The experimental curves (partial pressures vs. time) have been compared with the computed ones, the corresponding rate constants of reaction steps being computed using a Matlab program.

Good results have been obtained with a model inspired from [4], in which propane adsorbed on O sites gives propene while that adsorbed on V sites gives rise to total oxidation products. Within this model, the addition of K reduces the values of all step constants, the most important variation concerning the second hydrogen abstraction step.

Acknowledgements

The authors thank Professor Grzybowska-Swierkosz (institut of catalysis, Krakow, Poland) for catalyst samples and fruitful discussions.

References

[1] R. Grabowski, B. Grzybowska, K. Samson, J, Sloczynski, J. Stoch, K. Wcislo, Applied Catalysis 125, 129-144 (1995)

[2] C. Mazzochia, C. Aboumrad, C. Diagne, E. Tempesti, J. M. Hermann and G. Thomas, Catalysis Letters 10, 181-192 (1991)

[3] S. Pietrzyk, M. L. Ould Mohamed Mahmoud, T. Rembeczky, R. Bechara, M. Czernicki, N. Fatah, Stud. Surf. Sci. Cat., 109, 263-271 (1997)

[4] T. Oyama, A. N. Desikan, W. Zhang, in " Catalytic Selective Oxidation ", ed. T. Oyama and J. Hightower, American Chemical Society, 1993, p. 16-30

OP-1-6

UNSTEADY-STATE PROCESSES IN AEROSOL CATALYST

M. Glikin, D. Kutakova, E.Prin

State Design and Research Institute for Chemical Engineering, KHIMTEKHNOLOGIYA
Post address: Gzerzinsky st.1, Severodonetsk, 349940 UKRAINE
Fax 38 06452 25367, e-mail prin@himn.etalon.lugansk.ua

The task to produce and to maintain the optimal structure and state of a catalytic surface during a chemical processes is the main problem in catalysis as it gives a possibility to control the rate and selectivity of chemical reactions.

Solving this problem for supported catalysts is complicated because of chemical conversion rate decrease owing to the intradiffusion retardation, catalyst pores plugging by cocks, polymers, salts and blocking active catalytic surface by these materials. Process selectivity is decreased due to the same factor influencing the mechanism of chemical conversion. The existing methods of catalyst regeneration do not assure reduction of the original catalyst surface properties.

The investigations led to the new organization of gas-phase heterogeneous catalytic chemical processes based on the use of fine-milled active catalytic material. Aerosol of catalyst fill the reaction volume and quasi-structures of the catalyst are created. Catalyst particles are influenced permanently by temperature and mechanical impulses. The high particle dispersity and catalyst activity are maintained by these factors and due to catalytic system recycling in the reaction unit. Such a catalytic system may be an individual chemical compound, mechanic mixture or alloy of individual chemical compounds.

The expected effect after the use of the catalytic small-particle aerosol can be associated with activity increase of the fine-grained catalyst compared to the conventional systems.

Chemical conversions on the fine-like catalyst (without any carrier) have been performed for the reactions of reduction, vinylation, deep and partial catalytic oxidation of organic and inorganic compounds.

The laboratory tests show unexpectedly high Aerosol technology efficiency. Substantial increase of aerosol catalyst activity compared to the best samples of supported catalytic systems tested in fluidized and fixed bed modes is found.

The investigation of two best samples of supported catalyst ($Pt/\gamma\text{-}Al_2O_3$, 0.6% Pt, $CuCrO_4/\gamma\text{-}Al_2O_3$, 30% $CuCrO_4$) and aerosol catalyst based on iron (III) oxide was carried out.

The tests were performed on the laboratory unit in the reactor of flow type (D=50mm) under condition of acetic acid deep oxidation reaction. Meanwhile the conversion degree was up to 99.98-99.99% at the carbon monoxide content of 20 mg/m^3 and absence of partial oxidation products in the off-gasses.

The result comparison of acetic acid oxidation on the classical catalytic system and in the aerosol catalyst shows extremely high activity of iron oxide aerosol catalyst. It exceeds the activity of industrial samples by five orders. Meanwhile the operation concentration of iron oxide was about 3 g/m^3, while it reaches 4 kg/m^3 for the platinum catalyst and 200 kg/m^3 for copper-chromium catalyst.

The experimental data analysis allows to suppose that under the described method conditions particle dimensions amount to several nanometers. The up-to-date scientific vision point at the influence of mechanic activation on catalyst surface properties connected with appearance of free radicals, atoms with unsaturated valency and coordination, deformation of interatomic bonds and atom recombination. The change of energetic particle surface properties compared to macro-particles are connected with their reduction to nanometer size. The electronic structure surface change, which influenced intensity of adsorption, was registered in a whole series of publications. Probably, this is the main reason of such considerable activity increase of aerosol of iron oxide catalyst in oxidation reactions.

REFERENCES

1. G.K. Boreskov. Heterogeneous Catalysis, M. Nauka, P. 237-248, 1988.
2. Yu. G. Shirokov. J. Applications Chemistry / 1997. Vol. 70. № 6. P. 961-967.
3. Seung Bin Park, Yun Chan Kang.//J. Aerosol Sci. 1997. Vol. 28. P. 473

OP-1-7

ROLE OF ADSORPTION HEATS AND ENTROPIES OF ORGANIC COMPOUNDS ON EFFICIENCY OF ADSORPTION CATALYTIC METHOD OF GAS PURIFICATION

Z.R. Ismagilov, M.A. Kerzhentsev and S.A. Yashnik

Boreskov Institute of Catalysis, SB RAS, Novosibirsk, Russia

For the purification of low-concentrated flue gases of industrial enterprises from toxic organic compounds, many researchers suggest to apply an adsorption-catalytic process based on the simultaneous use of the adsorption and catalytic properties of oxide catalysts in the combination with a periodic reverse of the flow direction of the flue gas [1-4].

The process consists of two main stages:

- Low-temperature adsorption of organic compounds on the granules of the deep oxidation catalyst;
- High-temperature deep oxidation of the adsorbed molecules and regeneration of the catalyst by a periodic heating of the catalyst bed in a regime with the reverse of the gas flow direction.

Chemisorption of given organic substances on the catalyst surface with the formation of intermediate compounds and their subsequent oxidation with oxygen to yield deep oxidation products – carbon dioxide and water – is the most important problem.

Equilibrium adsorption-desorption processes between the gas flow and the catalyst surface also affect the process in general and should be taken into account during the optimization of the process. This is especially important for purification of gases which contain a mixture of different organic compounds.

We have attempted to evaluate experimentally adsorption heats and entropies of several hydrocarbons on typical deep oxidation catalysts by gas chromatography [5].

The measurements were performed in the temperature range of 150-300°C in a 60-90 cm^3/min helium flow. $Cu_2Cr_2O_4/\gamma\text{-}Al_2O_3$ and $MgCr_2O_4/\gamma\text{-}Al_2O_3$ catalysts in the form of spherical granules (d = 0.4-0.6 mm) with the active phase content 20% were used as adsorbents. Cyclohexane, n-hexane, benzene, toluene and p-xylene were used as the adsorbates.

The absolute values of the adsorption heats on the alumina-copper-chromium catalyst grow in the row cyclohexane – n-hexane – benzene. The transition from saturated hydrocarbons to the aromatic ones results in the increase of the adsorption heat by more that 10 kJ/mol, proving the participation of the aromatic ring in the formation of adsorbate-surface complexes. The growth of the absolute adsorption heat values in the row benzene – toluene – p-xylene is connected with the increase of the electron density in the π-system of the aromatic ring resulting from the introduction of electron-donor inductive substituents with the consequent increase in the strength of the adsorbate-surface complexes.

The adsorption heats on the alumina-magnesium-chromium catalyst grow in the same row as on the alumina-copper-chromium one, with the only exception of p-xylene.

Absolute values of the adsorption entropies of these organic compounds on the alumina-copper-chromium and alumina-magnesium-chromium catalysts show the same tendencies as the adsorption heats.

The order of adsorption entropies determined experimentally is in a good agreement with the results of the statistical analysis of the adsorption of these molecules in the frames of models with different degrees of freedom of molecules in the gas phase and in the adsorbed state.

On the basis of the data obtained, it is possible to conclude that the hydrocarbons studied will desorb from the catalyst surface at different temperatures due to the significant differences in the adsorption heats. Therefore, during unsteady-state oxidative purification of a real multicomponent mixture, some compounds desorbed from the catalyst surface can move in front of the others and in front of the heat front in the adsorption-catalytic reverse process. For optimization of the purification process, differences in the adsorption heats of organic compounds should be taken into account.

References

1. A.N. Zagoruiko, A.S. Noskov, O.V. Kostenko: Russian patent 95112956 (1995).
2. A.N. Zagoruiko, O.V. Kostenko, A.S. Noskov: *Chem. Eng. Sci.*, **51**, 2989 (1996).
3. A.S. Noskov, L.N. Bobrova, G.A. Bunimovich, O.V. Goldman, A.N. Zagoruiko, Y.S. Matros: *Catal. Today*, **27**, 315 (1996).
4. A.N. Zagoruiko, OV. Kostenko, P.G. Tsyrulnikov, V.N. Tomilov, V.S. Salnikov, A.S. Noskov: in *Proc. Int. Conf. "Khimreaktor-13"*, Novosibirsk, 1996, V. 1, p. 204 (in Russian).
5. V.G. Stepanov, A.F. Bedilo, M.V. Zheivot, A.A. Liakh, G.G. Ponomarev, S.A. Yashnik: in *Materials of XXVII All-Union scientific student conference*, Novosibirsk, 1989, p. 58.

OP-1-8

UNSTEADY STATE STUDIES OF OXIDATION AND HYDROGENATION PROCESSES

S.L. Kiperman, N.A. Gaidai, N.V. Nekrasov, M.A. Botavina, Sh.E. Duisenbaev

N.D. Zelinsky Institute of Organic Chemistry, RAS,
117913 Moscow V-334, Leninsky Prospect, 47, PHONE: 1354147, FAX: 1355328,
E-mail: kip@cacr.ioc.ac.ru

Process investigations under nonstationary conditions are one of important steps of kinetic models development and elucidation of the reaction mechanism. Such studies were realized to the reactions of CO oxidation and xylene total oxidation as well as acetylene hydrogenation.

The experiments were carried out in special gradientless reactors of little volume at atmospheric pressure. The relaxation curves describing a transition of the system to a new steady state after a jump change of corresponding conditions give evidence of reaction mechanism. The analysis of curves obtained allows to characterize the observed relaxations in all studied reactions as own ones.

CO oxidation was studied on a platinum-alumina catalyst specially in the region of hysteresis loops being a result of steady state multiplicity [1,2]. The reaction rate is described by the equations corresponding to different process laws on various parts of the hysteresis loops. The amount of CO_2 formed from CO preliminary introduced on the catalyst surface is sharply decreased after the intermediate treatment by helium during a short time and then oxygen. However the amount of CO_2 formed is practically not changed on CO introduction onto the surface with preliminary adsorbed oxygen layer treated then by helium during a different time. The experimental results with successive repeated introduction of CO and then oxygen show the possibility of appearance of different states of catalyst surface. It can be one of the reasons of steady state multiplicity. There are two maximums on the relaxation curves after a replacement CO and intermediate blowing off by He for a different time and without any blowing off by reaction mixture. The values of these maximums are considerably exceeded the stationary level. This evidences the existence of some forms of adsorbed carbon monoxide that leads to steady state multiplicity. The relaxation curves which characterize a response of the system to a replacement of the oxygen by reaction mixture with blowing off by He for a different time and without any blowing give evidence about participation of some forms of adsorbed oxygen in the reaction under the conditions of steady state multiplicity. All the data obtained correspond to the new step scheme proposed and the kinetic description of the process.

The investigation of CO oxidation law on a hopcalite catalyst shows that both reaction components interact through adsorbed state [3]. The oxygen adsorption on a hopcalite is less strong than on the platinum catalyst. Intermediate treatment of the surface with adsorbed oxygen by He during 15 sec is sufficient to decrease CO_2 quantity significantly after CO introduction. The data of nonstationary experiments show that 13-15% of oxygen in the lattice can take part in the reaction.

Nonstationary effects in total oxidation of xylene were studied on an industrial catalyst (palladium supported on stainless steel) [4]. Relaxation curves show that the reaction products are formed when the adsorbed xylene was replaced by oxygen but they are not formed in opposite case when the oxygen was replaced by xylene. It means that adsorbed oxygen quantity is not sufficient to form the products of total oxidation. The maximum is observed on the relaxation curves which are characterized a response of the system to a replacement of the adsorbed oxygen by the reaction mixture. The maximum value of reaction rate corresponds to optimal relation of surface concentrations of xylene and oxygen. In this case the rate of the reaction exceeded the stationary rate. It is possible when nonlinear mechanism is realized and the reaction proceeds at full coverages [5].

Acetylene hydrogenation was studied on palladium-alumina catalyst also under nonstationary conditions. Relaxation curves obtained after a replacement of the adsorbed hydrogen by reaction mixture are characterized by a maximum. It means that the surface interaction of acetylene and hydrogen is a rate determining step. The relaxation curves show that acetylene occupied the most part of the surface and the reaction proceeds in the full coverages region.

Process realization in nonstationary regimes can be more advantageous than those under stationary conditions because the level of products quantities formed in the first case can be higher as compared with the steady state one.

These results confirm that studies in unsteady state region allow to reveal essential peculiarities of catalytic reactions and to obtain new data on their mechanism.

References

1. E.G.Novikova, N.A.Gaidai, N.V.Nekrasov, E.A.Katsman, S.L.Kiperman. Progress in Catalysis. 1996. V. 5. P. 95.
2. E.G.Novikova. Kinetic description of steady state multiplicity during carbon monoxide oxidation on platinum. Thesis. Moscow, 1997.
3. T.Yu.Sergeeva, E.G.Chuvatkina (Novikova), S.L.Kiperman. Kinet. Katal. 1998. T.39.
4. N.V.Nekrasov, M.A.Botavina, T.Yu.Sergeeva, A.S.Dryakhlov, S.L.Kiperman. Kinet. Katal.. 1998. T.39
5. E.J.R.Neer, A.J.Kodde, H.Uil, A.Bleik. Canad. J. Chem. Eng., 1966, V.74, N 5, P.664.

OP-1-9

FORMATION AND DYNAMIC PROPERTIES OF MOBILE LIQUID METAL-CARBON INTERMEDIATES UPON THE LOW-TEMPERATURE CATALYTIC GRAPHITIZATION OF AMORPHOUS CARBON BY Fe, Co AND Ni

Oleg P. Krivoruchko and Vladimir I. Zaikovskii
Boreskov Institute of Catalysis, Pr. Akademika Lavrentieva, 5,
Novosibirsk 630090, Russia
E-mail: opkriv@catalysis.nsk.su, Fax: +7(383 2) 35 57 56
Tel: +7(383 2) 35 02 62

Amorphous carbon usually transforms to graphite at temperatures above 2500-3000°C. In the presence of catalysts, carbon materials are graphitized quicker and at lower temperatures. If Fe, Co or Ni are used as catalysts, the liquid-phase graphitization occurs at $T \geq 1500$°C in the contact zone "melted metal-amorphous carbon" via the "dissolution-precipitation" mechanism [1,2].

We have observed and experimentally studied a phenomenon of liquid metal-carbon intermediate generations during the solid-phase interaction between iron, cobalt and nickel particles and amorphous carbon, the samples being heated in vacuum at the temperature that is 500-900° lower than that of pure metal melting or their eutectic with carbon [3,4]. The experiments were performed *in situ* in the column of electron microscope with the use of a heating device and video recording of the processes dynamics. The corresponding video film will be presented during the talk.

Fe, Co or Ni hydroxide particles were deposited on the amorphous carbon films (200-300 A thick). On heating, oxides are generated and reduced to metals by carbon of the film. The situation becomes critical, as the particle transforms to a metal state and the temperature comes to 600-700°C. Under these conditions, the particle absorbs carbon and transforms to an unusual liquid state, and start chaotic movement in the carbon film volume. The processes of the particle formation is characterized by the presence of transition and quasistationary regimes. In the system "metal particle - amorphous carbon surface", an efficient interaction mechanism is realized, resulting in the activation of C-C bond, breaking of carbon atoms from the support and their dissolution in metal "at the moment of formation". When the dissolved carbon achieves the limit concentration, the structure of solid phase metal particles becomes unstable. The particles transform into the liquid phase and form abnormally saturated solutions of carbon in metal (to 50 at.%). A significant decrease in the melting temperature of the particles, compared to the melting temperature of the pure metals, is determined by bond weakening and increase of the number of broken bonds between metal atoms, which result from their interaction with dissolved carbon atoms. It should be noted that in equilibrium systems the metals of the iron group or alloys with carbon are in the solid state on heating to 1100°C. At 700°C, a carbon solubility in these metals attains 0.2-0.4 at.% [5]. The unusual liquid quasistationary state can be realized and maintained only under dynamic conditions, when metal-carbon particles moving is accompanied by amorphous carbon absorption and graphite layers deposition. The movement of liquid particles is periodical stipulated by oscillations in the rate of amorphous carbon graphitization. With liquid particles Fe-C, Ni-C and Co-C, the quasistationary rates of amorphous carbon graphitization are respectively $1.6 \cdot 10^{-5}$, $1.6 \cdot 10^{-7}$ and $4.8 \cdot 10^{-7}$ mol/cm^2 s at 700°C. At comparable temperatures, these rates are 2-4 orders of magnitude higher than the stationary rate of carbon diffusion through solid metals of the iron subgroup [5].

We have observed the effects of self-organization of liquid metal-carbon particles with respect to their size: dominating particle sizes become comparable with the carbon film thickness in the course of time. The particles, that lost their mobility, transform to the solid state, whose phase composition is similar to that of carbides and/or metals.

"Amorphous carbon - liquid metal-carbon particles - graphite systems" are open, essential non-equilibrium and self-organizing physicochemical systems. The liquid particles act as catalytic intermediates in the low-temperature graphitization of amorphous carbon.

The work was financially supported by Russian Foundation for Basic Researches (grant No 96-03-33890).

References

1. Marsh H., Warburton A.B.// J. Appl. Chem. 1970. V.20. P.133.
2. Oya A., Marsh H.// J. Mater. Sci. 1982. V.17. P.309.
3. Krivoruchko O.P., Zaikovskii V.I., Zamaraev K.I. Dokl. Akad. Nauk (Russia), 1993, 329 (6), 744-748.
4. Krivoruchko O.P., Zaikovskii V.I.// II Conference "Modern Trends in Chemical Kinetics and Catalysis", November 21-24, 1995, Novosibirsk, Russia. Abstracts. Part II(1). P.261-262. Novosibirsk: Boreskov Institute of Catalysis. 1995.
5. Lander J.J., Kern H.P., Beach A.L.// J.Appl.Phys. 1952. V.23. N 12. P.1305.

OP-1-10

Understanding the Dynamics of Heterogeneous Catalytic Reactions: Exact Computational Technology

Mark Lazman

HYPROTECH
300 Hyprotech Centre 1110 Centre Street North,
Calgary, Alberta CANADA T2E 2R2

mark.lazman@hyprotech.com

High fidelity dynamic simulation of modern days requires adequate and reliable kinetic models. These models should be able to reproduce the observed behavior in the wide range of time scales. The conventional way of building the kinetic model based on the solution of inverse kinetic problem may be not always successful if applied blindly. The issues involved range from the numerical problems as stiff differential equations to the problems of model identifiability. In this situation the analysis of the model could be very fruitful. It could provide the time scales for the processes that drive system as well as initial guesses or even analytic estimates of the parameters. There are also possibilities for *a priori* determination of those parameters and their combinations that could be reliably estimated from the given experimental conditions. Finally the study of steady state multiplicity, self-oscillations and more complex dynamic phenomena that are inherent for many important catalytic reactions is impossible without understanding of corresponding dynamic model.

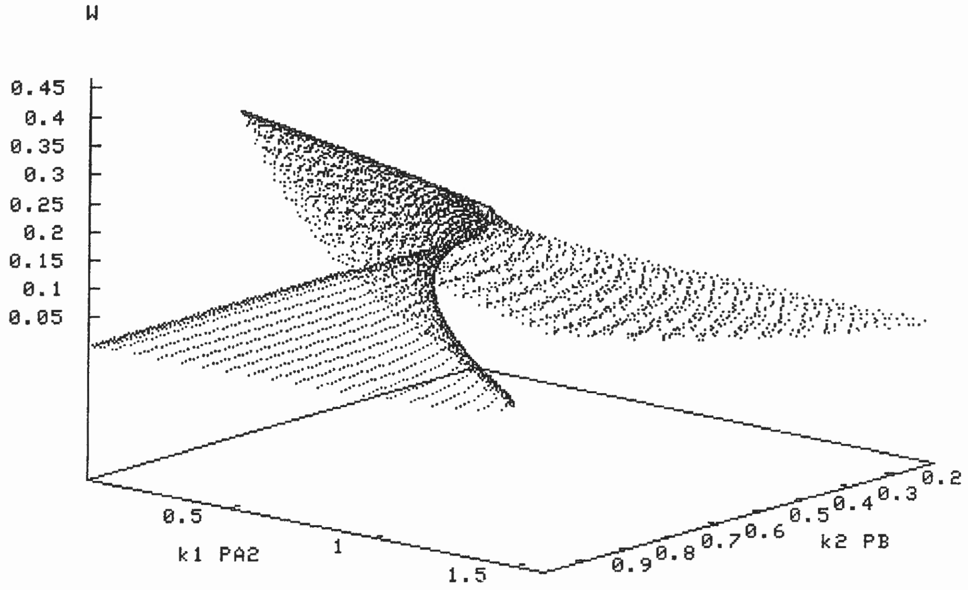
Analysis of the model addresses the issues as

- ➢ Time scales of major subsystems governing model dynamics
- ➢ Characteristics of the slow and fast motions
- ➢ Number of (quasi-) steady states in the feasible region
- ➢ Their dependence on parameters
- ➢ Stability and bifurcation boundaries
- ➢ Effect of the reaction mechanism on the observed behavior
- ➢ Dependency of the process characteristics on the parameters
- ➢ Identifiability of model parameters

The set of methods that solve the problems stated above combined with their implementation could be called the *Exact Computational Technology*. It allows the computer-assisted transformation, simplification and qualitative understanding of the model. ECT is based on the results of elimination theory, multidimensional complex analysis, theory of integral manifolds, and, computer algebra. This paper discusses ECT application to both steady state and dynamic problems concerned with models of heterogeneous catalytic reactions.

Steady state analysis

The figure below presents a 3D image of the object: complex multi-step heterogeneous catalytic reaction. Depending on the parameters (partial pressures of the gaseous components A_2 and B) the surface reaction could have 1 or 3 (quasi-) steady states. This situation could not be described in the conventional language of explicit kinetic equations based on the hypothesis of rate limiting step. The generalization required: in early 1980th author proved that Mass Action Law kinetic model of the single route catalytic reaction could be reduced to the single polynomial equation in terms of reaction rate: the *kinetic polynomial.* The zeroes of this polynomial are values of the steady state reaction rate. The developed theory resulted in the computer algebra implementation of the algorithm that builds the polynomial [1, 2]. Reduction to the single equation allows to answer many questions stated above: number of roots, their dependence on the parameters and reaction mechanism as well as parameter identifiability [1].



For general polynomial models we developed the modified implementation of the Groebner Bases method [2] that allows the transformation of the system of polynomial equations to the "triangular" form similar to the results of Gaussian elimination for linear system.

There is a light at the end of the tunnel even for general transcendent system, for instance, non isothermal catalytic reactor: application of Kronecker formula allows the reduction of the problem to the location of zeroes of single polynomial [2].

Dynamic analysis

Elementary steps of catalytic reactions can often have the reaction parameters of different order of magnitude. This situation has strong impact both on the observed kinetic behavior and on the methods of its analysis. The theory of integral manifolds proved to be a powerful tool for analysis of singularly perturbed systems that represent the model in this case. Combined with variable elimination method it allows obtaining explicit results for important models. Several patterns of steady state, quasi-steady state and dynamic kinetic dependencies will be discussed:

- Slow reaction: slow relaxation in the case of Rate Limiting Step
- Fast reaction: the fingerprints of fast surface reaction of two different adsorbates
- Slow exchange and Fast reaction: Five steady states in Catalytic CSTR
- Slow and Fast: Relaxation self oscillations in the system with buffer step
- Fast desorption and even faster surface reaction: the dynamics of Hydrogen oxidation

References

[1]M.Z.LAZMAN,G.S.YABLONSKII, Kinetic Polynomial: A new concept in Chemical Kinetics
IMA Proceedings, 1989, Patterns and dynamics in Reactive Media, Springer Verlag, 1991, p.117-149

[2] M.Z.LAZMAN, Finding all the roots of Nonlinear Algebraic Equations: A Global Approach and Application to Chemical Problems. 15th IMACS World Congress on Scientific Computation, Modelling and Applied Mathematics : Berlin, August 1997, v.6, p. 329- 334.

OP-1-12

Measurement and modeling of the transient adsorption, desorption and diffusion processes in zeolites

T.A. Nijhuis, L.J.P. van den Broeke, J.M. van de Graaf, M. Makkee,
A.D. van Langeveld, F. Kapteijn, and J.A. Moulijn

Delft University of Technology
Department of Chemical Engineering, Section Industrial Catalysis
Julianalaan 136, 2628 BL Delft, The Netherlands
Tel: +31-15-2786458, Fax: +31-15-2784452, E-mail: t.a.nijhuis@stm.tudelft.nl

The adsorption of different gases on zeolites was studied using the Multitrack system. Multitrack is a transient apparatus designed for testing catalysts on a very short timescale. By using high speed (100 µs) pulsing valves a small amount of gas (order of 10^{17} molecules) is pulsed through a small amount of sorbent material (up to 1 gram), located in an ultra-high vacuum system. The reactor can be operated up to 1273 K. Using three high-speed (1 MHz sampling rate) mass-spectrometers the gas-pulse response leaving the reactor can be measured.

By pulsing a gas to an adsorbing catalyst the pulse shape of the gas will change (broaden) because of the continuous adsorption and desorption of the gas molecules on the sorbent, and diffusion into the sorbent pores. This adsorption/desorption process was studied for a number of gases and zeolites, for example alkanes on silicalite-1. Using the pulse-response of a non-adsorbing gas through the same catalyst bed as a reference experiment, the rate of adsorption, desorption and diffusion can be determined simultaneously by a modeling process. Figure 1 demonstrates the result of some measurements, together with the fitted model, for the adsorption of *n*-butane on silicalite-1. It can be seen the model describes the measurements well.

A unique characteristic of this method, is that although the method by itself is macroscopic (*i.e.* its measurements include all processes from the diffusion in the gas phase outside the zeolite particles until the diffusion of the adsorbed phase inside the particles), it yields diffusivities in excellent agreement with those determined by microscopic methods, such as Pulse-Field-Gradient NMR. Other macroscopic methods (*e.g.* using membranes or with chromatographic techniques) report diffusivities up to two orders in magnitude lower than the ones determined using microscopic methods. An explanation for these differences in diffusivities can be found in external diffusion limitations or influences of a carrier gas

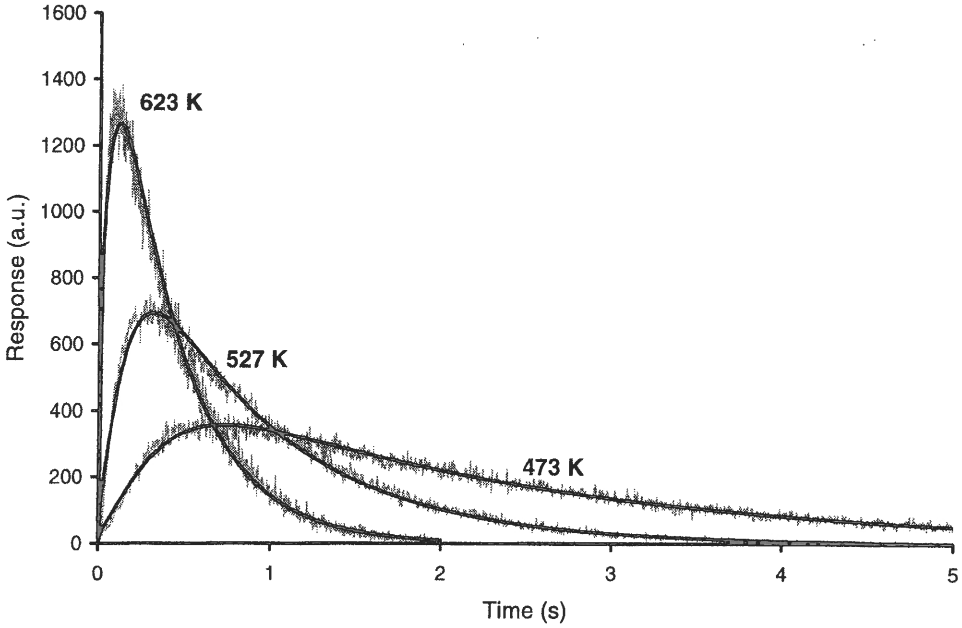


Figure 1. Measured and modeled pulse responses of n-butane over a bed of silicalite-1 at 473, 527, and 623 K.

influencing the macroscopic measurements. The present method using Multitrack, however, does not have these problems, since a carrier gas is not used and the experiments are performed in the Knudsen diffusion regime, thereby by definition excluding the possibility of external diffusion limitations.

The equilibrium constants for adsorption and the heats of adsorption determined using this method agree very well with reported values. It is shown the absolute rate constants for the adsorption and desorption processes can be determined, which is difficult using conventional methods. Furthermore, it is shown that for fast adsorbing species (*e.g.* methane, ethane, propane, and *n*-butane on silicalite-1) the absolute rate of adsorption is equal to the collision rate of the molecules with the sorbent, as can be calculated using the kinetic gas theory. More bulky components, such as *i*-butane, on the other hand, have a much lower rate of adsorption, which can be explained by a lower sticking coefficient as a result of a kind of steric hindrance during the adsorption process.

Concluding it can be said that the presented method for determining simultaneously the adsorption, desorption, and diffusion parameters, is an excellent method for the determination of all relevant parameters of the intrinsic adsorption and diffusion behavior of gases in microporous materials. The diffusivities determined using this macroscopic method are the actual diffusivities, not influenced by external processes, which is also the case for diffusivities obtained using microscopic methods, such as PFG-NMR. The equilibrium constants for adsorption obtained are in good agreement with reported values, the absolute rate constant for adsorption can be correlated to the theoretical adsorption rate, as can be calculated using the kinetic gas theory.

OP-1-13

On the oxygen promoting effect in the reaction of NO reduction with CH_4 on Co/ZSM-5

L. Pinaeva[a], A. Suknev[a], E. Sadovskaya[a], Y. Schuurman[b], T. Décamp[b], V. Goncharov[a], B. Balzhinimaev[a], and C. Mirodatos[b]
[a]Boreskov Institute of Catalysis RAS, pr. Lavrentieva 5, Novosibirsk, 630090, Russia, e-mail: ICCCT@catalysis.nsk.su.
[b]Institut de Recherches sur la Catalyse, 2 ave Albert Einstein, F-69626 Villeurbanne, France, e-mail: mirodato@catalyse.univ-lyon1.fr.

The promoting effect of oxygen in the reaction of NO reduction with CH_4 on Co/ZSM-5 catalyst is usually related to formation of NO_2 or $NO_{2,ads}$ that is necessary for methane activation [1,2]. So, the nature of adsorbed NO_x species on different types of zeolites as well as possible intermediates were extensively studied by IR spectroscopy for last years.

We used transient response techniques including TAP reactor, steady-state isotopic transient kinetic analysis (SSITKA), *in situ* DRIFT and FTIR spectroscopies to elucidate the mechanism of N_2 production, focusing at the oxygen insertion into both adsorbed species and reaction products.

Temperature programmed desorption (TPD) performed in NO+He and NO+O_2+He flows showed that in the presence of O_2 the band at 2130 cm^{-1} usually related to $NO_2^{\delta+}$ weakly bonded with the bridging Si(OH)Al hydroxyl groups of zeolite was actually composed of at least two distinct bands. In the presence of gas phase over the catalyst the first component of the band disappeared almost completely at about 260°C. The remaining absorption band was stable up to 500°C at least, in a similar way as the band at 1940 cm^{-1} which developed at 260°C and was ascribed to mononytrosyls bonded with Co^{2+} ions (Co^{2+}(NO)).

Transient experiments performed at 450°C in the DRIFT cell showed that the surface coverage with $NO_{x,ads}$ species increased by one order of magnitude in the presence of oxygen while the concentration of mononitrosyls decreased substantially. So, this effect is due to the formation of $NO_2^{\delta+}$ species arising from the oxidation of Co^{2+}(NO) that could be located, for example, on the interface between Co clusters and Si(OH)Al hydroxyl groups. TAP data on NO and NO+O_2 pulsing on the oxidized surface showed that $NO_2^{\delta+}$ were substantially more strongly bonded with Co^{2+} compared with mononitrosyl groups. Neither nitrite nor nitrate complexes were observed in the spectra during the transients. Correlation observed between the intensities of bands related to Co^{2+}(NO), $NO_2^{\delta+}$ as well as CO_2 in the transients from both He(+O_2) and He+NO(+O_2) to the reaction mixture confirmed our assumption that both Co^{2+}(NO) and $NO_2^{\delta+}$ species bonded with Co^{2+} participate in the activation of CH_4 molecules.

Replacing of $^{16}O_2$ to $^{18}O_2$ and vice versa in the reaction mixture flowing over the catalyst proceeded very fast. No substantial oxygen exchange (revealed by the transient formation of $^{16}O^{18}O$) was observed in the O_2 molecule. In the mean time, ^{16}O substitution by ^{18}O was observed in about 28% of the NO molecules but considerably delayed after the oxygen switch in the gas phase (fig.1a). In turns, isotope distribution is determined by the prominent oxygen exchange observed in NO molecule in the experiments on the replacing of $^{14}N^{16}O$+He to $^{15}N^{18}O$+He. The rate of nitrogen isotope exchange was comparable with the rate of NO adsorption / desorption. Like to the experiments with labeled O_2 the quantity of oxygen that could be exchanged was about ten times greater then the quantity of supported cobalt. Bridging Si(OH)Al hydroxyl groups of the zeolite were supposed to participate also in this exchange. Indeed, the exchange rate on H/ZSM-5 was estimated to be comparable to that on Co-ZSM-5 while the amount of exchanged oxygen was several times less. Formation of substantial quantities of strongly bonded $NO_2^{\delta+}$ absorbed species with non-equivalent oxygen atoms seems to explain a retardation of the exchange observed in the presence of oxygen (fig.1b).

Isotope insertion into CO_2 in the experiments with both $^{16}O_2/^{18}O_2$ and $^{14}N^{16}O/^{15}N^{18}O$ proceeded in step with oxygen exchange in NO. $^{16}O/^{18}O$ distribution in CO_2 molecule ($C^{16}O_2$:$C^{16}O^{18}O$ was 1:1, $C^{18}O_2$ resulted from CH_4 oxidation with $^{18}O_2$ only) is the obvious proof of that oxygen in CO_2 molecule would be inserted both from $NO_2^{\delta+}$ and Co^{2+}(NO) but not directly from gaseous O_2.

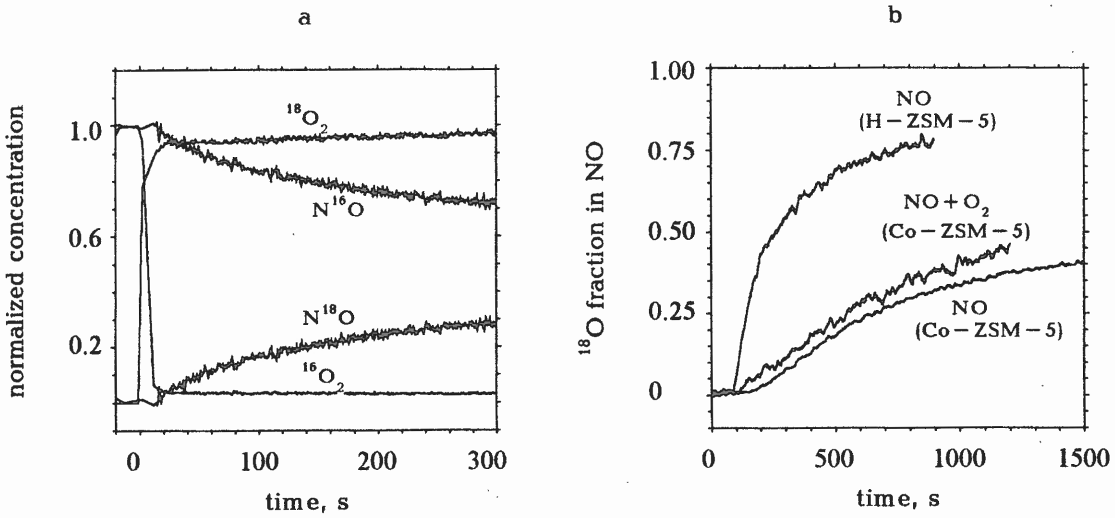


Fig.1. a)Responses of components of the reaction mixture after replacing of $^{16}O_2$ to $^{18}O_2$ and b) ^{18}O fractions in NO after replacing of $^{14}N^{16}O$ to $^{15}N^{18}O$ in different mixtures.

References.

1. A.W. Aylor, L.J. Lobree, J.A. Reimer, A.T. Bell. 11th International Congress on Catalysis-40th Anniversary. Studies in Surface Science and Catalysis, vol.101.1996. p.661-670.
2. A.Yu. Stakheev, C. W. Lee, S.J. Park, P.J. Chong. Catalysis Letters 38(1996) 271-278.

OP-1-14

INVESTIGATION OF THE CATALYTIC DECOMPOSITION OF NO AND N_2O WITH TRANSIENT TECHNIQUES

Katariina Rahkamaa and Tapio Salmi
Laboratory of Industrial Chemistry, Åbo Akademi, FIN-20500 Åbo, Finland,
Fax:+358-2-2654479, E-mail:Katariina.Rahkamaa@abo.fi

Keywords: NO_x abatement, transient techniques, kinetics

Introduction

Catalytic abatement of nitrogen oxides is an important process in exhaust cleaning. The most difficult nitrogen oxide to be decomposed is NO. Principally a straightforward way to remove NO would be the self-decomposition,

$$NO \rightarrow 1/2\ N_2 + 1/2\ O_2.$$

Analogously, nitrous oxide, N_2O, is decomposed:

$$N_2O \rightarrow N_2 + 1/2\ O_2.$$

The main obstacle in the self-decomposition is, however, the strong oxygen adsorption on most of the catalysts, which blocks the active NO_x-adsorpton sites and leads to a rapid decline of the catalyst activity. Therefore, the selective catalytic reduction (SCR) has turned out to be a more successful way to remove NO. Typical reducing agents are CO, hydrocarbons and H_2:

$$2\ NO + 2\ H_2 \rightarrow N_2 + 2\ H_2O.$$

Exhaust catalysts typically operate under transient conditions, under a variation of the gas composition and temperature. In order to elucidate the transient behaviour of a typical monolith exhaust catalyst, dynamic step response experiments of NO_x decomposition were carried out in the present study.

Experimental

The kinetics and mechanism of the decomposition of NO and N_2O was investigated with transient step response techniques in the presence and in the absence of a reducing agent (H_2). The experiments were carried out on a Rh/Al_2O_3 and Rh/CeO_2 catalyst mounted on a metallic monolith (Kemira Metalkat). The rolled monolith was placed in a cylindrical glass tube, through which the reacting gases were flowing. The gas flows (NO, N_2O, H_2, Ar) were controlled with mass flow controllers (Brooks 5850S) and the outlet gas flows were analyzed with a quadrupole mass spectrometer (Carlo Erba Instruments Q.T.M.D.). The experiments were carried out at atmospheric pressure and within a temperature interval of 150 - 350 °C.

Results and discussion

Following transient response experiments were carried out: self-decomposition of NO and N_2O and reduction of NO and N_2O with H_2. After a hydrogen pretreatment, the reaction flow was switched on. The reaction was allowed to continue until a steady state was attained, after which the inert gas (Ar) flow was switched on. Typical response curves are displayed in Figs. 1-2. The results show a time lag between the N_2 and O_2 responses in the N_2O decomposition, indicating the oxygen adsorption capacity of the catalyst (Fig. 1). In the selective catalytic reduction of NO with H_2, an overshooting H_2 response was detected (Fig. 2), suggesting that NO adsorption is more rapid than that of H_2. A detailed mathematical modelling of the transient responses, based on surface reaction mechanisms, will be presented in the final paper.

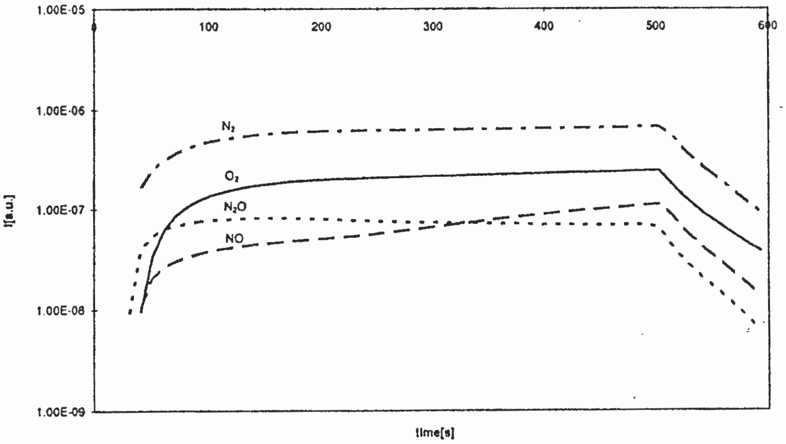


Figure 1. Step response experiment with a mixture of 1%N_2O/Ar at 350°C on a Rh/Al_2O_3.

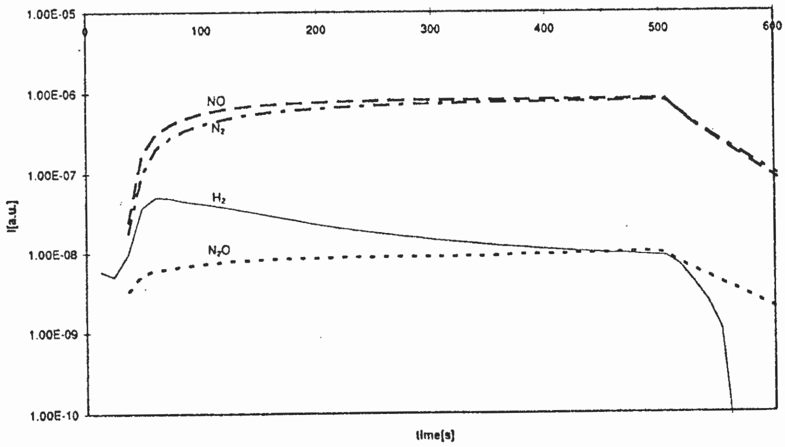


Figure 2. Step response experiment with a mixture of (1%NO+1%H_2)/Ar at 150°C on a Rh/Al_2O_3.

OP-1-15

Incubation, acceleration, retardation, reanimation and deactivation: The dynamic kinetic regimes of conversion of methanol and hydrocarbons on zeolite H-ZSM-5

Hans Schulz and Ming Wei
Engler-Bunte-Institut, Universität Karlsruhe, Kaiserstraße 12, 76128 Karlsruhe, Germany

Conversion of methanol to hydrocarbons and their further reactions to secondary products on the zeolite H-ZSM-5 can proceed in fundamentally different kinetic regimes which are highly dynamic and several of them instationary, depending on reaction time and on temperature and being controlled by the pore architecture and the respective spacial constraints of the zeolite [1-4].

The following kinetic regimes have been observed and characterized: **I**.a) Preinitiation, where methanol is converted to dimethylether and water only. **I**.b) Incubation, where hydrocarbons are being formed from methanol and these selectively produce a retardate in the zeolite pores. **II**) Acceleration, where the retardate takes part in the conversion and thereby strongly speeds up the reaction rate. **III**) Retardation, where the reaction rate declines because of excessive pore filling via trapping of bulky molecules. **IV**) The regime of reanimation shows the unique feature of regenerating high catalyst activity through conversion of the retardate into smaller molecules which can diffuse in the pores and leave the catalyst particles. **V**) The deactivation/coking regime of H-ZSM-5 which is unique as proceeding solely through growth of external coke seeds by reaction with methanol.

As an example **figure 1 left** shows the conversion of methanol and the yield of volatile hydrocarbons and hydrocarbon-retardate with the catalyst H-ZSM-5 at 270°C reaction temperature as a function of time. The episode of the kinetic regimes incubation (**I**), acceleration (**II**) and retardation (**III**) are indicated on top of the figure. In **figure 1 right** catalyst life time and retardate yield are presented as a function of reaction temperature. The regime **IV**, reanimation of the catalyst, is characterized by declining retardate selectivity and increasing catalyst life time with increase of

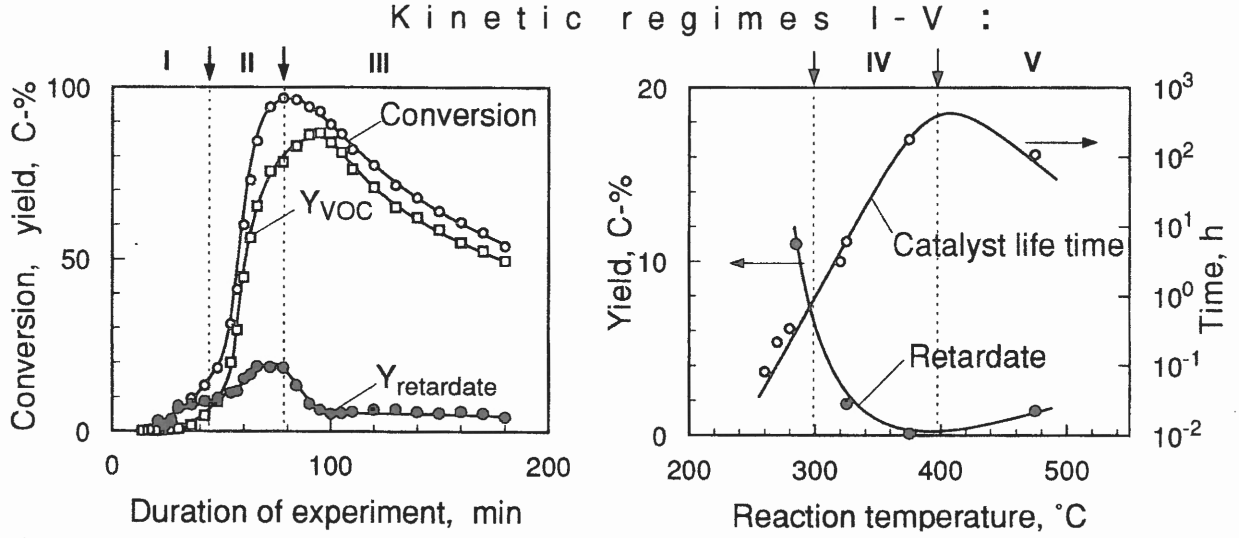


Figure. 1 *Conversion of methanol on H-ZSM-5 zeolite catalyst and identification of 5 different kinetic regimes;* ***left:*** *Conversion and yields of volatile hydrocarbons and retardate as a function of time at low reaction temperature (270 °C)* ***right:*** *Yield of retardate and catalyst life time as a function of reaction temperature ($p_{Methnol}$ = 2.5 bar, WHSV = 1 h^{-1})*

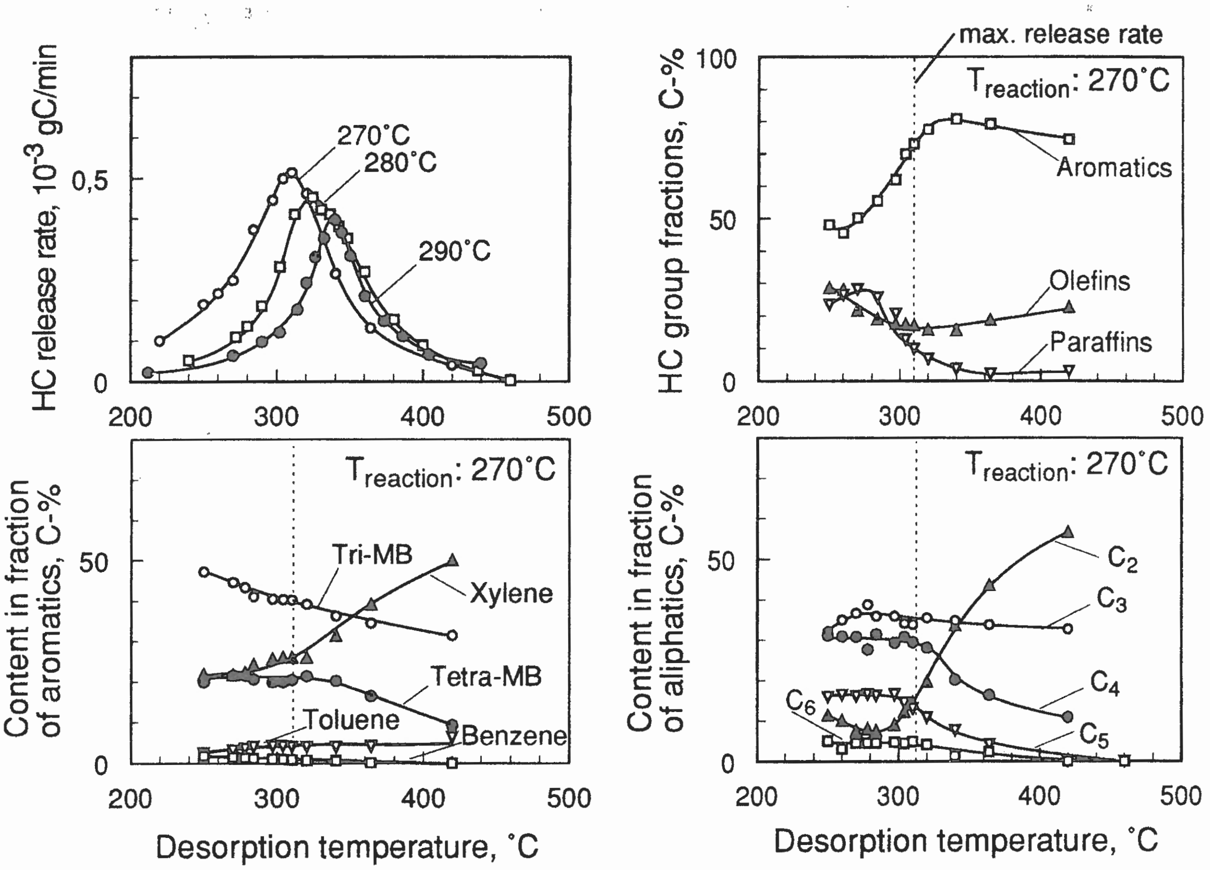


Figure. 2 *Hydrocarbon release rate and released product composition as a function of time/temperature* (2°C/min) *for a H-ZSM-5 catalyst deactivated at low temperature methanol conversion*

temperature. Finally in regime **V** (**fig. 1 right**) catalyst life time declines due to external increasing coking. Further characterization of the regime of reanimation is possible through thermal (temperature programmed) treatment of catalyst samples which had been used/ deactivated at low reaction temperature (270, 280 and 290°C) as shown in **figure 2**. The hydrocarbon release curves (**fig. 2, above, left**) show a maximum at 300-350°C as indicative for a retardate reaction to molecules of high diffusivity. The diagrams show selectivities which drastically change with time/temperature of regeneration/reanimation.

The several kinetic regimes of methanol and hydrocarbon conversion in the H-ZSM-5 pore architecture, the nature of their instationarity and the modifying role of the zeolite spacial constraints will be presented and discussed in the lecture.

References:

[1] H. Schulz, W. Böhringer and S.-W. Zhao, Proceedings 9th international zeolite conference, Montreal, (1992)

[2] H. Schulz and S. Nehren, Erdöl Kohle Erdgas Petrochem., 39 (1986) 93

[3] H. Schulz, S.-W. Zhao and H. Kusterer, Stud. Surf. Sci. Catal., Vol. 60, Elsevier, Amsterdam, (1991) 281

[4] H. Schulz, K. Lau and M. Claeys, Applied Catalysis A: General 132 (1995) 29

OP-1-16

MECHANISMS OF CO_2 REFORMING AND PARTIAL OXIDATION OF METHANE INVESTIGATED WITH PULSED REACTION TECHNIQUE

Toshimitsu Suzuki, Na-oki Ikenaga, Naoko Matsui, and Kiyoharu Nakagawa

Department of Chemical Engineering, Kansai University,
Suita, Osaka Japan 564

Phone+81-6-368-0865 FAX+81-6-388-8869, e-mail tsuzuki®ipcku.kansai-u.ac.jp

Introduction

Recently to reactions of carbon dioxide have been paid much attention, in view of reduction or chemical utilization of carbon dioxide, one of the global warming gases. Among them, carbon dioxide reforming is one of the promising reactions to give synthesis gas having a lower H_2/CO ratio.

Also much attention has been focused on the direct partial oxidation of methane to H_2 and CO using group VIII transition metal loaded catalysts. This process is slightly exothermic and proceeds at a lower temperatures, in contrast to highly endothermic steam and CO_2 reforming reactions. Thus thermal efficiency would be improved as compared to conventional processes.

We have found that ruthenium loaded on lanthanum oxide catalyst exhibited a very high catalytic activity on the CO_2 reforming of methane, and that iridium loaded on titania showed an excellent catalytic activity in the partial oxidation of CH_4 at low temperature.

This paper deals with the pulsed reactions of methane and CO_2 with Ru/La_2O_3 catalyst and transient responses reactions of methane and oxygen by measuring the catalyst bed temperatures of various metal loaded catalysts, in order to reveal reaction mechanisms of CO_2 reforming and partial oxidation of methane.

Experimental

Pulsed or transient response reactions were carried out with a quartz made fixed bed flow reactors equipped with sample injection loops. Temperature of the catalyst bed was controlled by monitoring the out side wall temperature of the reactor. Two very thin walled sheathed thermocouples were inserted into the catalyst bed in order to measure temperature at the front edge and rear end of the catalyst bed. This provided information about temperature changes in the catalyst bed by introducing different reactant gases. The effluent gases from the reactor tail was sampled by a quadrupole mass spectrometer every one second intervals. In a certain run, $^{13}CO_2$ was used to separate the CO from methane and $^{13}CO_2$.

Results and discussion

In the CO_2 reforming of methane with Ru catalyst, significant effect of support was observed. Among the supports investigated, La_2O_3, Y_2O_3 and ZrO_2 exhibited very high activities. On the other hand, Al_2O_3 and SiO_2 showed poor activities with a large amount of carbon deposition.

After steady flow of CO_2 was supplied on to Ru(5 wt%)/La_2O_3 and Ru(5 wt%)/Al_2O_3 for 5min at 600 °C, CO_2 was switched to an Ar flow to sweep out CO_2, and the pulse of methane (1 mL) was introduced. In both cases, responses of H_2 and CO were observed with unreacted CH_4. Response to CO was much weaker with Ru/Al_2O_3 and that with Ru/La_2O_3 was continued to observed after the CH_4 pulse passed through the catalyst bed. When the opposite reaction sequence (CH_4 steady flow followed by CO_2 pulse) was applied to the same catalysts. No hydrogen uptake was observed in both catalysts with small responses of CO, but a symmetrical CO_2 response was observed for the Ru/Al_2O_3 system. Unsymmetrical tailing responses of CO_2 and CO were observed in the Ru/La_2O_3 catalyst. Into a CH_4 steady flow or into a CO_2 steady flow CO_2 and CH_4 pulsed reactions with respective catalyst system were carried out.

In all the runs, CO_2 was concluded to be adsorbed onto La_2O_3. CH_4 would rapidly be dehydrogenated to give H_2 and CH_x on the Ru surface. Spillover of CO_2 from the support afforded CO and H_2. However, judging from very small responses of H_2, CH_x species would almost be carbon. Adsorption of CO_2 onto the support was measured by the pulsed method. Only La_2O_3 showed appreciable adsorption and delayed desorption, ZrO_2 exhibited slight adsorption of CO_2 but no adsorption was observed for Al_2O_3 and Y_2O_3 at 600 °C. However, except Al_2O_3 slight temperature rises in the catalyst bed was observed due to heat of adsorption of CO_2 on to the support. All these results suggested that in the CO_2 reforming of methane activation of CO_2 on the support played an important role.

In the partial oxidation of methane to CO and H_2 two possibilities were proposed; the first one is the direct path shown in equation (1), and the second path is two step process complete oxidation of methane to CO_2 and H_2O followed by steam and CO_2 reforming of methane to CO and H_2.

$$CH_4 + 1/2\ O_2 \rightarrow CO + 2H_2 \qquad (1)$$
$$CH_4 + 1/2\ O_2 \rightarrow CO_2 + 2H_2O \qquad (2)$$
$$CH_4 + CO_2 + 2H_2O \rightarrow 2CO + 4H_2 \qquad (3)$$

A large number of indirect evidences were shown to interpret respective paths. We have measured temperature changes of the catalyst bed by introducing pulses of CH_4 and O_2 mixture with carrier gas or oxygen pulses into a CH_4 steady flow. In the Ir/TiO_2 catalyst a large and rapid temperature rise was observed at the front edge of the catalyst, indicating that complete oxidation of methane occurred. When the same technique was applied to Rh/TiO_2 catalyst, which is reported to be an active catalyst for this reaction, a small temperature drop was observed at the front edge of the catalyst. This seems to indicate that at the front edge of the catalyst dehydrogenation of CH_4 to H_2 and CH_x occurred. At the rear end of the catalyst slight temperature rise was seen indicating possibility of direct reaction path.

Thus non-steady reaction technique is one of the interesting and useful methods to elucidate reaction paths in the methane conversion reactions.

OP-1-17

DEEP OXIDATION OF METHANE ON ALUMINA-MANGANESE CATALYST IC-12-40

P.G.Tsyrulnikov, V.S.Salnikov, V.A.Drozdov

Omsk Branch of the Boreskov Institute of Catalysis

N.A.Chumakova, V.K.Ermolaev, I.V.Malakhova

Boreskov Institute of Catalysis

Alumina-manganese catalyst IC-12-40, which is stable to 1000°C, may be used to burn methane from colliery wells in the reverse-process accompanied by heat recover [1]. Catalyst IC-12-40 is produced in industrial batches at AO "Katalizator" in Novosibirsk. When the catalyst was tested in the reverse-process n-butane combustion at 700°C, reaction was found to continue in the inert bed, where temperature attained 1060°C, as the gas flow direction was switched to the opposite one [2]. This fact was assumed to relate to the gas phase occurrence of catalytic oxidation reaction on ceramic Raschig rings.

In the present study we intended to determine, if the gas phase reaction occurs during deep methane oxidation over IC-12-40.

For the purpose we used:

- kinetic method performing reaction at various methane concentration (0.5-4.5 vol. %) and temperatures (400-750°C), CH_4:O_2 ratio ranging from stoichiometric to large oxygen excess. Flow-circuit setup had quartz reactor. We studied the catalyst of various fractional composition and also its mixtures with quartz inert granules of different size. For comparison we studied solely gas phase oxidation.
- ESR of matrix isolated methane oxidation products.

We have found that

- no homogeneous process occurs at all temperatures and methane concentration studied, only heterogeneous one, whose kinetics follow equation $W = 1.2 \cdot 10^6 \cdot \exp(-21300/R \cdot T) \cdot C$, where W is reaction rate, cm^3 CH_4/g·s, C is the current methane concentration in molar parts;
- gas phase oxidation becomes essential, when the temperature exceeds 700°C;

- catalyst presence significantly decreases the rate of the gas phase oxidation;
- ESR method shows no radicals to form at 700°C, RO_2 radicals are found to form at 720°C, when solely gas phase oxidation becomes possible.

Kinetic data obtained were used for reverse-process modeling. A model and algorithm are suggested for the theoretical studying of the heat front propagation inside the fixed bed with separated heterogeneous catalytic and gas phase zones. The latter may become important at 700-900°C.

Therefore, independently of methane oxidation conditions reaction occurring on IC-12-40 remains heterogeneous.

The authors would like to acknowledge the financial support from Russian Science Foundation, Grant N 95-03-08915a.

1. Yu. Sh. Matros, L.L. Gogin, V.S. Lakhmostov, T.V. Mulina, Ye.F. Stefoglo, 3d All-Russian Conf." Unsteady State Processes in Catalysis ", 1986, p.120-121 (in Russian).
2. V.A. Drozdov, L.L. Gogin, P.G. Tsyrulnikov, Yu. Sh. Matros, " Unsteady State Processes in Catalysis", International Conference, Abstracts, Novosibirsk, 1990, p. 249-250.

OP-1-18

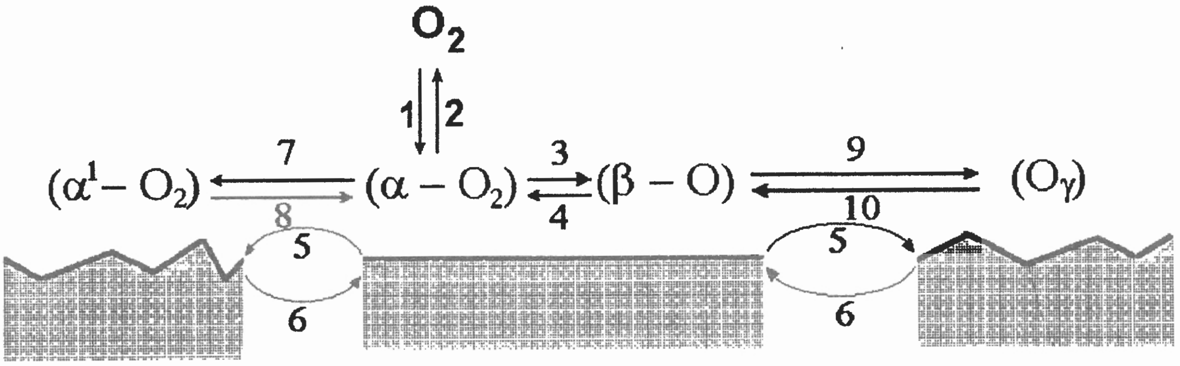
THE TEMPERATURE BEHAVIOUR OF THE OXYGEN SPECIES ON SILVER SURFACE

E.A. Ivanov, A.I. Boronin, S.V. Koscheev and G.M. Zhidomirov

Boreskov Institute of Catalysis, Novosibirsk 630090, Russia

The temperature behaviour of the oxygen species on silver surface has been investigated. Four main types of oxygen forming at different temperatures and oxygen pressures have been discriminated: $(\alpha - O_2)$ - molecular oxygen ($E = 530.0$ eV, $T_{des} = 380 - 400$ K) [1], $(\beta - O)$ - atomic oxygen ($E = 528.4$ eV, $T_{des} = 580 - 600$ K), $(\alpha^1 - O_2)$ - quasi-molecular thermally stable oxygen ($E = 530.5$ eV, $T_{des} = 800 - 900$ K) [2], (O_γ) - atomic thermally stable oxygen ($E=529.0$ eV, $T_{des} > 900$ K) [3]. A kinetic model describing the formation and transformations of the oxygen forms and taking into account the surface amorphization have been proposed.

The mechanism of the formation of adsorbed oxygen forms depending on temperature can be presented by the following general scheme.



From the kinetic point of view, the mechanism of the oxygen interaction with the silver surface can be divided into three blocks. The first block determines adsorption-desorption and dissociation of oxygen on regular surface. The second block determines the transformation of the surface from the regular to the disordered state and vice versa, representing the processes of surface amorphization and annealing of defects. The third block determines the oxygen diffusion from regular to disordered surfaces and vice versa. The kinetic model also includes stages of the reversible oxygen diffusion into the bulk. However, this process does not make any changes in the oxygen adsorption kinetics under equilibrium conditions.

The case when the adsorption and formation of different oxygen forms on the silver surface takes place under equilibrium conditions at a constant oxygen pressure in the gas phase is considered. All the unknowns have been defined through constants of stages. This is one of few cases when a non-linear system of equations can be solved in a final form through the system parameters, i.e. constants of stages. Note that all constants are used as ratios of constants of forward and reverse reaction stages. The oxygen pressure was varied in the calculations.

The calculated curves describe changes in the concentrations of oxygen adsorption forms depending on temperature under the equilibrium between the gas phase oxygen and surface oxygen at oxygen pressures in a wide range from 0.01 to 1000 mbar. One can see that all four forms have typical temperature intervals of existence. In the temperature range of 300-500 K molecularly bound (α - O_2) and atomic oxygen (β - O) is observed on the regular ordered surface, whereas at $T > 700$ K similar forms (α^1 - O_2) and (O_γ) exist on the defect surface. In the intermediate region at $T = 500 - 700$ K, a quasi-molecular thermally stable form (α^1 - O_2) is formed together with the atomic forms on the silver surface. Also an experimental effect of the oxygen pressure, which consists in the fact that the (α - O_2) -form and thermally stable states (α^1 - O_2) are observed only after oxygen treatments at elevated pressures, is described quite well.

Acknowledgement. The present work was supported by Russian Foundation for Basic Research (grants 95-03-09676, 96-03-34200 and 96-15-97571).

REFERENCES

1. R. B. Grant and R. M. Lambert: *Surf. Sci.*, **146**, 526 (1984).
2. A. I. Boronin, S. V. Koscheev, V. F. Malakhov, G. M. Zhidomirov: *Catal. Lett.*, **47**, N2, 111(1997).
3. X. Bao, M. Muhler, Th. Schedel-Niedrig and R. Shlogl, *Phys. Rev*. B. **54**, N3, 54 (1996).

Section 2.

Dynamics of Chemical Reactors

THE EFFECTS OF TEMPERATURE AND CONCENTRATION FLUCTUATIONS ON CATALYST PARTICLE CONVERSION IN THE METHANOL AND AMMONIA SYNTHESES

Odd Andreas Asbjornsen
SKARPODD Co., P.O. Box 1642, N-7002 Trondheim, Norway
Phone: (*)47 7359 3720, fax: (*)47 7359 8390, e-mail: oaaite@tev.ntnu.no
Magne Hillested
Statoil Research Center, Postuttak, N-7005 Trondheim, Norway
Phone: (*)47 7358 4395, fax: (*)47 7358 4345, e-mail: mhi@statoil.no

Most heterogeneous catalytic reactions show optimal conditions of bulk conditions, i.e. conditions that give maximum flux of a desired product from the catalyst surface. The reason for the optimum is found in the combination of reaction kinetic and transport properties for the heat and mass transfer to the catalyst particle. A well known example is the theoretical optimal temperature in the ammonia synthesis reactor, but this profile applies to the surface of the catalyst, and not necessarily to the bulk of the gas. Similarly, there is a theoretical optimal profile of the hydrogen to nitrogen ratio, which is lower than stoichiometric 3/1. The reason for this is found in the transport property of hydrogen being much higher than that of nitrogen. Similar conditions may be found in the methanol synthesis, but this is not so evident because two reactions contribute to the production of MeOH, while the ammonia synthesis has only one dominating reaction.

The optimal conditions and the effectiveness of catalyst particles are known to be influenced by temperature and concentration fluctuations in the bulk of the reacting gases. Such fluctuations may be caused by differences in effectiveness factor and catalyst activity between the particles, and by incomplete mixing of the incoming gas flow. From an operational point of view, it is of interest to evaluate the order of magnitude of the effects mentioned. An essential contribution of this paper addresses this issue with respect to two important industrial reactions, the ammonia and the methanol synthesis. The approach considers the root of the nonlinearity first, namely the reaction kinetics on the surface of the catalyst particle. If the phenomena are insignificant here, they are not likely to be of significance to the total reactor operation either. This approach is similar to the one used for catalyst particle stability studies by Asbjornsen and Hillestad [1].

From statistics it is known that that fluctuations imposed on non-linear systems cause a mean value shift in the system response. This mean value shift is proportional to the variance in the fluctuations and to the second derivative of the response function with respect to the fluctuating variable. If a process is running at optimum conditions, e.g. at a maximum where the second derivative is negative, the effect of fluctuations is always a reduction of the optimum. This was shown by Steensland et al. for several catalytic reactions [2]. The present paper presents the results of some investigations of the phenomena mentioned and the effects they may have on industrial catalyst particles in the ammonia and methanol synthesis.

Fluctuations in the state of the bulk of the gas affect the catalyst particle in two modes, the steady-state and the dynamic mode. How strong the effects are depends upon the frequency spectrum of the fluctuations. If this is a high frequency spectrum, only the outer layer of the particle will be affected, as the fluctuation decay very rapidly into the core of the particle.

Therefore, two aspects are of interest for the efficiency of the catalyst particle. First the very low frequency range of the fluctuations, which affect the steady state conditions throughout the catalyst particle. If the particle happens to operate at optimal temperature and composition, the effect of the low frequency fluctuations will always be a reduction in conversion. From a production point of view, this effect shows up as a decrease in catalyst activity if the particle operates near optimum. Therefore, a misleading interpretation may be the result, even though the activity actually has not changed. Secondly, the dynamic effect of the high frequency fluctuations are of interest. Depending upon the power spectrum of the fluctuations they will propagate into the particle to a certain depth, the more shallow depth the higher the frequency is. This means that the outer layer of the particle may follow the fluctuations, while the inner core will be at steady-state. The linearized dynamics of the particle is used for this investigation; similar to the approach used by Asbjornsen and Hillestad [1].

The effects of mean value shift and the optimal conditions for the flux of methanol and ammonia respectively, are due to the non-linear kinetics and the equilibrium conditions. Due to the stoichiometric balances, there is a linear subset of the material and energy balances, for which the mean values are unaffected by the fluctuations. The first step is therefore to search for mean value shifts and optimal conditions in the rate expressions, as shown by Denbigh [3] for the theoretical temperature profile in the ammonia reactor. This approach is extended to the H_2/N_2 ratio in the ammonia synthesis and the H_2/CO_2 ratio in the methanol synthesis. The Temkin Pyzhev kinetic model evaluated by Nielsen [4] is used for the ammonia synthesis, and the Busshe Froment [5] kinetic model is used for the methanol synthesis.

The phenomena discussed in the paper are indeed of importance for the interpretation of experimental results, as the effect of turbulence may blur the parameter estimates, even the interpretation of the kinetic mechanisms and the catalyst activity. It is also of industrial interest to evaluate the order of magnitude of the effects mentioned, in particular on important processes like the methanol and ammonia syntheses. Those processes are the examples for an illustration of the effects. The fact that the mean values of a linear subset of the cause and effect model of the particle dynamics are not affected by any mean value shift, only the kinetics, makes it possible to evaluate the likely effects from the kinetic models themselves, as shown by Asbjornsen and Hillestad [1] for the eigenvalues of the catalyst kinetics.

References

1. Asbjornsen, O.A. and M. Hillestad (1997): "Reaction Invariance and Stability in Catalyst Particles for Production of Methanol." *AIChE Journal*, Vol. 43, No. 4, pp. 1082-1090.
2. Steensland, T., O. A. Asbjornsen, and S. G. Terjesen (1968): "The Effect of Incomplete Mixing on the Degree of Conversion in Adiabatic Fixed Bed Cold Shot Reactors." *Chemical Reaction Engineering*, Pergamon Press Ltd, Oxford, U.K.
3. Denbigh, K. (1965): *Chemical Reactor Theory – An Introduction*. Cambridge University Press, Cambridge, U.K.
4. Nielsen, A. (1968): *An Investigation on Promoted Iron Catalysts for the Synthesis of Ammonia*, 3rd edition, Jul. Gjellerups Forlag, Copenhagen, Denmark.
5. Vanden Bussche, K. M. and G. F. Froment (1996): "A Steady State Kinetic Model for Methanol Synthesis and the Water Gas Shift Reaction on a Commercial $Cu/ZnO/Al_2O_3$ Catalyst." *Journal of Catalysis*, Vol. 161, pp. 1-10, 1996.

Using Neural Networks to Model Fast Dynamic Systems

J.L. Fontaine, A. Germain

Laboratoire de Chimie Industrielle de l'Université de Liège
Institut de Chimie B6, Sart Tilman, B-4000 Liège, Belgium
Phone number : +32 / 4 366 35 86
Fax number : +32 / 4 366 35 45
E-mail : jl.fontaine@ulg.ac.be

Modelling fast or complex dynamic phenomena has proven to be sometimes difficult and time-consuming, especially when sharp temperature profiles are encountered. In such conditions, mathematical models are often numerically unstable, and the results are hard to obtain and their physico-chemical meaning can be questionable.

We have studied the combustion of hydrogen with air in a fixed-bed reactor, using palladium supported on alumina as catalyst. The reactor is strongly cooled by thermostatised water with high flow rate. With H_2 / O_2 ratios between 5 an 50, and residence time of the gases between 0.1 and 0.5 second, this system is characterised by sharp thermal profiles when stabilised, and its dynamic behaviour is leaded by thermal inertia.

The mathematical modelling of this system is determined by its thermal characteristics, and especially by the coupling of heat release during combustion and heat sensitivity of the reaction rate. The axial dispersion of the heat is also an important parameter. Owing to these characteristics, we modelled this reactor by a set of serial batch reactors whose depth is defined by the mean size of the catalytic particles. This system is quite heavy and time consuming, but it provides two mains advantages : its physico-chemical signification is obvious, which allows to obtain reliable and readily interpretable results, even for discontinuous systems, and, most of all, it works for the difficult conditions encountered here.

Owing to the hypothesis of thermal inertia limitation, in order to determine the temperature and concentrations profiles in the reactor at time t, we need to know these profiles at previous time, t-Δt, and to calculate the hypothetical stationary profiles corresponding to the operating conditions at time t. Analysing the dynamic behaviour of the studied system, we found that we need to calculate profiles every 2 or 3 seconds during the transient phases. But according to the mathematical model used, our computer needed from 6 to 300 seconds to model one stationary working point. And then, even if the developed mathematical model is very interesting in order to be able to understand the behaviour of such a system, it cannot be used to control it when operating under dynamic conditions.

Our laboratory is working for some years with static neural networks in the field of chemistry. As other authors, we found that these ones provide a powerful tool, allowing to model very complex systems when physico-chemical models are not available or too complex to be of practical use. The reliability and the generalisation abilities of well-built neural networks allowed us to lead qualitative investigation about very complex systems, to bring to the fore unexpected phenomena and to discriminate between chemical reaction paths.

A huge advantage of the neural networks, once fitted, lies in their intrinsic speed. Then, very complex system can be modelled numerous times within a few seconds, even with a personal computer. Moreover, for such complex systems, fitting a good neural network does not need more time than to set and to adjust a physico-chemical model.

In order to be able to model the dynamic behaviour of the studied system, we needed to use a dynamic neural network. Such networks use some of the outputs that they calculated before as inputs, to determine the new outputs. Actually, such networks integrate its results over time and can take into account dynamic changes of the operating conditions of the system. It is rather difficult and time-consuming to fit, but the obtained results are quite reliable, and the model runs fast enough to be able to anticipate even the behaviour of fast systems. This ability can be used to finely regulate such dynamic processes, or to avoid the process to diverge.

We obtained very good results using dynamic neural networks. The best one was able to predict quite well temperature and concentrations profile, on a generalisation basis. It allows to reproduce the influence of slow or fast changes in the operating conditions, and the obtained profiles are always in good agreement with experimental data and is always consistant with chemico-physical rules.

THE DYNAMIC INSTABILITY AND STABILIZATION OF PACKED-BED REACTORS

Michael Menzinger and Vladimir Z. Yakhnin
Department of Chemistry, University of Toronto, ON, M5S.3H6
phone & fax: (416) 978.6158; e-mail: menzinger@chem.utoronto.ca

Packed bed reactors with exothermic reactions tend to amplify input perturbations of feed temperature, concentration of flow, i.e. to be dynamically unstable. This gives rise to the notorious moving hot spots which may compromise the safe and efficient reactor operation and it also determines the dynamic response to periodic external forcing. The instability results from the autocatalytic nature of the reaction heat and from the difference of the velocities of the convective transport of the heat and matter which arises from the reactor packing that acts as thermal reservoir. The development of intrinsically more stable packed bed reactors showing a reduced trasient reponse is of considerable importance.

The instability has a convective character. This means that an incoming perturbation is amplified as it is conveyed downstream and is finally washed out by the flow, leaving the reactor in its asymptotically stable steady state. If the noise persists, as is usually the case, the reactor displays noise-sustained, stochastic pattern of temperature and composition waves that ride on the steady-state background. Perturbations are amplified selectively in a resonant manner. Low frequency perturbations slightly displace the steady state as a whole and high frequency perturbations are suppressed by heat conduction. The reactor is most susceptible to perturbations of intermediate frequencies, leading to a resonant domain of moving hot spot activity.

Fig.1 illustrates the evolution of the low amplitude, periodic perturbation of input temperature along the reactor: curve (1) represent a snapshot of the transient temperature wave, (2) are the upper and lower envelopes of (1), and (3) is the steady-state temperature profile. Curve (4) is the difference of upper and lower envelopes (2), i.e. the amplitude of excursion from the steady state (3). It is a local measure of the strength of the convective instability.

The adverse impact of dynamic (and static) instabilities can be minimized through external control systems, the use of mild operating conditions (dilute feeds, low space velocities) or the development of intrinsically more stable reactors. One strategy involves an appropriate choice of catalyst particle size. We describe alternative ways of enhancing the dynamic stability of catalytic reactors. Figure 2 illustrates the capability of this stabilization procedure. It shows the response at the exit of a packed bed reactor to low amplitude white noise perturbations of the inflow temperature. The thin line shows the large-amplitude response of the conventional reactor, and the heavy line illustrates the stabilization that is achieved, under otherwise identical operating parameters (e.g. throughput) of the stabilized version.

OP-2-3

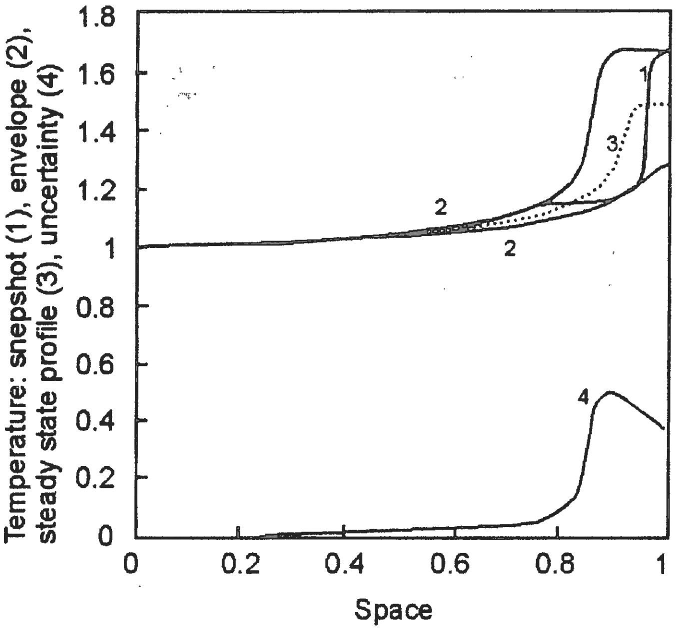


Fig.1

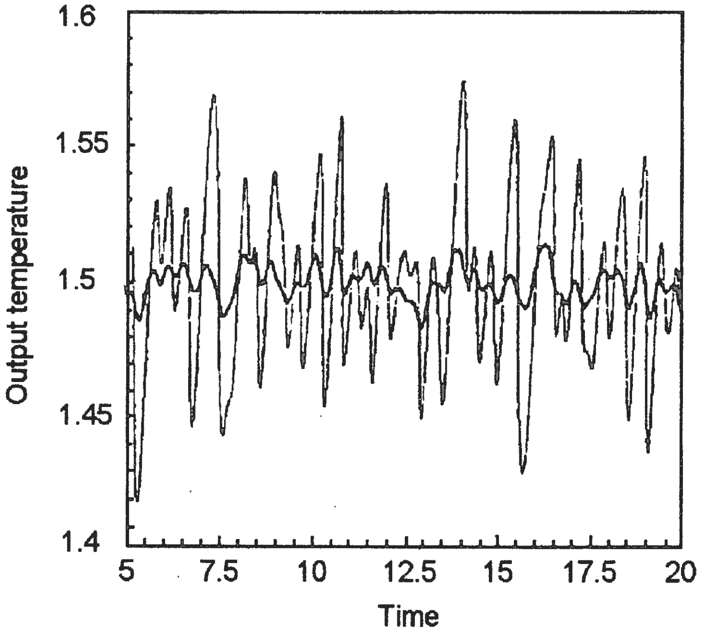


Fig.2

Section 3.
Forced Unsteady-State Operation

Effects of Diffusion on Periodic Operation Performance of NO-CO Reaction over Supported Noble Metal Catalysts

Takashi AIDA, Ryoichi KOBAYASHI, Duangkamol NA - RANONG, Hiroo NIIYAMA
Department of Chemical Engineering, Tokyo Institute of Technology
O-okayama, Meguro-ku, Tokyo 152, Japan
Tel: +81-3-5734-2140, Fax: +81-3-5734-2883, E-mail: taida@chemeng.titech.ac.jp

Most of the investigations under periodic operation of catalytic processes have been made based upon the intrinsic rate of the reaction at the active sites. However, the mode of concentration change under periodic operation of feed concentrations may be considerably varied through the flow reactor and the catalyst pellet if effects of adsorption, diffusion or mixing is significant. Cho *et al.* reported that adsorption and diffusion was not so influential on the global rate of CO oxidation over Pt/Al_2O_3 pellet with various loading depth under periodic operation at constant periods of 1 and 2 s (Cho, 1983; Cho and West, 1986). In this paper, effects of adsorption and diffusion on the global rate of NO-CO reaction over supported noble metal catalysts were investigated by experiments and model calculations. Improvement of the performance of NO-CO reaction under periodic operation have been reported for supported noble metal catalysts, especially platinum (Muraki and Fujitani, 1986).

In order to investigate the effect of intrapellet diffusion, egg-shell type (ES) and egg-white type (EW) of Pt/Al_2O_3 were prepared by the method established (Becker and Nuttall, 1979) from H_2PtCl_6 aqueous solution and Al_2O_3 (JRC-ALO-4, cylindrical, 1.5 mm-diameter, 10 mm-length). A variety of packing order of two different catalysts which show different behaviors under periodic operation were tested. This is regarded as giving information of the effects of diffusion and mixing through the flow reactor. Egg-shell type of Pt/Al_2O_3 and Rh/Al_2O_3 were employed as the catalysts. Periodic operation experiments were conducted by a flow system equipped with solenoid valves. NO and CO diluted by He were alternately fed to the reactor, that is to say box wave (on-off) feeding, with time-averaged C_{NO} and C_{CO} of 500 ppm and 2500 ppm, respectively and with s (split) of 0.5. Total flow rate was 100 ml-NTP·min^{-1}. Reaction temperature was 300 °C. Behaviors of the adsorbed species under the transient condition were observed by a FT-IR with a small diffuse reflectance cell (similar to DRIFTS reported by Marwood *et al.*, 1994).

Model calculation for the effect of intrapellet diffusion was made with the differential reactor approximation using mass conservation equations assuming a simplified mechanism and parameters described in the previous report (Aida *et al.*, 1997). It should be noted that the parameters were chosen to satisfy strong adsorption of CO on Pt and surface reaction controlling under steady condition. For the variation of the packing order of the catalysts, an integral reactor was assumed.

Fig. 1 shows the experimental results for the effect of the intrapellet diffusion on the conversion of NO. There appeared a significant difference between the results of ES and EW at the periods longer than 20 s. ES showed a much higher conversions than EW at long periods. This distinct difference could not be explained only by diffusion of the reactants in the catalyst pore because the time constant of diffusion was calculated as 0.1 s. The similar tendency to Fig. 1 appeared in the calculation results indicating that adsorption.

OP-3-1

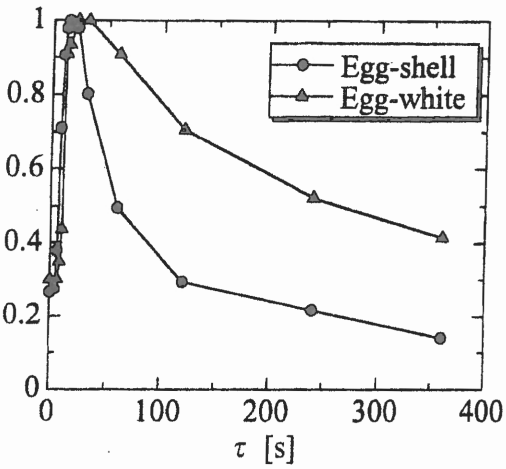


Fig. 1 Effect of intrapellet diffusion on the conversion of NO under the periodic operation of NO-CO reaction over Pt/Al_2O_3. Reaction temperature was 300℃.

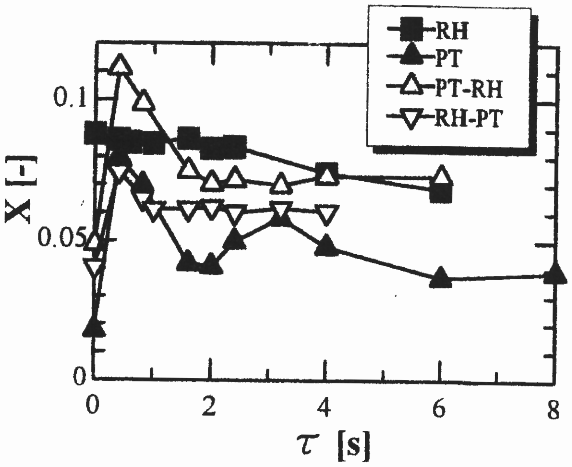


Fig. 2 Effect of the packing order of Pt/Al_2O_3 and Rh/Al_2O_3 under the periodic operation of NO-CO reaction. Reaction temperature was 150℃. Neat Pt/Al_2O_3 and Rh/Al_2O_3 were also shown.

diffusion and surface reaction were dependent on each other.

Results for the variety of the packing order of the catalysts were shown in Fig. 2. The order of PT-RH which means Pt/Al_2O_3 and Rh/Al_2O_3 were packed at the inlet-side and the outlet-side of the reactor. respectively, showed higher conversion of NO than the reversed packing order. Pt/Al_2O_3 showed a distinct periodic operation effect, whereas a slight dependency on the period was observed for Rh/Al_2O_3. The results indicated that the mode of the concentration change under the periodic operation was varied through the reactor possibly due to the diffusion or the mixing of gases fed.

The results obtained here reveals that the effects of adsorption, diffusion and mixing of reactant gases become more considerable under the periodic operation than the steady operation.

References

Aida, T., R. Kobayashi and H. Niiyama, *Kagaku Kogaku Ronbunshu*, to be published (1997a)

Becker, E. R. and T. A. Nuttall, Studies Surf. Sci. and Catal., vol. 3, ed. by P. Jacobs and G. Poncelet, pp. 159, Elsevier, Amsterdam (1979)

Cho, B. K., *Ind. Eng. Chem. Fundam.*, **22**, 410(1983).

Cho, B. K. and L. A. West, *Ind., Eng. Chem. Fundam.*, **25**, 158(1986)

Marwood, M., R. Doepper and A. Renken, *Chem. Ing. Tech.*, **66**, 971(1994)

Muraki, H. and Y. Fujitani, *Ind. Eng. Chem. Prod. Res. Dev.*, **25**, 414(1986)

CYCLIC OPERATION OF THE OXIDATIVE DEHYDROGENATION OF PROPANE

D. Creaser(1), B. Andersson(2), R.R. Hudgins(1), P.L. Silveston(1)

(1) Dept. of Chemical Engineering; University of Waterloo; Waterloo, Ontario, N2L 3G1, Canada

(2) Dept. of Chemical Reaction Engineering; Chalmers University of Technology; S-412 96, Göteborg, Sweden

Introduction: Many metal-oxide oxidative dehydrogenation catalysts are, at least temporarily, active for the reaction without the presence of gas phase oxygen. Apparently, the catalyst surface and bulk oxygen are sufficient to drive the reaction. Vrieland and Murchison [1] have studied the oxidative dehydrogenation of butane during cyclic operation consisting of alternate feeding of oxygen and butane. They have reported some impressive results for this mode of operation with butane selectivities of up to 80% at 50% butane conversion. In this work we have examined the cyclic operation of the oxidative dehydrogenation of propane with a V-Mg-O catalyst. The transient kinetics of the reaction reveal at what conditions cyclic operation of the reaction result in an improved yield for propene compared to steady-state operation.

Experimental: A quartz microreactor was used containing 30 mg of V-Mg-O catalyst. The reaction temperature was 510°C, the total flowrate 50 ml min^{-1} STP and pressure near atmospheric. A four-way valve located upstream of the reactor allowed feed to the reactor to be switched between gas mixtures containing 6% propane and 6% oxygen in helium. A quadrupole mass spectrometer monitored the transient responses of each component.

Results: Comparisons of the performance of the reaction under steady-state and transient operation without gas-phase oxygen indicated that the propene selectivity of the reaction was superior in the absence of gas-phase oxygen even at the same levels of conversion of propane. These findings suggested that cyclic operation of the reaction was a promising strategy for obtaining improved yields of propene. Figure 1a shows the transient responses of the products during cyclic operating at a 130 s cycle period and a 1:1 cycle split. The products have an overshoot response during the propane-feed half of the cycle. Immediately after exposure to propane, the activity is high due to the high concentration of surface oxygen. As the supply of

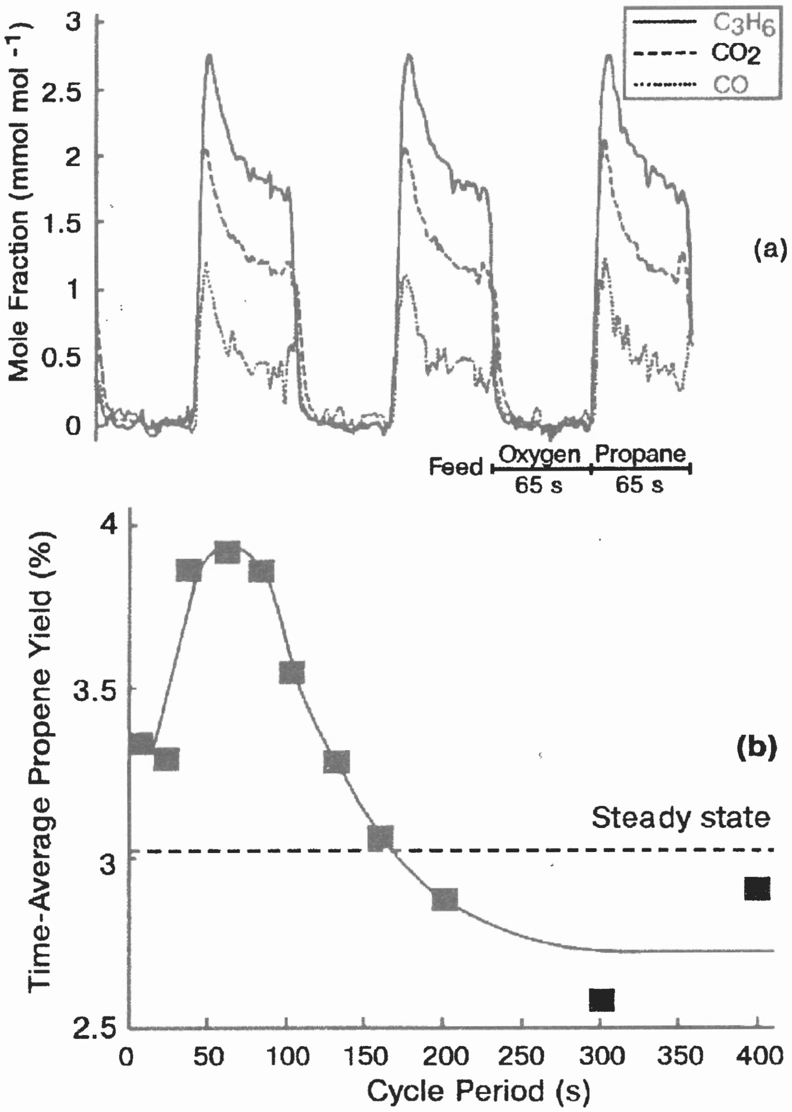


Figure 1. Product transient responses (a) and propene yield during cyclic operation (b)

surface oxygen is depleted the product concentrations decrease rapidly. The propene selectivity was from 70 to 80 % throuhout most of the period of reaction. Figure 1b shows the propene yield for cyclic operation compared to the yield obtained at the time-average steady state conditions which consist of constant feed concentrations of 3% propane and 3% oxygen. At long cycle periods the propene yield is lower than at steady-state conditions. However, due to the overshoot response of the products, as the cycle period is shortened, the time-average propane conversion increases and at a cycle period less than 150 s, the propene yield for cyclic operation exceeds that for steady-state. At very short cycle periods, less than 40 s, the propene yield decreases sharply, due to mixing and dispersion effects in the reactor that cause the feed to be no longer truly cyclic and more like steady-state.

Conclusions: It was found that by cyclic operation of the reaction at a 1:1 cycle split, a higher propene yield could be obtained compared to comparable time-average steady state conditions, at a range of cycle periods.

References:

[1] G.E. Vrieland, C.B. Murchison, Appl. Catal. A, 134 (1996) 101.

OP-3-3

Reactor performance enhancement under periodic operation for the ethanol dehydration over γ-alumina, a reaction with a stop-effect

Serge Golay, Ralf Doepper and Albert Renken
Institute of Chemical Engineering, EPFL, CH-1015 Lausanne, Switzerland
phone: +41-21-693 31 81; fax: +41-21-693 3190; e-mail: albert.renken@epfl.ch

The ethanol dehydration to ethene on γ-alumina presents a stop-effect behaviour, i.e. a drastic increase of the reaction rate when the feed concentration of a reactant is switched to zero. This temporary increase of the reaction rate under transient conditions was first reported by Koubek et al. [1] for the catalytic dehydration of alcohols and the deamination of amines on aluminas, zeolites or more generally, on amphoteric metal oxide catalysts. It was shown in a previous work [2] that it can be best described by a two sites model.

$$A + S_1 \xrightarrow{k_1} AS_1 \qquad \text{A: ethanol} \qquad (1)$$

$$A + S_2 \xleftrightarrow{K_2} AS_2 \qquad \text{E: ethene} \qquad (2)$$

$$AS_1 + S_2 \xrightarrow{k_3} E + W + S_1 + S_2 \qquad \text{W: water} \qquad (3)$$

$$2A \xrightarrow{k_4} D + W \qquad \text{D: diethylether} \qquad (4)$$

The ethanol can adsorb either strongly on acid sites (Eq. 1) or weekly on basic sites (Eq. 2), and a free basic site is required for the ethene formation (Eq. 3). The diethylether formation can be described, for simplicity, by a quasi-homogeneous reaction term (Eq. 4). At steady-state the reaction rate is slow due to the low concentration of free S_2 sites. The desorption of the weekly adsorbed species under inert gas is responsible for its temporary increase.

In Figure 1, the influence of the initial ethanol concentration on the ethene formation is shown. It can be seen that an optimum steady-state exists at low initial ethanol concentration, due to the educt inhibition. The maximum ethene concentration reached during the stop-effect can be up to 20% higher than this maximum steady-state concentration. Therefore the use of forced concentration oscillations of the inlet feed may lead to an increase of the reactor performance in comparison to its optimum steady-state value.

Theoretical calculations have already been presented by Thullie and Renken [3] for a differential reactor. It was shown that under relaxed steady-state conditions and with an optimum cycle-split, the rate enhancement factor increases monotonically beyond the maximal rate for optimum steady-state conditions. The relaxed steady-state operation requires the use of very short periods hardly obtainable from a practical point of view, due to the fact that the residence time distribution of the reactor usually mask them. Therefore the objective of this work was to study the use of periodic operation in an integral reactor to determine whether a reactor performance enhancement is possible under realistic conditions.

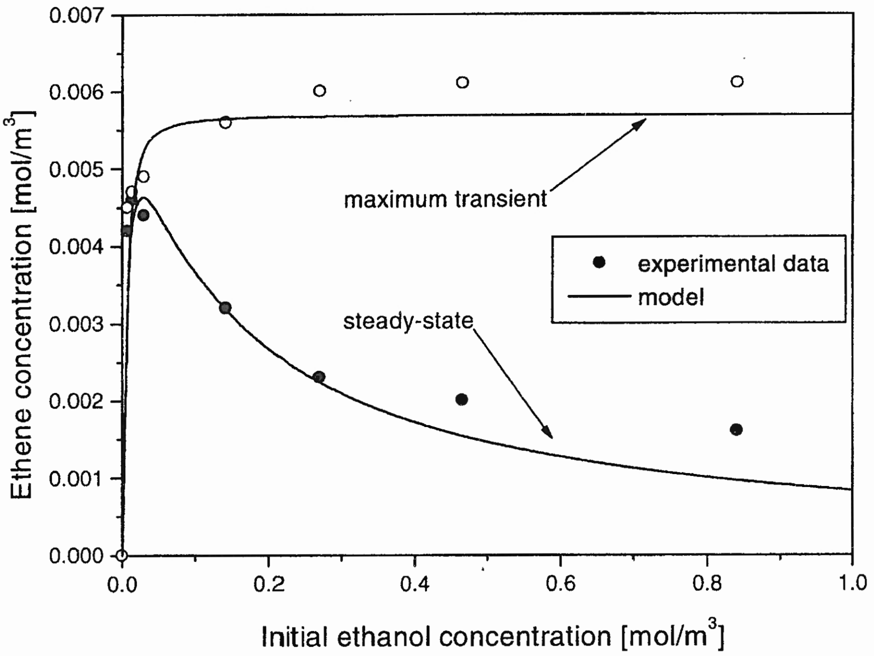


Figure 1. Influence of the initial ethanol concentration on the ethene formation in an integral tubular reactor (T_R=180°C, Q_{tot}=200ml(NTP)/min). =steady-state concentration, o maximum transient concentration.
$k_1=2.0\cdot10^{-2}m^3/kg\cdot s$, $K_2=7.15m^3/mol$, $k_3=4.80\cdot10^{-5}mol/kg\cdot s$, $k_4=1.1\cdot10^{-3}m^3/kg\cdot s$, $n_4=1$, $Z_l=0.86mol/kg$, j=0.84.

The average ethene performance was measured as a function of the three main variables that arise in periodic operation: period, split and mean initial concentration. Each parameter effect will be discussed carefully to develop a methodology for the determination of the optimal conditions for the periodic operation. The predictions based on the simulations calculated with model parameters determined on transients will be compared to the periodic experiment results.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the funding from the Swiss National Science Foundation and the Max Buchner Forschungsstiftung, Frankfurt, Germany

REFERENCES

1. J. Koubek, J. Pasek and V. Ruzicka, in New Horizons in Catalysis, Elsevier-Kodansha, Amsterdam-Tokyo, 1980, p. 853
2. S. Golay, O. Wolfrath, R. Doepper and A. Renken, in Studies in Surface Science and Catalysis, 109, Elsevier, Amsterdam, 1997
3. J. Thullie and A. Renken, Chem. Eng. Sci., 46(1991)1083

Selective Hydrogenation of Ethyne in a Pressure Swing Reactor

A.J. Kodde and A. Bliek

Department of Chemical Engineering, Nw.Achtergracht 166, 1018 WV Amsterdam, University of Amsterdam, The Netherlands, E-mail: sec@chemeng.chem.uva.nl, Tel: +31-20-525 5265, Fax: +31-20-525 5604.

Introduction

The *in-situ* removal of reaction products from the reaction medium is an established way to prevent subsequent further reaction to undesired products or to promote an equilibrium to shift in the desired direction. Such *in-situ* removal may have a continuous nature, as in case of reactive distillation or for membrane reactors, but it may also be achieved through discontinuous operation. One case of *in-situ* separation which is discontinuous is the selective adsorption onto solid adsorbents, which needs to be followed by a regeneration step. In the present work we propose and analyze the use of a mixed bed of adsorbent and catalyst particles to achieve simultaneous reaction and temporal in-situ removal. Regeneration of the adsorbent is achieved by operating the fixed bed in a pressure swing mode, with adsorption during the high pressure half-cycle and desorption (regeneration) during the low-pressure half-cycle. In this way a transient pressure swing process is obtained, with promise of enhanced selectivity or conversion. In principle, similar advantages can be expected as have been demonstrated for membrane reactors. However as a perm-selective barrier as in the case of membrane reactors is absent, the technical feasibility of realizing such a process increases and current practice in pressure swing separation shows that pressure swing operation is realistic.

Whereas pressure swing reactors have received some attention in case of equilibrium limited reactions [1], its use in irreversible reactions has only marginally been explored. In a theoretical analysis we have shown that selectivity enhancement is indeed achievable in consecutive reaction schemes[2] using a Pressure Swing cycle employing co-current regeneration and purge steps.

Selective hydrogenation of ethyne

In this work selectivity enhancement in a consecutive reaction is studied experimentally using the selective hydrogenation of ethyne to ethene.

$$C_2H_2 + H_2 \xrightarrow{Pd/Al_2O_3} C_2H_4 + H_2 \xrightarrow{Pd/Al_2O_3} C_2H_6$$

The removal of ethyne from the ethene stream obtained in cracking plants is an important step in the manufacture of polymer grade ethene. Ethyne hydrogenation must be be highly selective since the ethyne content has to be reduced to less than 5 ppm, while higher ethene losses are economically intolerable.

This reaction is catalyzed by palladium based catalysts and proceeds at low temperatures[3]. In adsorption based *in-situ* separations this is important in view of the sufficient adsorption capacity at these temperatures. Low alumina MFI zeolites exhibit a selective adsorption towards acetylene over ethene due to differences in adsorption kinetics. Improvement of the selectivity is based on increased residence time of ethyne in the unit.

We have developed a mathematical model of PSR unit using experimentally determined parameters for both catalyst and adsorbent.

Results of mathematical modelling as well as experimental data on a small scale PSR unit concerning the performance of the pressure swing reactor are presented. The adsorbent selectivity required is a critical parameter. Factors like productivity, selectivity enhancement and purity of the product streams will be discussed.

References

[1] Chatsiriwech, D, E. Alpay, L. S. Kershenbaum, C. P. Hull and N. F. Kirkby, Enhancement of Catalytic reaction by pressure swing adsorption, *Catal. Today*, **20**, 351-366, (1994)

[2] A. J. Kodde, A. Bliek, Selectivity Enhancement in Consecutive Reactions using the Pressure Swing Reactor, *Stud. Surf. Sci. Cat.*, **109**, 419-428, (1997)

[3] A. N. R. Bos, K. R. Westerterp, Mechanism and kinetics of the selective hydrogenation of ethyne and ethene, *Chem. Eng. Proc.*, **32**, 1-7, (1993)

OP-3-5

SO₂ OXIDATION METHOD. MATHEMATICAL MODELING TAKING INTO ACCOUNT DYNAMIC PROPERTIES OF THE CATALYST

N.V. Vernikovskaya, A.N. Zagoruiko, A.S. Noskov

Boreskov Institute of Catalysis, Novosibirsk, 630090, Russia

In Boreskov Institute of Catalysis a method of sulphur dioxide oxidation in sulphuric acid production is offered [1] which allows to lower the SO_2 concentration in waste gases to 50 ppm. The method is based on the use of the unsteady state of the catalyst. The main difference of this method from conventional methods of "double contact - double absorption" is the organization of the second stage. It consists of two catalyst beds (Fig.1). The feed to each bed is cycled between air used for catalyst activation and gas mixture after intermediate absorption. The directions of air and gas mixture filtration are opposite. The air after catalyst bed is fed to sulphur burner.

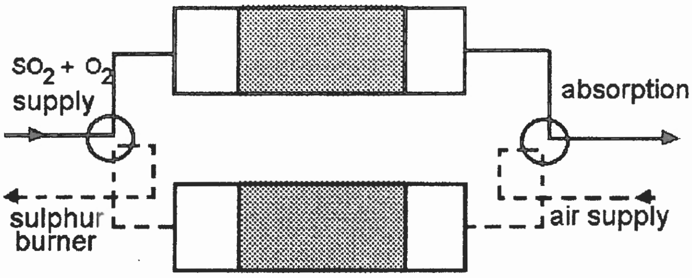


Fig.1. Schematic diagram of the second stage of "double contact - double absorption" method [1].

This report is devoted to mathematical modeling of this scheme taking into account unsteady state of the catalyst. The unsteady state kinetic model of SO_2 oxidation over vanadium catalyst [2] is used to describe dynamics of the catalyst state. We use one dimensional heterogeneous mathematical model [3] to describe the processes in the catalyst bed. This model assumes plug flow in the reactor. An active component of the catalyst is in a liquid molten state and the model takes into account the inertia of the liquid phase concentration of SO_3 and of the reaction intermediates, the inertia of the solid phase temperature. Equilibrium states of fast processes of SO_2 and O_2 dissolution in the melt and those of active component formation are present in the model.

We investigate how the SO_2 conversion (average over the period when reaction mixture is blown through the catalyst bed) depends on the space time, the input temperature of the gas mixture and air, the period of filtration, the input SO_2 concentration.

Figure 2 shows the dependence of the average SO_2 conversion on the input temperature of gas mixture and air. One can see, that at short periods conversion slightly depends on the input temperature in the interval from 100°C to 600°C (line 1). As the period increases, the temperature range where conversion is maximum, narrows and shifts to higher temperatures (lines 2-4). But at long periods the SO_2 conversion can be increased even under low input temperature if we increase the space time (compare lines 3 and 3a). Conversion attained either at short periods and space times (t_p=2.5 min; τ_s=1 s) or at long periods and space times (t_p=10 min; τ_s=4 s) far exceeds the equilibrium value and ensure the output residual concentration of SO_2 less than 50 ppm. It can be explained in the following way. Large quantities of SO_2 are sorbed onto the active component of vanadium catalyst when it is exposed to gas mixture, and besides sulphur dioxide oxidation the formation of inactive with respect to SO_2 vanadium complexes occurs. This results in a reduction of catalyst activity. In order to activate the catalyst, air is fed into the catalyst bed. The SO_2 desorption starts, the formation of active with respect to SO_2 vanadium complexes occurs and catalyst activity increases. As the air blow direction is opposite to gas mixture one the high temperature zone does not leave the catalyst bed, so the process can be effectively carried out even under low input temperature.

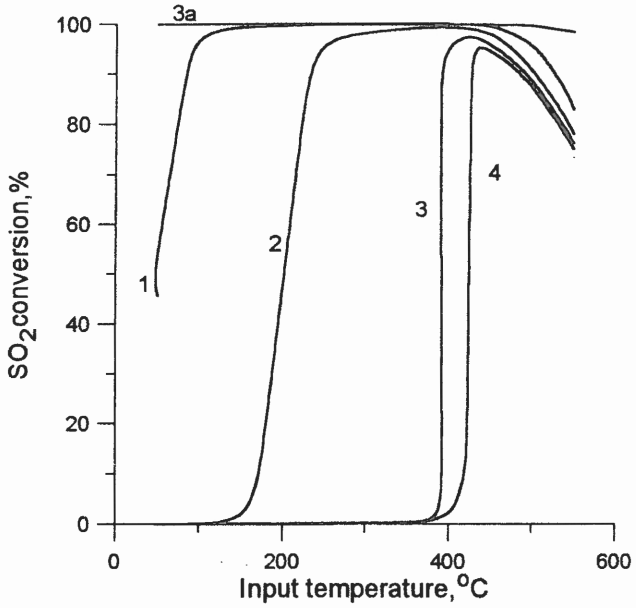


Fig.2. The dependencies of the average SO_2 conversion on the input temperature for different periods of filtration (t_p) and space times (τ_s):
τ_s = 1 s: t_p = 2.5 min (1), t_p = 5 min (2), t_p = 10 min (3), t_p = 15 min (4);
τ_s = 4 s: t_p = 10 min (3a);
C_{SO_2} = 1 % vol., C_{O_2} = 3 % vol. (when gas mixture supply);
C_{O_2} = 21 % vol. (when air supply);

References: [1]. Goldman O.V., Bunimovich G.A., Zagoruiko A.N., Lakhmostov V.S., Vernikovskaya N.V., Noskov A.S., Kostenko O.V. // Patent RF N2085481, C01B17/76, B.N21, 1997, [2].Balzhinimaev B.S., Ivanov A.A., Lapina O.B., Mastikhin V.M., Zamaraev K.I.//Faraday discuss. Chem. Soc., 87, 133-147, 1989; [3].Bunimovich G.A., Vernikovskaya N.V., Strots V.O., Balzhinimaev B.S., Matros Yu.Sh. //Chem. Engng. Sci., v.50, No 4, pp. 565-580, 1995.

High Yields in the Catalytic Partial Oxidation of Natural Gas to Formaldehyde: Catalyst Development, Reactor Configuration and Operation Mode

A. Parmaliana[1], F. Arena[1], F. Frusteri[2] and A. Mezzapica[2]
[1]Dipartimento di Chimica Industriale, Università di Messina – Italia
[2]Istituto CNR-TAE, Messina – Italia

Among the various catalytic routes proposed during the last decades for the conversion of the natural gas to higher hydrocarbons, fuels or oxygenates, the direct partial oxidation to formaldehyde (MPO) has attracted a great research effort since the need to find a viable alternative to the current multi-step process for producing HCHO. The research interest has been generally addresses to disclose active and/or selective catalysts /1/, while no or limited attention has been devoted to the reactor and process configuration as well as to the optimisation of the operating conditions. In particular, the issue dealing with the kinetic control of the process has been often neglected in spite of its crucial relevance for the attainment of high yields to HCHO.

The superior performance of silica based oxide catalysts in the MPO reaction is generally recognised /1,2/. We have largely contributed to this issue highlighting the factor controlling the reactivity of bare commercial silica samples and silica supported MoO_3 and V_2O_5 catalysts as well as the reaction pathway and the nature of active sites /3-5 /. Furthermore, we have already documented how high HCHO yield values, adequate for the industrial exploitation of the reaction, can be achieved operating in non steady-state mode by means of a dynamic control of the process which hinders the evolution of the partial oxidation towards the formation of CO_x /6/.

Several original attempts have been recently made for enhancing the yield in the direct catalytic conversion of methane into higher hydrocarbons or oxygenates /7-8/. However, since the higher reactivity of the reaction products with respect to CH_4 molecule, yield values to C_2 and CH_3OH and/or HCHO so far reported are limited to 20-25% and 2-3 %, respectively. In particular, the recycle of the reaction mixture along with the separation or selective adsorption of the product resulted in significant improvements in the C_2 yield in methane oxidative coupling /9/. No similar approaches have been still reported in the literature for maximising the HCHO yield in MPO reaction.

This paper is aimed to outline the research activity performed to develop silica oxide catalysts suitable for pre-industrial exploitation of the MPO reaction as well as to assess the influence of reactor configuration and reaction mode on the HCHO yield. Basic insights about the need **(i)** to perform the reaction in non steady-state conditions under dynamic control of the reactor and **(ii)** to adopt a catalytic system which possesses peculiar features in terms of activity and stability along with a moderate oxidising power will be also provided.

The performance of silica based oxide catalysts in the T_R range 600-720 °C has been evaluated by using continuous flow reactor (CFR) and continuous flow recycle reactor (CFRR). The tuning of the recycle ratio ($R= r_f / r_r$ where r_f and r_r refer to feed flow rate and recycle flow rate respectively) and GHSV has permitted to attain very high HCHO yields. Then, the optimum recycle ratio as well as the influence of the reaction temperature, GHSV, feed composition and reactor configuration on the catalytic performance of such SiO_2 based catalytic systems have been ascertained.

It is noteworthy to consider that HCHO yields up to 17% (CH_4 conv., 33%; HCHO sel., 52%) have been obtained operating in the continuous flow recycle mode. Such HCHO yield values are one order of magnitude higher than those so far vindicated for the direct conversion of methane to oxygenates in continuous running reaction systems.

Considering the potential for the industrial exploitation of the MPO process, the following critical issues have been addressed:

1. Reactor configuration;
2. HCHO Separation System

A Preliminary process scheme along with the economical feasibility of the MPO process are also discussed.

References

1. R.G.Herman, Q. Sun, C. Shi, K. Klier, C-B. Wang, H. Hu, I.E. Wachs and M.M. Bhasin, Catal. Today, 37(1997)1
2. A. Parmaliana, F. Frusteri, A. Mezzapica, M.S. Scurrell and N. Giordano, J. Chem. Soc., Chem. Commun., 9(1993)751
3. A. Parmaliana, V. Sokolovskii, D. Miceli, F. Arena and N. Giordano, J. Catal. 148(1994)514
4. F. Arena, N. Giordano and A. Parmaliana, J. Catal. 167(1997)66
5. A. Parmaliana, F. Arena, F. Frusteri, G. Martra, S. Coluccia and V. Sokolovskii, 3rd World Congress on Oxidation Catalysis , Stud. Surf. Sci. Catal. 110(1997)347
6. A. Parmaliana, F. Frusteri, A. Mezzapica, D. Miceli, M.S. Scurrell and N. Giordano J. Catal. 143(1993)262
7. M.L.M. Green, S.C. Tsang, P.D.F. Vernon and A.P.E. York, Ind. Eng. Chem. Res. 32(1993)1030
8. Y. Liu and S. Shen, Appl. Catal A : General, 121(1995)57
9. A. Machocki, Appl. Catal. A: General, 146(1996)391

Section 4.

Reactors with Flow Reversal

OP-4-1

AMMONIA - OFF GAS PURIFICATION BY REVERSE-PROCESS

L.N.Bobrova, A.S.Noskov, E.S.Borisova

Boreskov Institute of Catalysis, SB RAS Novosibirsk, 630090, Russia,
***Fax:** (3832)357678, **E-mail:** bobr@reverse.nsk.su*

Ammonia, as well as SO_2 and NO_x is involved in the course of the acidification of our environments. This impurity is inherent in the waste of both agriculture and industry, for example, production of the fertilizers. The utilization of ammonia is economically attractive, as a rule, at the concentration in excess of 1 %v/v. In the present work the removal of ammonia from the oxygen-containing gas with low temperature by the reverse-process [1] is discussed. There are some peculiarities of the catalytic oxidation of ammonia in the reverse-process, which are to be taken into account at the process engineering. The ammonia oxidation occurs in the directions:

$NH_3 + 0.75\ O_2 = 0.5N_2 + 1.5\ H_2O$ - 76 kcal/mol
$NH_3 + O_2 = N_2O + 1.5\ H_2O$ - 64 kcal/mol
$NH_3 + 1.25\ O_2 = NO + 1.5\ H_2O$ - 54 kcal/mol

The final products are defined primarily by selectivity of the catalyst used. For the time being the catalyst developed peculiar to the mild ammonia oxidation to nitrogen has been unknown. Some difficulties should be overcome to develop such catalyst. For example, reactivities in ammonia conversion for metals, metal oxides, and a composite oxide catalysts increase coincident with a decrease in the selectivity to nitrogen. Furthermore, ammonia has very high sticking coefficient. The adsorption property and the surface capacity of the catalyst to ammonia are of great importance to the developing and operation of the reverse-process. Figure show certain of results obtained at the study of such phenomenon by mathematical simulation. One-dimensional two phase mathematical model taking into account the dynamics of catalyst surface according to the kinetic scheme

$NH_3 + [\ ] \leftrightarrow [NH_3]$
$[NH_3] + 0.75\ O_2 \rightarrow 0.5\ N_2 + 1.5\ H_2O + [\ ]$

has been used for analysis. At the operation of reverse-process the temperature on the ends of catalyst bed can change over wide limits. During time between reversing the gas flow through the fixed beds the ends of catalyst bed are heating from 208 to 343 ^{0}C and cooling thereafter (see Figure A). Ammonia surface coverage on the same part of the catalyst bed follows the temperature (B). After reverse flow the front of the catalyst bed become the back along the gas flow trend. Ammonia accumulated on the catalyst can desorb and be observed at the outlet.

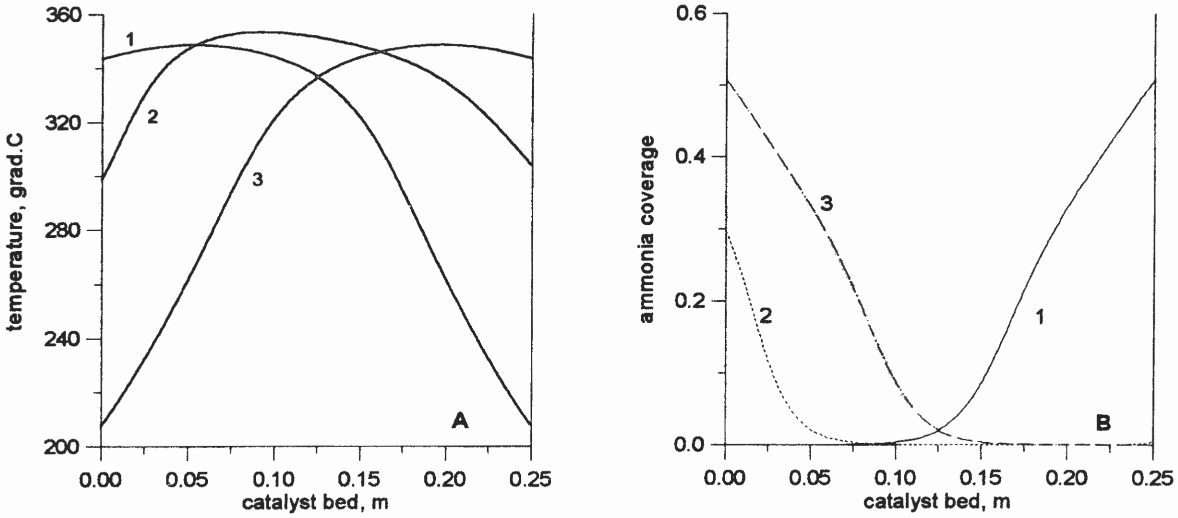


Fig. Temperature (A) and ammonia coverage (B) profiles versus catalyst bed. Total inert bed - 0.8 m. Gas temperature input -100 ^{0}C, ammonia concentration input -0.3 % v/v, time between reverse -8 min.

Theoretical study of the ammonia removal by catalytic oxidation on the reverse-process principle have been experimentally verified in the pilot plant on capacity of 30 nm^3/h. The 0.1%Pd/7%V_2O_5/Al_2O_3 [2] and 10%V_2O_5/Al_2O_3 (AVK-10) catalysts were chosen for the test. The Raschig rings with a size of 15x15x3 were used as a heataccumulating inert material. Autothermal high-temperature cyclic regimes performed at ammonia concentration of 2-8 g/nm^3 in air and the input temperature of 10 ^{0}C.

Table

Catalyst (5x10)	Contact time, s	Time between reverse, min	Maximal temperature, ^{0}C	Ammonia conversion , %	Selectivity to N_2O, %
10%V_2O_5/Al_2O_3	0.62	14	550	98.5	4
0.1%Pd/7%V_2O_5/Al_2O_3	0.5	34	430	98.5	4.7

The results presented in Table show that at the same ammonia conversion the catalyst load of 10%V_2O_5/Al_2O_3 exceeded one as compared with 0.1%Pd/7%V_2O_5/Al_2O_3. In addition, to provide the high conversion the time between reversing the gas flow through the fixed beds was to diminished (see Table).

References.

1. Matros Yu.Sh., Bunimovich G.A., Noskov A.S., Catal.Today, 17 (1993) 261.
2. L.A.Sokolova, O.V.Nevskaya, N.M.Popova, T.M.Ldokova, T.A.Kravchenko: Russ. Pat. 2050186, (1995).

CATALYSTS FOR VOC CONTROL UNDER UNSTEADY-STATE OPERATION

V.A.Chumachenko, G.G.Isaeva, T.V.Mulina and M.G.Makarenko
Katalizator Company, 1 Tikhaya Str., Novosibirsk 630058, Russia
Phone: +7(3832) 329445, fax: +7(3832)332252, e-mail: vic@katcom.nsk.ru

Catalysts to be used in various applications of VOC control under unsteady-state conditions should meet some specific requirements, mainly:

- high activity with respect to various contaminants in gas mixture;
- stability with respect to jumps of temperature and concentration during periodic reaction waves migration;
- low pressure drop along the catalyst bed;
- high resistance against catalytic poisons, possibility of multiple *in situ* regeneration.

A brief analysis of the catalysts' behavior in industrial plants for VOC & CO removal has been made in [1]. Technological aspects of the process for VOC control in gas containing sulfur poisons have been presented in [2].

This paper (i) concentrates upon more detailed study of the commercial Cu-Cr-Al oxide catalyst state during long-term operation in the presence of sulfurous compounds; (ii) provides a new approach to the sulfur-resistant catalyst development and testing; (iii) compares alternative Mn-Al oxide catalysts of various geometrical forms.

Samples of commercial ring-shaped catalyst ICT-12-8 were taken from DynaCycle® reactor for cleaning of asphalt production gases [2]. Samples that were in service 10, 27, 35 months (#2, #3, #4) and underwent multiple sessions of regeneration *in situ* have been tested and compared to the fresh one (#1). Also, sample #4 was calcinated in air flow during 4 hours at 600 ^{0}C (#4a) and 750 ^{0}C (#4b).

Experimental study included: catalytic activity measurements in a model reaction of n-butane complete oxidation; porous structure and specific surface; XRD phase analysis; differential thermal analysis (DTA); X-ray micro-analysis.

Decay in activity was caused by the presence of H_2S, CS_2 and other sulfur-bearing compounds converting to sulfur oxides in the course of VOC removal. Catalyst activity after 35 months decreased by the factor of 4-4.5 compared to the fresh one, and reached «the plateau» value that was high enough to maintain a satisfactory performance of the reactor.

DTA showed the existence of weakly adsorbed compounds of carbon and sulfur, revealing the endothermic effect within 150-600 ^{0}C. Also, in the range 600-810 ^{0}C there were found both endothermic and exothermic effects that could be attributed to a more strong interaction of sulfur compounds with the active components of the catalyst, as well as to a sulfatization of alumina support.

XRD phase analysis of the catalyst #4 showed the presence of initial γ-Al_2O_3, CuO and $CuCr_2O_4$. Besides, new phases of $Cu_2Cr_2O_4$, $Cr_2(SO_4)_3$, $CuSO_4.nH_2O$, $Cu_{1.93}S$ and $Al_2(SO_4)_3$ could be identified. Phase composition of the catalyst #4b (regenerated at 750 ^{0}C) included γ-Al_2O_3 (probably, traces of θ-Al_2O_3), CuO, $CuCr_2O_4$. Its activity has been substantially restored in 2.5 times.

Sulfur and carbon distribution across the particle wall thickness was investigated by the method of X-ray micro-analysis. Local and average mass fractions of elements were measured. Maximum content of sulfur in fragments reached 8.85%, carbon - 21.2%. Average values were, respectively, 2.59% and 3.57%. After regeneration (sample #4b) sulfur content decreased to 0.36%, carbon content - to 1.2%.

Physical-chemical studies of Cu-Cr-Al catalyst provided new data for understanding of deactivation and regeneration processes. These results are in a good correlation with kinetic measurements and industrial experience. Catalyst ICT-12-8 proved to be still rather active after 3-year work in quite unfavorable conditions.

Chemical analysis of the samples #2, #3, #4 confirmed our previous observations that compounds of Cr (VI) have been completely reduced to Cr (III) during on-stream operation. However, many legislation laws do not allow the presence of highly toxic Cr (VI) compounds in a fresh catalyst. That is the reason that search of a sulfur resistant Cr (VI) - free catalyst is still one of the main challenges for unsteady-state processes progress in future.

The next section of the paper gives some preliminary results of development and testing a catalyst that should meet requirements mentioned above. Our approach is based on CuO as a major constituent of active component and a support stable to sulfur compounds. Copper oxide can also react with SO_2 and SO_3 (in excess of air) at 300-500 ^{0}C forming sulfates, thus decreasing the catalyst activity at rather low temperatures. However, at higher temperatures 600-650 ^{0}C they will easily destroy to initial copper oxide and activity will increase.

Testing procedure consists of (1) steady-state kinetic measurements in the reactions of CH_4, C_3H_8 and C_4H_{10} complete oxidation; (2) study of the catalyst activity in CH_4 oxidation during several cycles of periodic SO_2 impact and catalyst regeneration.

The last section of the paper is devoted to hydrodynamic and kinetic studies of Mn-Al oxide catalysts formed as 15x15 mm Raschig rings (#1) and as 25x25 mm rings with 3-mm cross-type walls inside (#2). Pressure drop along the beds filled with catalysts #1, #2 was measured in the range of linear gas velocities 0.2 - 3.2 m/s. Coefficient of the air resistance for catalyst #2 was higher than that for catalyst #1 by factor of 1.28. However, the activity (in n-butane oxidation) related to a volume of catalyst #2 was much higher than that of catalyst #1. Critical crushing strength of the catalyst with walls inside was more favorable, as well.

Catalyst #2 being commercialized in definite cases gives an opportunity either to replace existing units by a smaller quantity of the catalyst, or to increase the total activity of the unit. Upgrading of regenerating thermal incinerators to regenerating catalytic reactors also seems to be a good choice.

Further investigation of oxide-type catalysts named in this paper is under way.

Authors wish to thank Prof. Yu. Matros for providing the catalyst samples, Dr. G.Goldenberg, Dr. O.Klenov and Dr. A.Abramov for experimental assistance.

References:

1. V.A.Chumachenko and L.Yu.Zudilina, Proc. of USPC-2, St.Louis, USA, 1995, P40.
2. Yu.Matros, V.Strots, G.Bunimovich, S.Medvetz, C.Roach, C.Covarik and V.Chumachenko, Proc. of CatCom'96, New Orleans, USA, 1996.

OP-4-3

EFFECT OF THE INTRAPARTICLE MASS TRANSPORT LIMITATIONS ON THE TEMPERATURE PROFILES AND CATALYTIC PERFORMANCE OF THE REVERSE - FLOW REACTOR FOR PARTIAL OXIDATION OF METHANE TO SYNTHESIS GAS

Krzysztof Gosiewski[a], Ulrich Bartmann[b], Marek Moszczyński[a] and Lesław Mleczko[b]

[a] Institute of Inorganic Chemistry - ul. Sowińskiego 11; 44-101 Gliwice - Poland
tel. (+48 32) 31 30 51 E-mail: gosiew@kuria.gliwice.pl

[b] Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum - Germany

Abstract

So far the reverse-flow reactors have been applied in industry mainly for catalytic SO_2 oxidation and volatile organic compounds removal from industrial flue gases. However, other possible applications are still being investigated. In the 90's an attempt at application of this solution for the methane conversion to synthesis gas was also undertaken in several research centres world-wide. The process occurs in the wide range of temperatures, often above 1300 K, so any industrial or pilot plant work should be preceded by careful mathematical simulation. Unfortunately, the solution encounters severe numerical problems, and the model cannot be easily solved with reliable results. The problem can be described by the set of Partial Differential Equations, at least some of them of parabolic type (depending on the assumptions made). The solution of the first version of the model, which applied *semi-implicit* Euler's method revealed that the steep gradients of the state variables in some parts of the bed make the problem numerically difficult. To obtain stable and reliable solution a very dense numerical grid should be applied. Moreover, in the region of a steep temperature rise and then its rapid decrease the accuracy of the solution was still dubious. The PDEX numerical package implementing a fully adaptive algorithm for parabolic partial differential equations developed in *Konrad-Zusse-Zentrum für Informationstechnik* in Berlin (see [1]) seemed to be more appropriate to the problem, since it gives solution with a numerical error assumed *á priori*.

The heterogeneous model for the heat and mass transfer consists of the following PDE's:

$$\underbrace{\varepsilon \cdot \rho_g \, c_{pg} \cdot \frac{\partial T_g}{\partial t}}_{\approx\ 0} = - \dot{n}_g \cdot C_{p,g} \frac{\partial T_g}{\partial z} + \alpha S(T_c - T_g) \qquad (1)$$

$$\rho_s c_k \frac{\partial T_c}{\partial t} = \lambda_e \frac{\partial^2 T_c}{\partial z^2} + \alpha S(T_g - T_c) + \rho_s \sum_j \eta_j \, r_j (-\Delta H_j) \qquad (2)$$

$$\underbrace{\varepsilon \cdot \rho_g \cdot \frac{1}{\dot{n}_g} \frac{\partial \dot{n}_{i,g}}{\partial t}}_{\approx\ 0} = \underbrace{\varepsilon \cdot \rho_g \cdot D_{eff} \frac{1}{\dot{n}_g} \cdot \frac{\partial^2 \dot{n}_{i,g}}{\partial z^2}}_{\approx\ 0} - \frac{\partial \dot{n}_{i,g}}{\partial z} + k_{g,i} \cdot S \cdot (x_{i,s} - x_{i,g}) \qquad (3)$$

for i = 1 to 6 (i.e. for the following components: CH_4, O_2, CO, H_2, CO_2, H_2O)

and algebraic equations taking into account the gas to solid mass transfer:

$$x_{i,s} = \frac{\rho_s \cdot \sum_j \upsilon_{i,j} \cdot \eta_j \cdot r_j}{k_g \cdot S} + x_{i,g} \qquad \text{where:} \quad k_{g,i} = \beta_i \cdot P \cdot / (R \cdot T) \tag{4}$$

with an appropriate commonly used initial and boundary conditions. The symbols appearing in the above equations will be described in the full text of the paper.

At present the model is solved taking into account the following reactions: total CH_4 oxidation to CO_2 , steam and CO_2 reforming and water gas shift reaction. The r_j reaction rate equations were developed based on kinetic studies in a micro-catalytic fixed-bed reactor at the University of Bochum for platinum catalyst. It is known from the literature that the process has severe diffusional limitations, so simplifying the problem the actual value of the effectiveness factor η_j for each reaction had to be implemented to the model. The wide range of the catalyst temperature along the bed results in significant change of η_j factors; therefore, the assumption of some average values could give unreliable results. A simplified internal diffusion model, (every reaction rate equation was linearized to the form : $r_j = k_j \cdot C_{ess}^n$ where: C_{ess} is the concentration of the "most essential" component for a particular reaction) made it possible to take into account the actual effectiveness factor values for each integration step. With such an assumption the effectiveness factor could be calculated for a planar geometry from the formulas:

$$\eta = \frac{\tanh \psi}{\psi} \qquad \text{where:} \qquad \psi = \sqrt{\frac{k}{D_{ef}}}$$

Simulations with the PDEX package have shown, that even if the heat and mass accumulation as well as axial dispersion terms in the gas phase (marked as ≈ 0 in eqns (1) and (3)) are negligibly small, the stability of numerical process is improved when these small values are introduced to the model.

The numerical simulations carried out in the present study have revealed that the nature of the process leads to the fact that lot of commonly applied model simplifications (i.e homogeneous model, neglecting of axial conductivity or dispersion terms, neglecting or simplifying the model of diffusional limitations) should be applied in this particular process with extreme caution. Some examples of influence of such simplification will be given in the paper.

Due to the very high temperature range which can appear in the reverse-flow reactor, any laboratory or pilot scale experiments could be extremely difficult. So mathematical simulations can give some insight into the problem but at the same time they should be treated as a very rough estimation of the process.

Another purely practical problem is to find out what advantage can be expected by using the reverse-flow concept to methane conversion. It seems obvious that when maximum temperature in the reactor will exceed 1700 K this advantage is at least doubtful. The paper will present influence of the inlet gas composition on the maximum temperature value. Especially the influence of the inlet H_2O molar fraction can have an important impact on the practical application of this technique.

---

1. U. Nowak, J. Frauhammer, U. Nieken *A Fully Adaptive Algorithm for Parabolic Partial Differential Equations in One Space Dimension* - Comp. Chem. Engng (1996) 20 pp. 547-561

OP-4-4

Investigation of Unsteady-State Methanol Synthesis by a Fixed-bed Reactor Operated in a Flow Reversal Mode

Guo yaoxing Chen xiaochun Li chengyue
Beijing University of Chemical Technology, Beijing 100029, P.R.China

Abstract

One of the most important advantages of flow reversal reactor is that a thermodynamically favorable axial temperature profiles for the reversible exothermic reactions, such as catalytic synthesis of methanol from either CO and H_2 or CO_2 and H_2, would be created. A few of studies on unsteady-state methanol synthesis by periodic flow reversal from syngas has been reported[1~3]. As a part of modeling and technological studies of unsteady-state methanol synthesis in a flow reversal reactor integrating one catalytic reaction section with two desulfurating sections, some experimental studies of operation performances are reported in this paper.

The experimental investigation was carried out in a bench-scale reactor, packed with a commercial copper-based catalyst of MK-101, which was structured in U-type so as to reduce space held and thermal losses. The sizes of the reactor are 20mm i.d. and 1360mm long. The volume, height and weight of the catalyst packed are 190ml, 600mm and 220g respectively. A desulfuration agent of ZnO was packed in the two end of the reactor and the height of every end was about 360mm. The fixed bed at the two ends of the reactor were devised as either noncatalytic desulfuration reaction section or gas-solid heat exchange ones. Figure 1 shows a schematic diagram of the experiment set-up. The flow rate of the gases were measured and controlled by a group of several mass flow-meters, the composition of the gas mixture and condensed fluid were analyzed by a MS-GC system. The transient axial temperature profile in the reactor were measured by a set of fourteen thermal couples via a pc-data acquisition system.

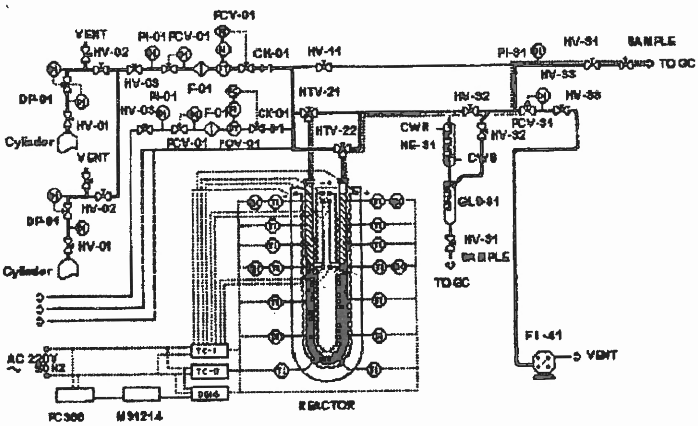


Fig. 1 : schematic diagram of the experiment set-up

A set of experimental conditions is summarized in Table 1

Table 1: Experimental study conditions

Pressure (MPa)	Concentration of ΣCO_x in feed mol%	Feed temperature (°C)	Gas velocity (m/s)	Period time (min)
2.0	4.0-12.0	17-18	0.20-0.40	20-40

The effects of period time, t_c, the concentration of ΣCO_x in feed mixture and gas velocity on the transient temperature profiles, the thermal wave propagation velocity, the maximum temperature and the conversions of ΣCO_x were investigated, the results obtained were discussed. As a few of examples, some results demonstrating the effects of concentration of ΣCO_x in feed and period time on the transient temperature profile and its maximum value are shown in figure 2 and figure 3.

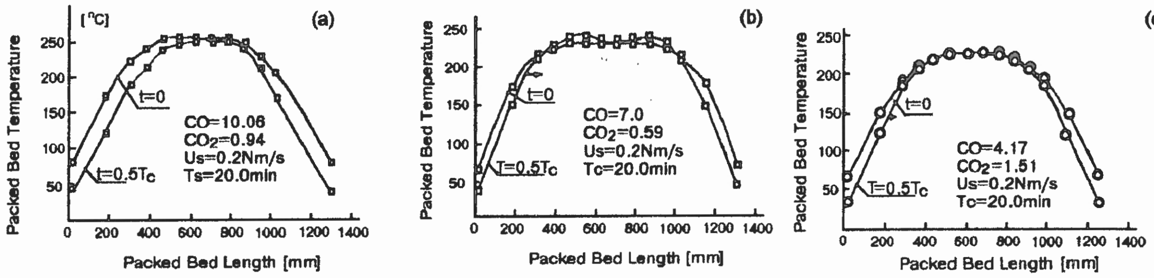


Fig. 2: Effects of concentration of ΣCO_x in feed, on experimental temperature profile and its maximum

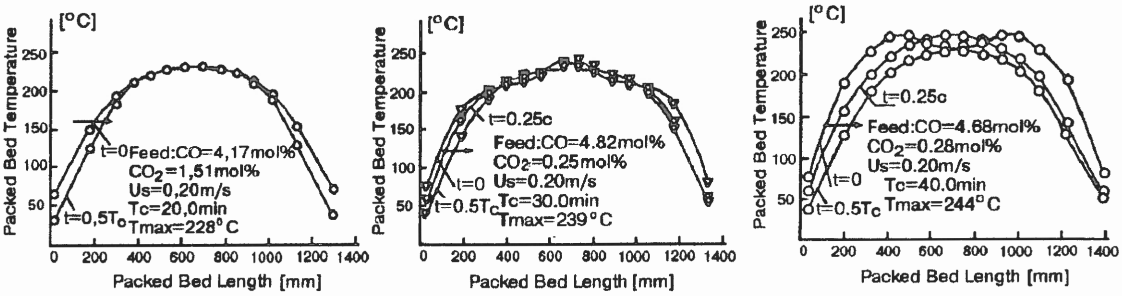


Fig. 3 Effects of period time, t_c on transient temperature profiles

An interesting phenomenon, the transient temperature run away during starting-up, was observed. Figure 4 illustrates this process for a set of experimental conditions given. It could probably be explained that transient and local overheat near the inlet of catalytic bed induced some of strong exothermic side reactions, for example, methanation as a lot of methane was detected in the tail-gas at the same time. This fact suggests us that the control of the transient hot spot is of great importance for a complex reaction system including some strong exothermic reactions.

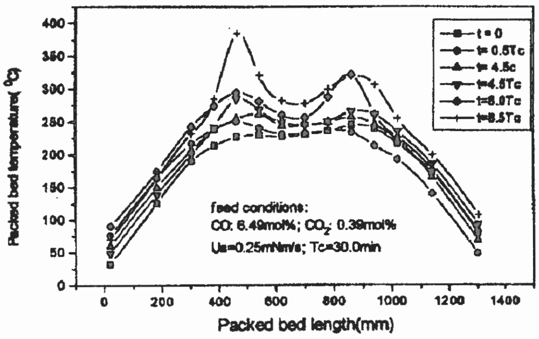


Fig. 4 Transient temperature run-away during starting-up

References:

1. Matros, Yu. Sh. "Catalytic Process under Unsteady-state Conditions", Elsevier Science B. V. Amsterdam, The Newtherlands(1989).
2. Neophytides, S. G. and Froment, G. F. "A Bench Scale Study of Reversed Flow Methanol Synthesi", ind. Eng. Chem. Res., 31, 1583-1589, 1992
3. Vanden Bussche, K. M., S. N. Neophytides, I. A. Zolotarskii and G. F. Froment. "Modeling and simulation of the Revers-flow operation in a Fixed-Bed Reactor for Methanol Synthesis.", Chem. Eng. Sci., 48,3335-3345(1993).

OP-4-5

Regenerative Catalytic Oxidation in environmental protection: an example of the application

Jerzy Haber, Tadeusz Machej
Institute of Catalysis and Surface Chemistry Polish Academy of Sciences,
ul. Niezapominajek, Pl-30 239 Kraków, Poland;
Phone: +48(12) 4252841, Fax: +48(12) 4251923; E-mail : nc machej@cyf-kr.edu.pl

Catalytic processes for total oxidation have found very wide application as methods for the purification of flue gases from different pollutants, such as volatile organic compounds (VOCs), carbon monoxide etc. They are more economical because of low energy consumption in comparison with the thermal non-catalytic methods.

15 years ago a regenerative catalytic oxidation (RCO) system was developed at the Institute of Catalysis and Surface Chemistry of the Polish Academy of Sciences in Kraków. The inlet gas containing the VOCs passes through a hot ceramic bed that heats the gas to the reaction temperature. The VOCs are then oxidized on the catalyst placed between two ceramic beds either autothermally (using only the heat of combustion of the VOCs) or with a small amount of supplementary heat. The hot exhaust gases leave the combustion chamber and pass through another ceramic bed, which is thereby heated to the outlet temperature. The flow direction of the gas stream is then reversed so that the ceramic bed that was heated by the exhaust gases is now used to heat incoming gases, while the flow direction is reversed regularly, producing a pseudo-steady-state operation.

The unit based on the RCO was applied in many different fields for cleaning the off-gases. Here we describe the cleaning of flue gases from a printing machine. The printing machine discharged, during operation, variable amount of gases due to number of printed colours and the rate of printing. Table 1 persents the flow rate of off-gases as a function of colour numbers and the rate of printing.

Table 1. Characteristics of off-gas

Number of colours	Flow rate, Nm^3/h	Rate of printing, m/min.
4	9300	150
5	11700	150
6	16100	50
6	17100	100
6	19200	150
7	21800	150
8	24000	150

OP-4-5

The concentration of the VOC also changes proportionally to the number of colour and the rate of printing. Table 2 presents this relationship.

Table 2. Concentration of VOCs in off-gas

Number of colours	Rate of printing, m/min.	Concentration of VOC as ΣC, g/Nm^3
6	50	0.8
6	150	1.8
7	100	2.3
7	150	2.8
8	100	3.8
8	150	4.9

The unit applied for cleaning characterized above off-gases, has nominal capacity 20,000 Nm^3/h. However, the unit is flexible and operate under variable flow rate within the limits - 50 %; +20 %, e.i. 10,000 to 24,000 Nm^3/h.

Table 3 presents examples of the unit operation under different printing conditions. In all cases the unit operated autothermally, i.e. without supplying external energy, producing the steady-state temperature of the catalyst.

The factors influencing efficiency of the heat recovery and cleaning efficiency will be described.

Table 3. Chracterization of the unit operation

Number of printed colours	Concentration of VOC as ΣC, g/Nm^3	Flow rate, Nm^3/h	Heat of reaction, kJ/Nm^3	Steady-state	
				Catalyst temperature, °C	Cleaning efficiency, %
6	0.68	16100	38.9	355	95.6
6	1.43	17100	68.7	400	98.7
6	1.61	19200	76.7	445	99.5
7	1.43	20000	69.1	405	99.0
7	1.99	21800	93.8	430	99.6

OP-4-6

Dynamic Features of a Reverse-Flow Reactor

J. Khinast and D. Luss
Department of Chemical Engineering
University of Houston
Houston, TX, 77204-4792
USA

Under most operating conditions a reverse-flow reactor (RFR) eventually converges to a symmetric period-1 operation so that the concentrations and temperature profiles after one flow reversal are a mirror image of those after the previous flow reversal. Recent simulations of a cooled RFR show that it may attain under certain conditions states with more complex periodicity, i.e., states with period n>1, and even complex quasi-periodic states. These states may complicate the operation and control of these reactors. The maximum temperature of such a complex stateoften exceeds that of a symmetric period-1 state and could deactivate the catalyst or even lead to safety problems by promoting undesired side reactions which do not occur under the symmtric period-1 operation.

We shall present a systematic, numerically efficient method for mapping parameter regions (operating conditions) for which the cooled RFR exhibits qualitatively different dynamic features. We illustrate this technique by determining the impact of the cooling capacity and flow-reversal period on the transitions from one dynamic feature to another. In the specific example we study quasi-periodic states exist for lower cooling capacities than those for which asymmetric period-1 states exist. In a narrow region of parameters both symmetric and asymmetric period-1 states are stable.

It is customary to model the behavior of the RFR in the limit of very high flow reversal frequency by a counter-current flow reactor with equal flow rates in the two flow directions. It is usually assumed that this reactor attains a symmetric state. It will be shown that this assumption is not always valid. Moreover, this limiting model may predict states which differ from those of the full model for very high flow-reversal frequency.

OP-4-7

Application of a Reversed Flow Reactor for the NO Reduction with NH_3 using Transient Kinetic Models

W. Sjoerd Kijlstra, Pieter Koopmans, Rik Bastiaens and Alfred Bliek*

Department of Chemical Engineering, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands;

* *To whom correspondance should be addressed; phone +31 20 525 6479; fax: +31 20 525 5604; e-mail: bliek@chemeng.chem.uva.nl*

Introduction

Reversed flow reactors are well known for their heat storage capacities in exothermic reactions. In much the same way, they can be utilised as mass storage units. One particular field of application of this principle is selective catalytic reduction (SCR) of NO using NH_3. In this reaction, a stringent stoichiometric dosing of NH_3 is essential. This is hampered by varying inlet concentrations of NO in flue gases derived from combustion installations. The NH_3 dosing problem may be reduced by making use of the NH_3 storage capacity of the catalyst.

In the present work, the potential of reversed flow operation is investigated, both by experimental work and computational modelling, for a $DeNO_x$ reactor loaded with a 2 wt% Mn/Al_2O_3 catalyst, which has proven to exhibit a high activity and selectivity for the SCR reaction at temperatures below 473 K [1]. In contrast to reversed flow modelling studies reported for this reaction so far, a microkinetic model is used, including separate adsorption and desorption constants instead of equilibrium constants obtained from steady state kinetic data.

Experimental

The reactor set-up contains two catalyst beds placed in series with a feed point for NH_3 addition in-between. The experimental conditions used are as follows: $C_{NO} = C_{NH3} = 500$ ppm, $C_{O2} =$ 2 vol%, balance He, T = 423 K, VHSV = 17800 hr^{-1}; switch time = 400 s.

Reactor modelling

The microkinetic model used has been discussed previously [2]. The catalyst beds are treated as plug flow reactors, assuming a flat velocity profile and a negligible axial dispersion, without any mass and heat transfer limitations (all assumptions checked by calculations). The same reaction conditions are used as in the experimental part of the study. The entire reactor is supposed to be at 423 K, and heat required or produced by the single reaction steps is not included in the model. The computer software package gPROMS [3] was used to solve the resulting set of coupled partial differential equations. The entire system is subjected to several discrete steps (v changes sign upon flow reversal, v and c_i change stepwise upon NH_3 addition in-between the two reactor beds), resulting in changing boundary conditions for the set differential equations. The package gPROMS is specifically developed to solve simultaneously continuous and discrete processes. It can do so 1) due to the ability to distinguish between differential and algebraic variables and 2) by analytical calculation of the Jacobian matrix.

Results and discussion

Experimental results show that at constant inlet concentrations a reversed flow reactor has a comparable performance as a conventional plug flow reactor with respect to NO conversion, selectivity towards N_2 and NH_3 slip.

Both experimental and modelling results indicate that adsorption and desorption of H_2O and formation of nitrates, which are neglected in all reported simulation studies so far, has to be accounted for at the low operating temperature used (423 K).

Remarkably, the use of the quasi steady-state approach in kinetic modelling is not reliable to predict the characteristics of transiently operated reactors. This becomes evident by the fact that changing individual reaction rate constants, while maintainng the equilibrium constants obtained from steady state kinetic data, leads to different reactor performances and concentration profiles. Hence, absolute values of individual adsorption, desorption and reaction rate constants are necessary.

In addition, some computational results will be presented on plug flow and reversed flow reactors with varying NO feed concentrations.

References

1. Kijlstra, W.S., Daamen, J.C.M.L., Van de Graaf, J.M., Van der Linden, B., Poels, E.K., and Bliek, A., *Appl. Catal. B: Environm.*7, 337 (1996).
2. Kijlstra, W.S., Brands, D.S., Smit, H.I., Poels, E.K., and Bliek, A., accepted for publication *in J. Catal.*
3. Barton, P.I., and Pantelides, C.C., *A.I.Ch.E.J.* **40**, 966 (1994).

OP-4-8

The Reversed Flow Operation of a Cross-Flow Solid Oxide Fuel Cell Monolith

Stylianos G. Neophytides
Institute of Chemical Engineering & High Temperature Chemical Processes
GR-26500 Patras, Greece

With growing environmental concerns and the need to secure energy supply, to provide cleaner and more efficient energy conversion technologies, fuel cells are doubtless one of the most promising technologies. They are in fact the alternative route to electrical power generation that does not entail combustion of fossil fuels and the associated emissions to the environment.

The prevailing technological outlook is that high process efficiency can be achieved under operating conditions being constant in space and time. However it was shown that, the transient operation of a co-current flow Solid Oxide Fuel Cell (SOFC) under forced periodic reversal of the flow, can lead to significantly improved and efficient operation of the SOFC [1]. Its main dynamic operational features are similar with those of the conventional catalytic fixed bed reactors which had been extensively reviewed by Matros [2].

In this study the reverse flow operation is theoretically applied in the case of a crossflow SOFC monolith (Fig. 1) for the H_2 electrochemical oxidation. The air and fuel channels cross each other. Each set of them sharing a common solid electrolyte plate constitutes a unit battery. The solid electrolyte is coated with the suitable electrocatalyst for O_2 reduction to O^{2-} (e.g. $La_{1-x}Sr_xMnO_3$) from the side of the air channels and the appropriate catalyst-electrode material (e.g. Ni-cermet) for the anodic reaction. All the unit batteries are connected in series.

Fig. 2 shows the temperature distribution in the monolith at the start and the end of a semicircle. Due to the crossing flow of the gas streams the temperature maximum is moving diagonally along the reactor. In general the simulation results show that the crossflow monolith appears to be even more efficient compared to the co-current flow.

References

1. S.G. Neophytides and A. Tripakis, CJChE, vol. 74, 719-728, (1996)
2. Matros Yu.Sh, Chem. Engng. Sci. 45, 2097-2102, (1990)

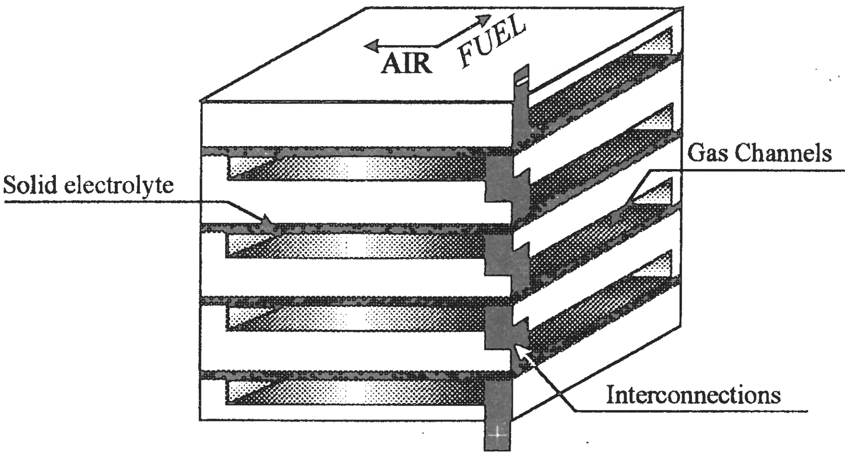


Fig. 1. Schematic diagram of the crossflow SOFC monolith

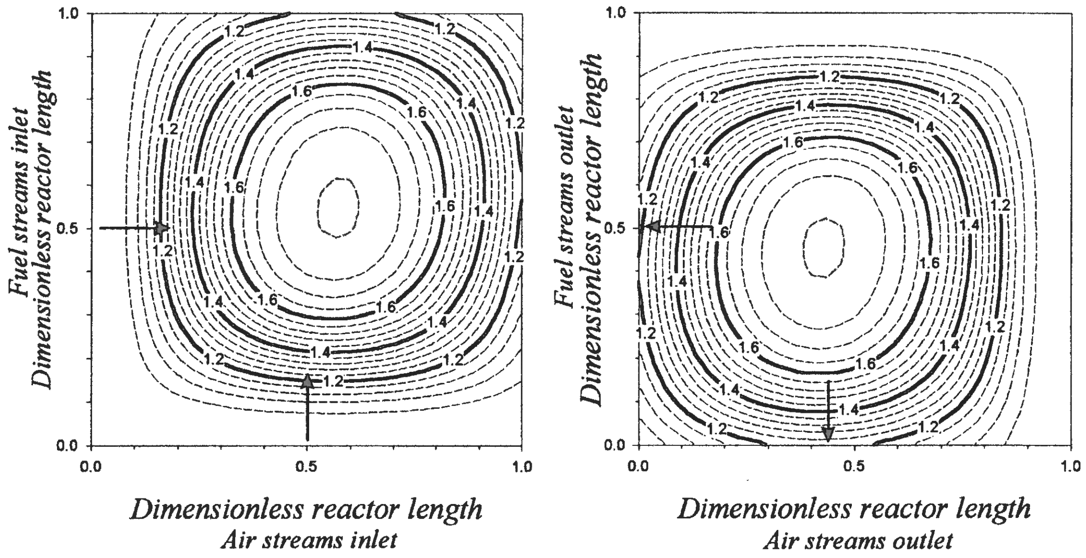


Fig. 2. Contours of the Temperature distribution along the monolith at start (a) and at the end (b) of a semicircle. The diagramms represent the dimensionless temperature $Ts=T/T_o$, $T_o=700$ K

OP-4-9

RECENT ADVANCEMENTS IN REGENERATIVE CATALYTIC OXIDIZER TECHNOLOGY

C.R. Roach[1], Q.V. Jackson[1], G.A. Bunimovich[2], V.O. Strots[2], Yu.Sh. Matros[2]

[1]*Monsanto Enviro-Chem Systems, Inc., P. O. Box 14547, St. Louis, MO 63178, USA*
[2]*Matros Technologies, 14963 Green Circle Dr., Chesterfield, MO 63017, USA,*

Regenerative catalytic oxidizer (RCO) technology employs the concept of periodic flow reversals in a fixed bed of catalyst [1,2] for oxidation of volatile organic compounds (VOCs). Fundamentals of the technology, such as reactor model and its parameters, methods for solving model equations, analysis of effects of different parameters on the reactor performance, as well as results of lab and pilot tests and some examples of commercial applications have been reported in a number of papers [1-3], and were recently summarized by Matros and Bunimovich [4].

The objective of the present work is to present theoretical and experimental results that lead to recent advances in the design and operation of commercial units. Examples of actual applications using these new developments are presented. The paper also discusses examples of comparison between plant data and mathematical modeling.

The design of RCOs is based on one-dimensional heterogeneous model of a fixed bed. The model includes such components as reaction kinetics, intraparticle diffusion, heat and mass transfer between the surface of solid material and bulk of gas phase. The most important dynamic factor is the heat capacity of the solid phase that determines the time scale of reactor cycle.

In most RCO applications, the catalyst bed is flanked by two beds of chemically inert, usually ceramic packing serving as heat retention and transfer media. There exists a variety of ceramic materials that can be used in RCOs. The packing can be either random (saddles, Raschig rings) or structured, such as corrugated wave plates and monoliths with straight channels. Geometrical parameters of these materials result in variations of heat transfer, heat retention and pressure drop properties. The analysis shows that straight channeled monolith is the most efficient material because laminar flow in narrow channels provides for high heat transfer rate at low pressure drop. In a typical RCO, the amount of monolithic ceramics may be 2.5-3 times less than that of conventional random packing. Corrugated wave ceramics takes up intermediate position between random packings and straight channeled monoliths. Process simulation results will be presented.

In real-life applications, VOC oxidation catalysts operate under variable, often extreme conditions that often lead to deactivation. There are many factors that affect the catalyst via various mechanisms, generally classified as poisoning, fouling, masking, and sintering. It is essential to understand the dynamics of catalyst deactivation and, whenever possible, develop ways for preventing it or for catalyst regeneration, preferably *in situ*.

One of the examples reported in the paper deals with poisoning of copper-chromium catalyst by sulfur compounds in an RCO installed at an asphalt making facility. Analysis of the literature indicated that the poisoning can be reversed by thermal regeneration. Experimental investigation of regeneration allowed to determine the optimum temperature and duration of regeneration.

There are several industries that release VOC-laden gases that also contain particulate matter: wood processing, painting, baking, some chemical processes. In an RCO, particulate matter may cause plugging of ceramic packing and/ or catalyst, catalyst deactivation, or even fires inside the oxidizer. The paper discusses the catalyst deactivation aspect of the problem. Using the results of pilot tests of RCO at a wood processing facility, experimental data and process simulation, it became possible to develop a procedure for catalyst regeneration, predict the process performance over an extended period of time, and develop a periodical bakeout strategy that ensures meeting the performance requirements.

Periodical flow reversal concept is routinely used in regenerative thermal oxidizers (RTOs) that destroy VOCs through homogeneous oxidation at 800 - 1000 °C. Recent analysis of two systems [5] showed that RCO technology has substantial operating cost advantages over RTO. This creates a possibility to retrofit the existing RTOs into catalytic units by installing catalyst bed in addition to the ceramic packing already in an RTO, or as a replacement of part of the packing. The paper discusses the advantages of such retrofitting and presents an example of such a retrofit. Comparison of experimental and simulation results is presented.

Treatment of very low concentrated gases requires a supply of heat energy to the catalyst bed in order to maintain the oxidation process. The most effective way to add this energy is installation of a burner (sometimes, electric heater) between two halves of catalyst bed. Different control strategies can be used for burner operation. According to one, the amount of fuel is controlled based on temperature reading in the catalyst bed. Another approach involves turning the burner on when the catalyst bed cools, and turning it off when the catalyst becomes heated. Simulation of such on-off control showed the existence of doubly periodical regime in the reactor with one period corresponding to flow reversals and another determined by burner operation. The simulation results and discussion of the two strategies will be presented.

References

1. Matros Yu.Sh. Unsteady Processes in Catalytic Reactors. Studies in Surface Science and Catalysis, v. 22, Elsevier, Amsterdam-Oxford-New York-Tokyo, 1985.
2. Matros Yu.Sh. Catalytic Processes under Unsteady-State Conditions. Studies in Surface Science and Catalysis, v. 43, Elsevier, Amsterdam-Oxford-New York-Tokyo, 1989.
3. Eigenberger G. and U. Nieken, Catalytic Cleaning of Polluted Air: Reaction Engineering Problems and New Solutions, Int. Chem. Engineering, Vol. 34, No. 1, pp. 4-16, 1994.
4. Matros Yu.Sh. and G.A. Bunimovich, Reverse-Flow Operation in Fixed Bed Catalytic Reactors, Catal. Rev.-Sci . Eng., Vol. 38, No. 1, pp. 1-68, 1996.
5. Matros Yu.Sh, G.A. Bunimovich, S.E. Patterson and S.F. Meyer, Is It Economically Feasible to Use Heterogeneous Catalysts for VOC Control in Regenerative Oxidizers. Catalysis Today, Vol. 27, pp. 307-313, 1996.

OP-4-10

Reduction-Oxidation-Cycling in a Reverse Flow Reactor: Given Constraints

H. Seiler, G. Emig
Universität Erlangen–Nürnberg
Lehrstuhl für Technische Chemie I
Egerlandstr. 3
D–91058 Erlangen (Germany)
Tel.: +49 – 9131 / 85–7429
Fax: +49 – 9131 / 85–7421
e-mail: seiler@rzmail.uni-erlangen.de

Scope of the Work

Forced unsteady-state operation of chemical reactors often leads to a higher efficiency in the use of mass or energy, e. g. by operating fixed bed reactors with periodic flow reversal [1] or by forced unsteady-state operation in the inlet composition which corresponds to separating heterogeneous catalytic oxidation reactions into two gas-solid reactions, a reduction and an oxidation step [2,3].

During an exothermal reaction taking place in an adiabatic fixed bed reactor, the released heat may be stored inside the bed by periodically reversing the flow direction. Because of this storage of energy the inlet temperature may be decreased without extinguishing the reaction, which is very useful in the catalytic purification of polluted air [4,5].

Operating oxidation reactions in reduction-oxidation cycles will lead either to pure products [6] because of separating the two feed components, or to higher yields where the reason is the absence of the adsorbed active oxygen on the solid's surface leading to total oxidation [2,3].

In this study, these two forced unsteady-state operation modes will be combined to get an highly efficient process. Now the solid is no longer a mere reservoir for heat, but for mass in form of oxygen, too. This leads to complicated dependencies between the state variables. Because of this complex behaviour, simulation studies prior to the experiments have the advantage that it is easier to get information about the behaviour of the system and to investigate the influence of several parameters like inlet conditions, reaction enthalpy and operational time constants. With this knowledge well defined experiments can be designed to verify qualitatively and quantitatively the behaviour of the whole system.

To enable more common studies, a suitable type of test reaction with one exothermic and one endothermic step was chosen (Fig. 1).

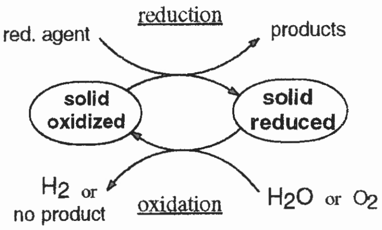


Figure 1: Reaction scheme – Cycle of the solid

The reaction rate will be described by a pseudohomogeneous kinetic model using power law expressions with first order in gas and solid, respectively.

$$\begin{aligned} \text{Reduction:} \quad & r_{red} &= k_{red}(T) \cdot c_{red} \cdot \Theta_{ox} \\ \text{Oxidation:} \quad & r_{ox} &= k_{ox}(T) \cdot c_{ox}(1 - \Theta_{ox}) \end{aligned}$$

with Θ_{ox} being the amount of oxygen in the solid with respect to the fully oxidized form of the solid and c_{red}, c_{ox} the gas phase concentrations of the reducing and oxidizing agent, respectively.

The basis for this test reaction is the steam iron process [6], which would be an economical process for producing, refining or storing hydrogen if it were to be carried out under lower inlet gas temperatures ($T < 800K$). Another advantage of the steam iron process is its independence of natural gas or oil, because it can be operated with gasified coal for which the known resources will last for a longer time. But it is easy to change kinetics and reaction parameters in the mathematical model to extend the found dependencies to develop a general theory.

The main interesting point in operating such processes (endothermic and exothermic step in a reduction-oxidation cycle) in a reverse flow reactor will be the energy efficiency, because the endothermic reaction step can be supplied with heat from the exothermic one which takes place at a different time. In addition, the constraints resulting from this special operation mode should be examined in theory and experiment.

Results and Discussion

To improve the discussed process with a cyclic operation of an adiabatic fixed bed reactor it is necessary to compare the cases with and without changing the flow direction. The model used for the simulations is instationary, one-dimensional, pseudohomogeneous, and ir considers the dispersion of heat and mass. The studies were done for sufficiently short cycle times where the solid was not fully reduced or oxidized to enable coupling between the reduction and the oxidation step over the solid phase in matter and heat.

The simulations during the periodic stationary state (transients have settled down) show that without flow reversal the outlet stream will reach nearly thermodynamic equilibrium which is determined by the ratio of the inlet concentrations. In addition, the heat released during the exothermic step cannot be used by the endothermic one. The behaviour in the outlet concentration can be explained by the fact that it makes no difference wether the reaction is operated in one or in two steps, because the oxygen content in the solid – as a result of the reaction steps before – will determine the possible gas conversion [7] (see also Fig. 2).

The change of the flow direction leads to outlet compositions which will be restricted by the state of the solid in the bed at the early beginning of the whole process. This results in the fact that the maximum obtainable gas conversion in the first reduction step is $(1.0 - x)$ if the oxidation degree $\Theta_{ox}(t_0)$ is x. So if the process is started with a fully oxidized bed $(\Theta_{ox}(t_0) = 1.0)$ the gas conversion can be increased up to 1.0, but only if the ratio of the inlet concentrations was chosen in a right range (see Fig. 2).

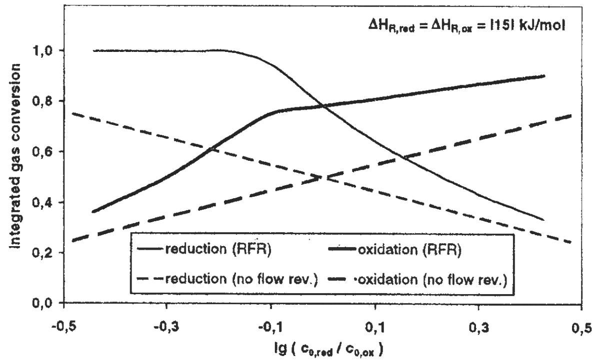


Figure 2: Conversion for reduction and oxidation versus logarithmic ratio of the inlet concentration for reduction and oxidation

The reasons for this behaviour can be found in the balances for mass and heat in the periodic steady state. In this state each point in the reactor must return to its initial state after one period (i. e. one reduction and one oxidation step with two changes of the flow direction). The amount of oxygen removed from the reactor during the reduction step must be equal to the amount of oxygen supplied by the oxidation reaction. Similarly, the heat generated by the reduction reaction must be equal to the heat removed from the reactor by the convective stream or consumed by the oxidation reaction. The adiabatic temperature rise is a measure for the heat released at total conversion. At complete gas conversion during the reduction step, the mass balance for one cycle determines a gas conversion during the oxidation step which is equal to the ratio of adiabatic temperature rises of the reduction and the oxidation (in absolute values). In general the following equation shows the relationship between the adiabatic temperature rises and the conversions of the two steps, considering the same time for each reaction step:

$$X_{ox} \cdot \Delta T_{ad,ox} = X_{red} \cdot \Delta T_{ad,red}$$

This equation is crucial for operating reduction-oxidation-cycles in a fixed bed reactor with periodic flow reversal, because the choice of the inlet concentration for each reaction step sets a limit to the conversion. This is particularly important at highly different reaction enthalpies. But here another problem is involved – runaway of the adiabatic fixed bed reactor during the start-up phase occurs if the exothermic step has the higher reaction enthalpy and if the absolute value of the adiabatic temperature rises (stand for the inlet concentrations) are too high.

The next step in the research work will be to propose criteria for the obtainable level of the time integrated conversion in dependence of the absolute value of reaction enthalpies and of inlet concentrations for a given set of reactor operation parameters like period time, residence time and ratio of the times for the two steps.

References

[1] Yu. Sh. Matros, Catalytic processes under unsteady-state conditions, Elsevier, Amsterdam (1989)

[2] L. Weismantel, J. Stöckel, G. Emig, Applied Catalysis A, Vol. 137, No. 1, pp. 129 (1996)

[3] O. Watzenberger and A. Hagemeyer, Patent DE 195 45 095 A 1 (1997)

[4] U. Nieken, Fortschrittberichte VDI, Reihe 3: Verfahrenstechnik, Nr. 328, VDI-Verlag (1993)

[5] L. van de Beld, Ph. D. Thesis, University Twente (1995)

[6] M. S. Casper, Hydrogen Manufacture by Electrolysis, Thermal Decomposition and Unusual Techniques, Noyes Data Corporation, Park Ridge, New York (1978)

[7] H. Seiler and G. Emig in G. Froment and K. Waugh (Eds.) *Dynamics of Surfaces and Reaction Kinetics in Heterogeneous Catalysis*, Elsevier, Amsterdam, p. 479 (1997)

Acknowledgements

The authors acknowledge support from the German Ministry of Education, Science, Research and Technologie (BMBF) – support number 03D0033C.

OP-4-11

MODELLING OF A ROTATING MONOLITH FORCED UNSTEADY STATE REACTOR FOR PROPANE DEHYDROGENATION

E. H. Stitt, S. D. Jackson, D.G. Shipley, F. King
ICI Katalco, PO Box 1, Billingham, Cleveland, UKTel +44 1642 522704 Fax +44 1642 522606 e-mail: hugh_stitt@ici.com

Introduction

The dehydrogenation of propane to propene is typically carried out over a catalyst at approximately 600°C and near atmospheric pressure. The reaction is equilibrium limited and highly endothermic, and therefore heat supply is required through the reaction. Side reactions include cracking to lower hydrocarbons and carbon with some polyaromatics formation. Catalyst regeneration is required due to deactivation caused by the "coke" deposition. Timescales between regeneration vary considerably for the comercial processes availalble.

In this study a promoted chromia catalyst, supported on a washcoated alumina monolith was used for characterisation. The catalyst was observed to exhibit very high beneficial activities (factor of 3-5) for a short time (60 – 100 secs) after regeneration and reactivation. Selectivities as high as 95% were observed during this inital period. Regeneration is carried out using air or dilute oxygen, during which the catalyst is also oxidised. The catalyst then requires reduction, using hydrogen, prior to feeding propane again. Both regeneration / oxidation and reduction steps are exothermic. The driver in the reactor design presented herein was to capitalise on this initial high activity and to utilise regenerative heat transfer in an unsteady state reactor

Rotating Monolith Reactor

The catalyst undergoes a dehydrogenation - regeneration (+ oxidation) - reduction cycle. The regeneration step however uses oxygen and this needs to be isolated, using an inert gas purge, from the propane and hydrogen feeds used in the reduction and dehydrogenation stages. The design concept is thus to use a catalytic monolith in the form of a "Wheel" that rotates through successive stationary feed segments, Fig.1. This enables utilisation of heat from the regeneration and reduction stages, transferred by the rotating monolith into the dehydrogenation zone. If required, fuel gas can be added during the oxidation stage. The speed of rotation is effectively set by the heat balance. The chromia loading on the catalyst has a significant effect as much of the heat generation arises from the oxidation - reduction of the catalyst. Fortuitously, at reasonable chromia loadings this gives dehydrogenation cycle times of the right order of magnitude required to utilise the observed high activities of freshly regenerated catalyst. Moving the catalyst through the flow zones facilitates exploitation of the unsteady state catalysis and regenerative heat transfer without the need for flow switching valves. The direction of the flows through the monolith is an important feature in the design. Fig.2 gives a schematic flowsheet, showing the streams flowing to and from the reactor, and the recuperative (essentially feed / product) heat exchangers required. The rotating monolith does of course require dynamic seals between the flow zones.

Fig.1 : Layout of Rotating Monolith Reactor

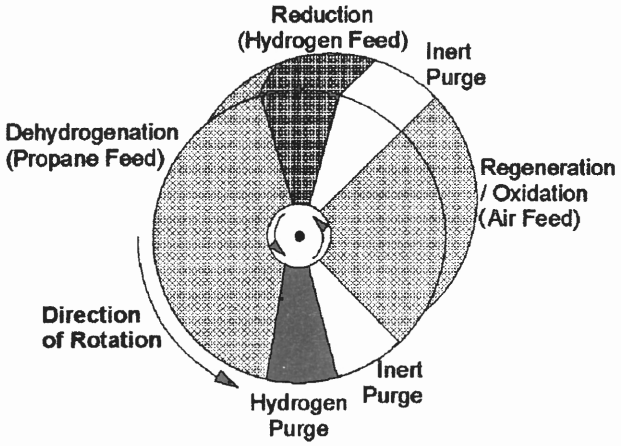
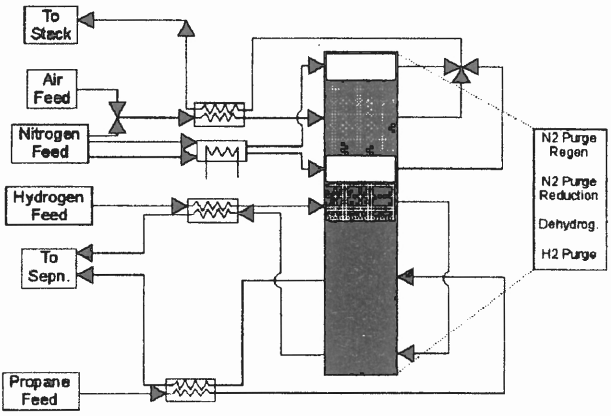


Fig.2 : Schematic Flowsheet PDH "Wheel" Reactor



Reactor Model

A FORTRAN model of the reactor was written to allow evaluation of the potential design. The cycling nature of the reactor means in fact that the overall reactor operates at steady state: that is, while the moving catalyst sees varying temperatures and feeds as it rotates, the condition at a given stationary point is constant. The model included the following features: Dehydrogenation Stage Reactions: Propane dehydrogenation and associated reactions were based on a set of assumed first order reactions. Calculations showed the reaction was unlikely to be diffusion controlled. The rate expressions were based on experimental data. Other Reactions: The coke and catalyst oxidation reactions were assumed to be "fast" (viz. reagent limited) as was the catalyst reduction reaction. The degree of oxidation / reduction of the chromia was based on measurements. Heat Transfer: Standard heat transfer correlations are used for gas - monolith heat transfer. Axial, radial and tangential conduction by the monolith are neglected. The modelling in fact showed heat transfer to be very good with gas-monolith ΔT's of $10^{O}C$ or less. Heat Balance: included reaction thermochemistry and flowing enthalpies of the gas and monolith. Rotational Pumping: As the monolith moves from one zone to the next it carries with it its inventory of gas feed in the previous segment. This stream mixing effect is included.

Reactor Design

Using the above model, a design study was carried out, to consider the effect of the major process variables. Variations on the flowsheet shown in Fig.2 were tried, including double pass arrangements for the propane feed. These were not successful. Rotation periods of 45 - 120 secs gave suitable designs. The presentation will include description of the model plus output including temperature and concentration / conversion profiles, in addition to conclusions from the reactor design and evaluation study.

OP-4-12

PARAMETRIC SENSITIVITY IN FIXED-BED CATALYTIC REACTORS WITH REVERSE-FLOW OPERATION

Wu[1] H., Rota[2] R., Morbidelli[3*] M. and Varma[4] A.

1. Ausimont R&D Center, Montedison, Via S. Pietro 50/A, 20021 Bollate (Milano), Italy.
2. Dip. Chim. Fis. App., Politecnico di Milano, Via Mancinelli 7, 20131 Milano, Italy.
3*. Chem. Eng. Dept./LTC, ETH Zentrum, CH-8092 Zurich, Switzerland. Tel 0041-1-6323034. Fax 0041-1-6321082. E-mail morbidelli@tech.chem.ethz.ch
4. Dept. of Chem. Eng., U. of Notre Dame, Notre Dame, IN 46556, U.S.A.

Abstract

After the successful application to SO_2 oxidation in the early 1980s (cf. Matros and Bunimovich, 1996), fixed-bed catalytic reactors operating with periodic flow reversal have received great attention during the last decade. The necessary condition for the stable operation of these units is to have one part of catalyst bed operating in ignited conditions, which creeps periodically between the two ends of the packed bed. It is clear that such stable conditions are achieved only in specific regions of the system parameter space. In particular, under certain operating conditions, slight variations in the system parameters (such as feed temperature, reactant concentrations, cycle period, etc.) may lead to complete extinction of the reactor. In these cases, the reactor is said to operate in the parametrically sensitive region. In practical applications, it is clearly desirable to avoid this operating region in the early stages of reactor design.

The present work is devoted to supply an effective method to identify such parametrically sensitive regions in various system parameter planes for reactors with reverse-flow operation. This method is an extension of the generalized criterion for parametric sensitivity, originally developed by Morbidelli and Varma (1988). In particular, the temperature maximum in solid phase, θ_s^* established after repeated operations, is chosen as the objective; then the normalized sensitivities of this objective with respect to variations of system parameters of interest are computed. The parametrically sensitive region is defined as the situation where the normalized objective sensitivity with respect to variations of any of the system parameters, reaches its maximum or minimum.

A typical example is shown in Figure 1, where values of the normalized sensitivity of the temperature maximum θ_s^* with respect to the heat of reaction parameter β, $S(\theta_s^*;\beta)$, are reported as a function of β for various values of the Damkohler number Da. It is seen that in

each case, the sensitivity exhibits a maximum at a specific β value, β_c, which then defines the parametrically sensitive region for the reactor operation. Moreover, for $\beta > \beta_c$, the reactor operates under the ignited conditions, and hence it is the reactor-working region, while for $\beta < \beta_c$, the reactor is in the extinguished conditions, indicating that the heat of reaction is insufficient for the reactor to operate in reverse-flow mode.

A transient heterogeneous model, accounting for mass and energy capacities in both gas and solid phases, is used in this study. Maps of the parametrically sensitive regions in various dimensionless parameter planes are presented. These graphics can be used in practice to find correct operating conditions so as to avoid the parametrically sensitive regions leading to reactor extinction.

References

Matros, Yu. Sh., and Bunimovich, G. A. (1996) Reverse-flow operation in fixed bed catalytic reactors. *Catal. Rev.---Sci. Eng.* **38**, 1.

Morbidelli, M., and Varma, A. (1988) A generalized criterion for parametric sensitivity: application to thermal explosion theory. *Chem. Eng. Sci.* **43**, 91.

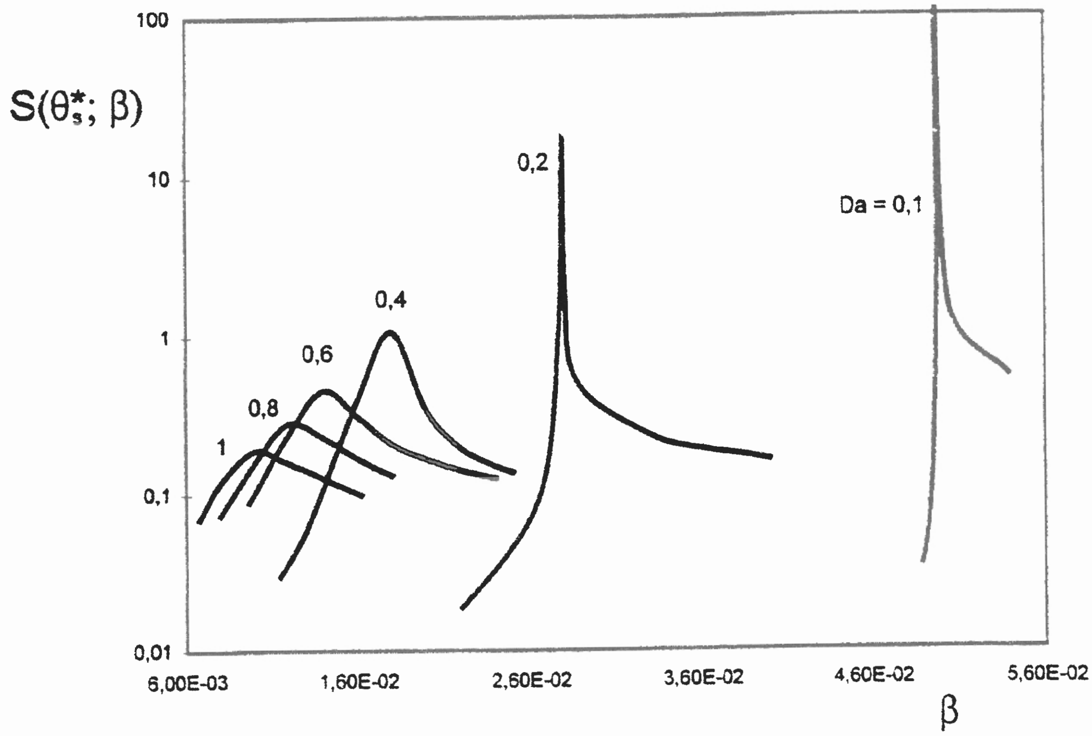


Figure 1 Normalized sensitivity of the temperature maximum in solid phase with respect to the heat of reaction parameter, $S(\theta_s^*;\beta)$, as a function of the heat of reaction parameter, for various values of the Damkohler number.

OP-4-13

Practical Studies of the Commercial Flow-Reversed SO_2 Converter

Wen-De XIAO Hui WANG Wei-Kang YUAN*

UNILAB Research Center of Chem. Reac. Eng., East China Univ. of Sci. and Techn., Shanghai, 200237, P. R. China. Phone & fax: 86-21-64252814, e-mail: sane@npc.haplink.com.cn

The unsteady-state SO_2 converter with flow-reversal has been commercialized to a large scale since the early 1980s by Matros and coworkers, and in 1993, a converter of this type was established in Shenyang Smelter, applying the Matros' technique, with its performance basically satisfactory. On August 1 this year, an other flow-reversed converter was constructed in Jiyuan Smelter to treat the lead waste gases by the UNILAB, with the gas flow rate of 20-40Nkm^3/hr, SO_2 concentration from 1.2 to 4.0% (vol), and the converter's inner diameter of 6.3m. Some practical problems, however, are still to be studied. In this paper, four problems are discussed related to the commercialization practices of the large-scale flow-reversed converter.

Buffering of the outlet temperature

The flow-reversed converter is characterized by periodic fluctuation of the outlet temperature(Xiao and Yuan, 1996). This behavior brings about three practical troubles. Expansion and contraction of the outlet shift valve by sharp heating and cooling causes the airtightness and the final SO_2 conversion deteriorate, and simultaneously the cooled sulfuric acid may appear in the outlet pipeline before the SO_3 absorber as the temperature is lower than dew point of the gases (about 105 ℃). Moreover, acid fog happens to the absorber and chimney.

To overcome this trouble, the UNILAB has proposed a proprietary device, named by outlet temperature buffer(OTB). The calculated results show that, when SO2=3%, u=0.35m/s, and cycle duration=20 minutes, the outlet temperature keeps on the inlet one, 60 ℃, during the former five minutes, and in the latter five minutes, it rises at a rate about 60 ℃ per minute, and finally up to 360 ℃, without the OTB. With OTB, however, the outlet temperature fluctuates little. In the Jiyuan converter 6.3m in diameter, the OTBs work very well with the outlet temperature almost stable around 150 ℃, provided that the SO_2 concentration fluctuates a little.

Control of the reactor temperature

The axial maximum temperature of the reactor determines to much extent its performance, which depends upon the inlet SO_2 composition and the gas superficial velocity, as proven by Matros (1989) and Xiao (1991).Generally, the SO_2 composition in smelter's waste gases is on average 2-3%(vol), and the maximum temperature may by over 600 ℃ at a velocity of 0.2-0.4m/s on adiabatic conditions. For better performance, the multiple-stage configurations with interstage heat exchangers were employed (Matros,1989; Xiao, 1991). The Jiyuan converter was divided into five stages with the end stages as OTBs and the interstage heat exchanger of 100m^2 in area. Two control loops are proposed and programmed into computer package, one loop for the cool duration introducing the cool raw gases into

---

*Author to whom correspondence should be addressed.

the exchangers by a bang-bang method, and the other for the cycle duration introducing the gases into the catalyst bed of the reactor in one direction by an adaptive method.

The cool duration control aims to make the maximum temperature between 530 and 560 ℃, so the cooling is opened when it over 560 ℃ and closed lower than 530 ℃, and the cycle duration control to make the maximum temperature locate near the end of the first catalyst bed when the flow shifted, so as to produce an relatively good temperature profile. These control strategies are proven very reliable by our experiences.

Flow distribution in the converter

There has been well established that the superficial velocity has great effect on the maximum temperature and final conversion of SO_2, and thus the well distributed flow in the flow direction is very necessary for flow-reversed converter. As velocity increased from 0.1m/s to 0.4m/s with inlet SO_2 concentration fixed to 3% (vol), for example, the maximum temperature is increased from 564 ℃ to 643 ℃, and the final conversion decreased from 96.8% to 85.5%. This behavior can not happen to the conventional steady-state converter.

Another reason for a fine distribution is that the catalyst bed may subside nearby the reactor wall by the upward and downward blowing, and furthermore the holes appear. This make the conversion deteriorate very quickly, and has taken place in Shenyang's flow-reversed converter, to the authors' knowledge, though it may not happen to the conventional one because of the one-way blowing downwards.

To deal with this trouble, an elaborately designed distributor was developed by the authors.

About the three-way valve

Three-way valves big as 2.0m in diameter are the critical devices for the flow-reversed SO_2 converters. In the UNILAB technique, there are three valves of this kind, among which two for cycling control and one for cooling control. Among the two for cycling, one is for the inlet gases without SO_3, and another the outlet gases with SO_3. To our experiences, the SO_3 valve requires much care.

In practice, the three-way valve is the type of piston with its stem up-and- down. When the stem upwards, the part adsorbing SO_3 is exposed to the surroundings of moisture, and thereby the concentrated sulfuric acid forms. On the conditions of concentrated sulfuric acid and relatively high temperature about 150 ℃, few steels can endure the corrosion. In the Jiyuan converter, the 317 steel stem is first used, corrosion behaves obviously and the gases with SO_3 vented form the seam between the stem and packing. Therefore, an improvement on the shift valves was proposed to isolate the stem from the moisture surroundings.

References

Matros, Yu. Sh., *Catalytic Processes under Unsteady-State Conditions*, Elsevier (1989).

Xiao, W. D., *Study on the Behaviors and Control of Unsteady-State Fixed-Bed Reactor with Flow Reversal,* Ph. D. Dissertation, East China Univ. Sci. & Tech.,(1991).

Xiao, W. D., and W. K. Yuan, Modelling and Experimental Studies on Unsteady-State SO_2 Converters, *The Canadian Journal of Chem. Eng.* Vol74, 772 (1996).

OP-4-14

CATALYTIC PROCESSES, APPLYING THE NONSTATIONARY STATE OF THE CATALYST SURFACE

A.N.Zagoruiko, A.S.Noskov
Boreskov Institute of Catalysis SB RAS
pr.Lavrentieva, 5, Novosibirsk, 630090, Russia
phone +7-3832-354591, fax +7-3832-357678, e-mail: zagor@caty.catalysis.nsk.su

Performance of catalytic processes in artificially created nonstationary conditions evidently provides the increase of catalytic technologies efficiency: to increase the rate of reactions, obtain higher selectivity, decrease energy consumption and both the operation and capital costs of the catalytic processes. In general it may be stated that transfer to «unsteady-state» philosophy expanded qualitatively the space for process developers fantasy. In practice it was revealed in appearance of principally new generation of catalytic technologies - reverse-processes [1], though the reverse-processes of the first generation (most successfully commercialized for VOC incineration and SO_2 oxidation) applied, essentially, only the heat nonstationarity of the packed catalyst bed. At the same time the account of «chemical» nonstationarity of the catalyst, from one hand, is obviously needed for the design and development of such process and, from the other hand, may be applied for development of novel technologies.

The first process, effectively using the nonstationarity of the catalyst surface, was Reverse-NO_x process for selective reduction of nitrogen oxides by ammonia. In this process the ammonia was fed into the center of the catalyst bed. Ammonia accumulation at the catalyst surface provided high stability of process operation under oscillating NO_x content, while adsorption of ammonia mostly in the central part of the bed prevented its desorption to the purified gas after the gas flow reversal.

Historically the purposeful development of new generation processes started from the SO_2 oxidation process. Here we used the nonstationary kinetic model, proposed by Prof. Balzhinimaev. Investigations showed that the melt of vanadia catalyst active component shows not simply catalytic properties, but as well absorption properties in relation to sulfur dioxide. Fig.1 shows the flow-sheet of the new process, applying absorption features of the catalyst [2].

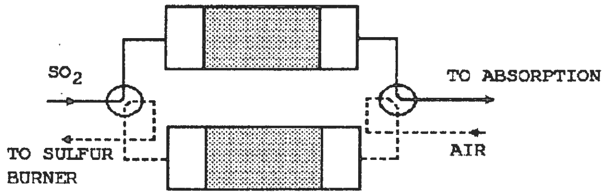


Fig.1
The flow-sheet of the SO_2 oxidation reverse-process, using periodical blowing of catalyst beds with air.

In this process the reaction mixture (containing, for example, ~1% of SO_2) is fed into the first catalyst bed, where sulfur dioxide absorbs at the catalyst surface, partly converting to SO_3, which afterwards is captured in the absorption tower. During some time the sulfur dioxide is practically absent in the outlet gases. When it appears at the outlet, the inlet mixture flow is switched to another bed, while the first bed is blown by air. The air desorbs the absorbed SO_2 and saturates the melt with oxygen, thus providing the over-equilibrium SO_3 yield in the next cycle. Outlet air stream, containing sulfur dioxide and sulfur trioxide are fed to the sulfur burner as feed air.

Process performance in such mode provides extremely high degree of gas purification from SO_2 (99.996%). Proposed process may be applied at the second stage of conventional DC/DA sulfuric acid systems with minimum expenses for reconstruction.

The next process, applying the nonstationarity of the catalyst surface is the adsorption-catalytic reverse-process (ACRP) for VOC incineration [3]. This process applies the ability of oxide catalysts not only to accelerate the oxidation reaction, but to adsorb VOC as well. Such admixtures are adsorbed at low (ambient) temperature and then are incinerated by periodical temperature increase. Adsorption duration is much longer than heating period, and the heating is necessary to reach the flash point temperature in some part of the bed and then the process may occur autothermally. All this provides low energy consumption of the purification plant.

The principally new feature of the process is application of reverse-flow technique in the incineration step, when the heating is performed by the means of the heater, situated in the central part of the bed. During the adsorption period the inlet gas is fed without flow reversals into the catalyst bed center, providing the accumulation of VOC preferable in this part of the bed, what leads to minimization of unoxidized VOC desorption from the bed ends during incineration, thus enabling achievement of high purification degree.

The presentation describes the process development steps: elaboration of nonstationary kinetic model, modelling of catalyst pellet with account of intraparticle diffusion limitations, process simulation, pilot and industrial testings. It may be stated that ACRP provides extremely low energy consumption in purification of lean waste gases (with VOC content below 200 mg/m^3). It may be seen (Fig.2) that energy consumption here decreases with decrease of VOC content, showing the behavior, opposite to conventional technologies.

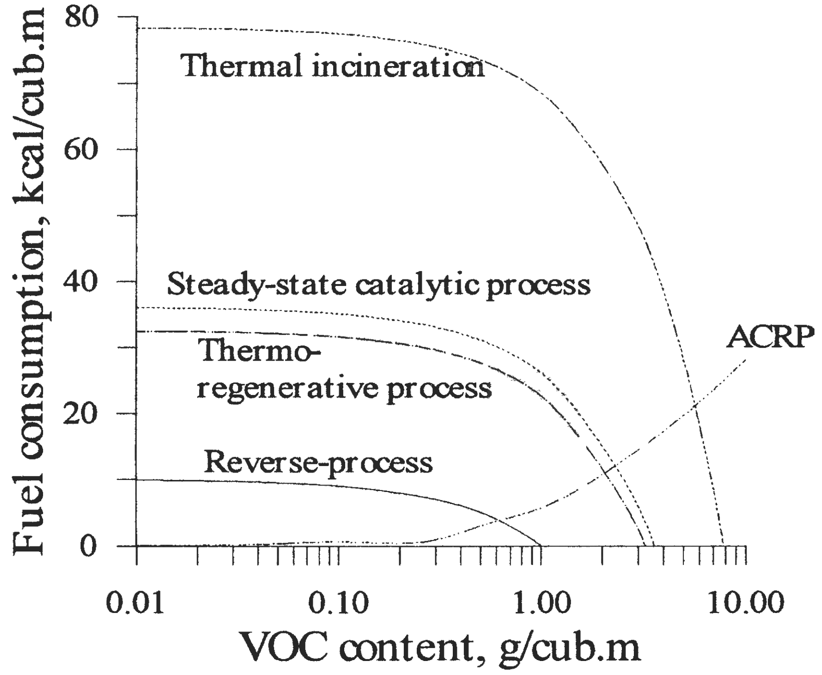


Fig.2

Comparative energy consumption for VOC incineration technologies.

In general it may be stated that purposeful application of catalyst surface nonstationarity gives the way for development of new generation of catalytic technologies. The presentation describes new possible applications of the idea.

References:

1. Yu.Sh. Matros, G.A. Bunimovich. Reverse-flow operation in fixed bed catalytic reactors. - Catal.Rev.-Sci.Eng., 38(1), 1996, pp.1-68.
2. O.V. Goldman, G.A. Bunimovich, A.N. Zagoruiko, V.S. Lahmostov, N.V. Vernikovskaya, A.S. Noskov, O.V. Kostenko. Russian patent #2085481, priority 30 May 1995.
3. Zagoruiko A.N., Noskov A.S., Kostenko O.V. Russian Patent Application No.95112956, 1995.

Section 5.

TAP (Temporal Analysis of Products) Reactor Studies

THE THIRD KINETIC STRATEGY

J.T. Gleaves, G.S. Yablonsky, Y. Schuurman*

Washington University, Department of Chemical Engineering,
Campus Box 1198, St. Louis, MO 63130
**Centre National De Recherche Scientifique, Institut de Recherche sur la Catalyse, Delegation Regionale Rhone-Alpes, Secteur Vallee du Rhone, 2 avenue Albert Einstein, BP 1335, 69626 Villeurbanne Cedex, France*

Heterogeneous catalytic processes are inherently more difficult to unravel than homogeneous processes because they involve more than one phase. Experimentally, it has been particularly difficult to obtain information about the fundamental chemical processes that occur in complex catalytic reactions. One of the primary problems is that the effects of transport and chemistry are interwoven and not easily distinguished from one another. The problem has spawned a number of experimental strategies designed to obtain kinetic information from heterogeneous catalytic reactions.

The most common strategy, used in steady-state experiments, is to eliminate the influence of transport characteristics on the process by operating at conditions that make transport very fast compared with the chemical processes. A second strategy, used in surface science experiments, involves eliminating transport effects by eliminating the gas phase.

This talk discusses a third kinetic strategy based on TAP vacuum pulse response experiments. In TAP experiments, gas transport effects are not eliminated as in the other two approaches. Transport occurs in the Knudsen flow regime and is governed by the collisions of gas molecules with catalyst particles. As a result, gas diffusivities are independant of gas composition or pressure. Variuos features of the TAP experiment, and its application to fundamental problems in heterogeneous are presented.

OP-5-2

The Role of Bronsted Acid Sites in the DeNOx Reaction – A Mechanistic Study applying the Temporal Analysis of Products Reactor and FTIR

Till Gerlach and Manfred Baerns
Institute for Applied Catalysis Berlin-Adlershof,
Rudower Chaussee 5, D-12484 Berlin, Germany
Tel.: +49 (0)30 6392 4444, Fax: +49 (0)30 6392 4454, e-mail: baerns@aca.fta-berlin.de

The deNOx reaction, i. e. the catalytic reduction of nitrogen oxides to nitrogen by hydrocarbons in an excess of oxygen is of high importance for the automotive industry in their efforts to meet the more stringent future emission standards. Present catalysts suffer from a lack of activity, selectivity and stability. Mechanistic studies on the reaction pathways of the deNOx reaction on existing catalyst formulations are considered to be helpful for defining the catalytic sites and to provide a rational basis for further catalyst improvement and development.

Although considerable progress has been recently achieved in the understanding of the deNOx reaction, the role of Bronsted acid sites and of NO_2 as a reaction intermediate as well as of surface intermediates formed in the reaction course are still being debated controversially. Furthermore, the differences in reduction efficiency between alkenes and alkanes are not completely understood.

The aim of the present study was to elucidate these phenomena. The reactions between NO_2 and propene well as propane as model hydrocarbons were investigated over a H–Mordenite (H–MOR) catalyst by means of pulse experiments in vacuum applying the Temporal–Analysis–of–Products (TAP) reactor and by FTIR experiments. Additionally, continuous flow experiments have been carried out which show that this catalyst is active for NO_2 reduction with a maximum activity at 350 °C with propene and at 450 °C with propane as reducing agents. Oxygen is not necessary for NO_2 reduction to N_2 over H–MOR.

TAP and FTIR experiments have shown that NO_2 as well as propene adsorb strongly on Bronsted acid sites, while propane is only weakly adsorbed below 300 °C. In the reaction between propene and NO_2 over H–MOR at 300 °C, organic nitrogen containing adsorbates like nitriles or isocyanates exist on the catalyst surface as shown by FTIR, these compounds stay adsorbed even after evacuation of the gas phase. In contrast, when propane is used instead of propene, no such adsorbates are formed at 300 °C. From a time resolved FTIR experiment it was derived that NO_2 adsorbed on Bronsted acid sites (ir band around 2200 cm^{-1}) reacts readily with propene and that a band at 2278 cm^{-1} is formed in this reaction which might be indicative of the formation of an organic nitrile or isocyanate compound (Fig. 1).

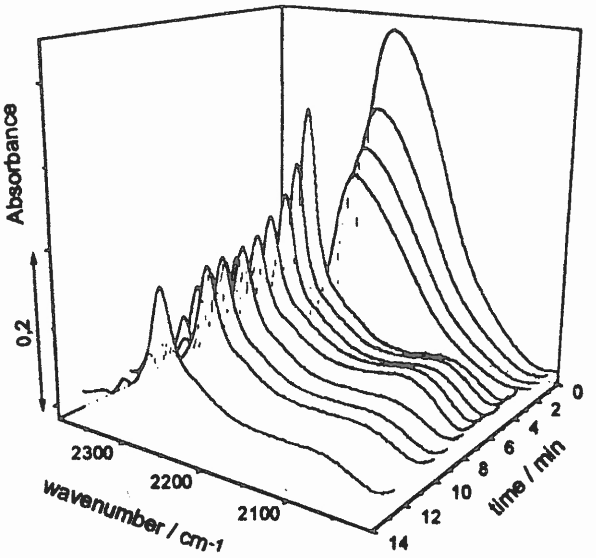


Fig. 1 Spectral changes observed in the 2000 - 2400 cm^{-1} region upon desorption of NO_2 from H-MOR and addition of propene after 3 min.

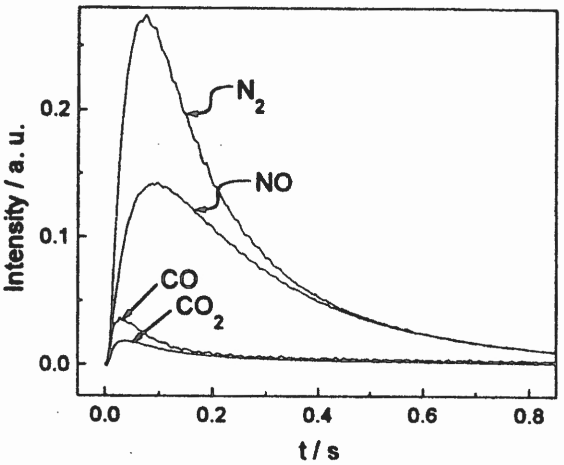


Fig. 2 Formation of N_2 on pulsing NO_2 over H-MOR pretreated in a flow of NO_2/C_3H_6 at 300 °C.

The reactivity of the adsorbates formed in the reaction between propene and NO_2 at 300 °C towards NO_2 was elucidated by TAP experiments. To achieve this aim, the catalyst was pretreated in the TAP reactor at 300 °C for 0.5 h under ambient pressure in a gas stream containing 1000 ppm C_3H_6 and 1000 ppm NO_2 in He. After evacuation of the reactor, NO_2 was pulsed over the pretreated surface. In the NO_2 pulses, the formation of N_2 together with NO and CO_x was observed (Fig. 2). This shows that during the pretreatment adsorbates were formed on the catalyst surface which react with NO_2 to form dinitrogen. It is likely that the adsorbates are the same as observed in the FTIR experiments.

The same experiment was repeated at different temperatures between 200 and 500 °C, and the activity of the catalyst towards N_2 formation during the pretreatments was monitored by means of a GC analysis of the exhaust gas at each temperature. In the NO_2 pulses after each pretreatment, the activity of the catalyst towards N_2 formation paralleled its activity towards N_2 formation during the pretreatment. Therefore it may be concluded that the adsorbates which react with NO_2 in the pulse experiments are the intermediates of NO_2 reduction under continuous flow conditions.

Preliminary results show that when propane is used instead of propene, the formation of such adsorbates requires temperatures above 300 °C. It will be a subject of further studies to investigate the activation of propane on Bronsted acid sites. Furthermore, the reactivity of some model intermediates such as acrylnitrile, ethylisocyanate and acrylamine towards NO_x will be investigated to elucidate the ability of functional groups like –CN, –NCO and –NH_2 to form N_2 when reacting with NO_x.

THE CONVERSION OF METHANOL TO OLEFINS: A TRANSIENT KINETIC STUDY

O. Dewaele, V.L. Geers, G.F. Froment and G.B. Marin*

Laboratorium voor Petrochemische Techniek, Universiteit Gent, Krijgslaan 281 (S5), B-9000 Belgium.

Tel +32 9 264 4917, Fax +32 9 264 4999, E-mail Guy.Marin@rug.ac.be

The conversion of methanol to olefins over a H-ZSM5-catalyst was studied by means of transient experiments in a TAP-setup. Three types of experiments were performed in vacuo between 623 K and 773 K: high pulse frequency steady state experiments, pulse experiments and step experiments.

During the high pulse frequency steady state experiments, methanol was fed into the reactor under vacuum by rapidly injecting methanol at a pulse rate of 40 pulses per second. The maximum reactant and product pressure in the reactor was below 100 Pa. The transport time in the reactor was independent of the feed rate because Knudsen diffusion is the dominant transport mechanism. The measured mass fragmentation spectrum of the effluent was deconvoluted using the reference spectra of different compounds. Methanol, water, dimethylether, methane, ethylene, propylene and butene were found to be the main products in the effluent. Some pentene and traces of hexene were also detected. The main olefin present was propylene. Three fragmentation peaks in the effluent spectrum at m/e 28, 29 and 30 remained after deconvolution. They correspond to the fragmentation spectrum of formaldehyde. The methane to formaldehyde ratio was found to be 1. This is in agreement with Hutchings et al. (1987) who explained the observed methane formation by a route leading simultaneously to formaldehyde. The latter was proposed to be very reactive since its formation was never observed. Lower methanol feed rates, resulting in a lower reactor pressure, give higher ethylene to propylene ratios in the reactor effluent. The propylene to butene and butene to pentene ratios were not affected by changing the feed rate.

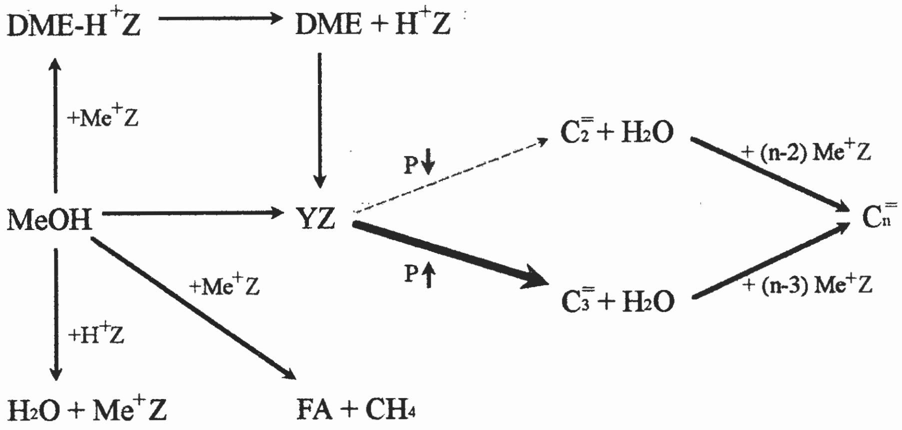
Single pulse experiments with methanol, ethylene and propylene were also performed. The methanol pulse experiments showed that water, formaldehyde and methane are rapidly produced from methanol: their responses are almost identical to the methanol response. This is not the case for the responses of dimethylether and the olefins. The rapid formaldehyde formation agrees with the model of Hutchings et al. (1987). The broadening of the

---

* author to whom correspondence should be addresed.

dimethylether and the olefin responses indicates that several stable surface intermediates are involved in their formation. The main objective of the ethylene and propylene pulse experiments was to identify the main primary olefins. Therefore, ethylene and propylene were pulsed into a continuous flow of methanol in vacuum obtained by injecting methanol at a high pulse frequency. The ethylene and propylene pulse sizes were kept small enough to avoid any significant change of the steady state of the reactor. The olefin distribution produced by ethylene did not correspond to the olefin distribution produced from methanol. The olefin distribution from propylene, however, mainly coincided with the distribution from methanol. Ethylene was not produced sufficiently fast from propylene to be detected during the propylene pulse experiments. These results show that gas phase propylene, and not gas phase ethylene, is the major source for the formation of the higher olefins.

Kinetic data on the olefin production was difficult to retrieve from the methanol pulse experiments because of the large average surface life time of the surface intermediates involved in the olefin formation. Therefore, step experiments were performed on a larger time scale than the single pulse experiments. The high pulse frequency feed of methanol was stopped after the steady state was obtained. The responses of propylene and ethylene show about the same shape. This indicates that there is a common rate determining step for the propylene and ethylene formation. A very rapid decrease of the methanol and dimethylether responses is observed. This is not the case for water and the olefins, whose responses decrease much slower (i.e. on a time scale which could not be observed in the pulse experiment). This leads to the conclusion that water is produced during or after the rate determining step of the olefin formation.



Reaction network consistent with the TAP-data

Reference:
Hutchings, G.J., Gottschalk, F., Hall, M.V.M., and Hunter, R., *J. Chem. Soc. Faraday Trans. 1*, **83**, 571-583 (1987)

OP-5-4

SELECTIVE AND NON-SELECTIVE OXYGEN SPECIES DETERMINING THE PRODUCT SELECTIVITY IN THE OXIDATIVE CONVERSION OF PROPANE OVER VANADIUM MIXED OXIDE CATAlYSTS

H.W. Zanthoff*[1], S.A. Buchholz[1], A. Pantazidis[2, 3] and C. Mirodatos[2]

1 - Rule-University Bochum, Lehrstuhl für Technische Chemie, D-44780 Bochum Germany
2 - IRC-CNRS, 2, Av. Albert. Einstein. F-69626 Villeurbanne Cedex, France
3 - present adress: TOTAL, Cert. B.P. 27, 76700 Harfleur, France

Introduction

The oxidative conversion of propane to propene or functionalized C_3-hydrocarbons, acrolein and/or acrylonitrile, is presently one of the most challenging subjects of alkane activation research. Numerous catalysts have been developed which are able transform the paraffin into the desired product. Among these catalysts those containing vanadium as key element are exhibiting highest performance for achieving high product yields. However, the local environment of the vanadium strongly influences the reaction pathways and leads to different product distributions. Vanadium-magnesium oxide catalysts were found to be very active and selective in the dehydrogenation of propane. Yields of propene up to 15.2 % (V(18.9 wt-%)/MgO; $X_{C_3H_8}$ =35.8%) [1] have been reported over this catalyst system. However, no oxygenates have been observed. Vanadium-phosphorus oxides exhibited high yields in partial oxidation of propane to acrylic acid (in the presence of water); yields of 10.5 % ($X_{C_3H_8}$= 24%) have been reported so far [2]. Vanadium-antimony oxides are well known as catalysts for the ammoxidation of propane to acrylonitrile [3]. Using this catalyst modified with other metal ions yields of acrylonitrile as high as 58.9 % [4] were obtained.

The following limiting factors for achieving high selectivities and yields with these catalysts have been predominantly discussed: the redox behaviour [5,6], the lattice structure of the oxide phases observed in these catalysts [5,7] and the thermodynamic stability of the bonds in reaction products compared to those in propane [8]. Only little attention has been paid to the role of reactive adsorbed oxygen in these catalysts. In the present work we investigated the influence of different oxygen species on the reaction pathways using vacuum transient techniques in the Temporal-Analysis-of-Products reactor. Experiments were performed in the presence and absence of oxygen, using isotopic labeled oxygen to distinguish between lattice and adsorbed oxygen. Model catalysts V(24 wt-%)/ MgO, $(VO)_2P_2O_7$ and different VSb_xO_y catalysts were used to investigate different local vanadium environments.

---

* Corresponding author, Tel. (+49) 234-700-4S18, fax. (+49) 234-7094-115

Results and Discussion

Under vacuum conditions in the absence of gas phase oxygen all catalysts are active in the oxidative conversion of propane. Therefore, it can be concluded that on all catalysts a Mars van Krevelen type of redox reaction is the working mechanism under these conditions. In the presence of gas phase oxygen, however, the three catalysts exhibit a different behavior. The VSb_xO_y catalysts show similar behavior as in the absence of gas phase oxygen, i.e. this catalyst exhibits only active lattice oxygen and the gas phase oxygen is necessary to reoxidize the active sites. For $(VO)_2P_2O_7$ a participation of short-lived adsorbed oxygen was observed, which mainly participates in the activation of propane and its total oxidation. This is in accordance with our previous investigations applying this catalyst for the partial oxidation of n-butane. On the V-Mg-O catalyst, however, a strong influence of short-lived adsobed oxygen species was observed. Again, these species participate in the activation of propane and the total oxidation.

The present results reveal that not only structural and redox properties control the reaction pathways towards the desired or undesired products, but also different environments of the vanadium lead to different active oxygen species that determine the catalytic performance. Furthermore, the higher selectivities obtained under vacuum conditions in the absence of gas phase oxygen over V-Mg-O and V-P-O catalysts suggest the application of the reactor/regenerator principle for these catalysts, where the catalyst is cycled and sequentially reduced/reoxidized while being kept in a near optimum redox state when exposed to the hydrocarbon. In this case the presence of non-selective adsorbed oxygen species might be suppressed or avoided.

Referenses

[1] Chaar, M.A.; Patel, D.; Kung, H.H.; J. Catal. 109 (1988), 463.
[2] Ai, M.; J. Catal, 101 (1986), 389.
[3] Morooka, Y.; Ueda, W.; in: Catalysis Band 11" Royal Chem. Soc., 1994, 223.
[4] Wu, X.Q.; Zhang, Q.; Dai, Q.L.; Hou, Z.Y; Lu, D.W.,- in: 3^{d} World Congress On Oxidation Catalyis; Eds. R.K. Grasselli, S.T. Oyama, A.M. Gaffney and J.E. Lerou, Elsvier, 1997, 1107.
[5] Kung, H.H.; Michalakos, P.; Owens, L.; Kung, M.; Andersen, P.; Owen, O.; Jahan, I.; ACS Symp. Ser. 523 (1993), 389.
[6] Zanthoff, H.W.; Schaefer, S.; Wolf, G.U.: Appl. Catal. A: General 164 (1992), 105.
[7] Mamedov E.A.; Cortes Corberan, V.; Appl. Catal. A: General 127 (1995), 1.
[8] Batiot, C.; Hodnett, B.K.; Appl. Catal. A: General 137 (1996), 179.

OP-5-5

CO_2 reforming in a TAP reactor.

II. Role of the metal on the reaction mechanism ; experiments and modeling

Y. Schuurman and C. Mirodatos
Institut de Recherches sur la Catalyse, C.N.R.S.
2, Avenue A. Einstein, F-69626 Villeurbanne Cédex, France

The reforming of methane by carbon dioxide into synthesis gas is known to be catalyzed by most of the group VIII metals of which Rh, Ru, Ir and Ni are the most active [1-3]. There is a general consensus that the rate limiting step is the step-wise activation of methane. The reaction of carbon dioxide, however, depends on the metal involved [2-4]. On nickel a dissociative CO_2 adsorption is observed into CO* and O*, followed by a surface reaction between C* and O* [3], while on Rh, Ru and Ir a direct reaction between CO_2 and adsorbed carbon is reported [2,4].

This paper describes TAP (Temporal Analysis of Products) experiments comparing different catalysts for the methane reforming : Ni/SiO_2, Ru/SiO_2, and Rh/SiO_2 in order to further elucidate both the role of the metal. In a TAP experiment pulses of reactants are introduced in an evacuated reactor. This technique gives detailed insights in the reaction mechanism [6].

Figure 1 shows the transient responses of the reactants and products on a pulse of $^{12}CH_4/Ar$ followed by a pulse of $^{13}CO_2$ obtained on Ni/SiO_2 at 600°C. The conversion of methane and carbon dioxide amounted to 87% and 96%. The production of hydrogen takes place on the methane pulse and this step can be written as follows :

$$^{12}CH_4 + xNi \rightleftarrows Ni_x{}^{12}C + 2H_2 \qquad (1)$$

Two distinct carbon monoxide pulses are observed on the labelled carbon dioxide pulse : 1) one corresponding to ^{13}CO formed instantly, 2) the second delayed, corresponding to ^{12}CO and presenting a long tail. Apparently there are two different routes for the production of CO, represented by :

$$^{13}CO_2 + Ni \rightleftarrows NiO + {}^{13}CO \qquad (2)$$

$$NiO + Ni_x{}^{12}C \rightarrow (x+1)Ni + {}^{12}CO \qquad (3)$$

A similar experiment was carried out over Ru/SiO_2. The same step (1) for the activation of methane was found. But, at variance with Ni/SiO_2, the ^{13}CO and ^{12}CO responses are identical, indicating that both molecules are formed in the same step, represented by :

$$^{13}CO_2 + Ru_x{}^{12}C \rightleftarrows {}^{13}CO + {}^{12}CO + xRu \qquad (4)$$

All carbon was removed from the Ru surface by pulsing $^{13}CO_2$ until the CO production had dropped to zero. Upon introduction of a pulse of methane over this surface, the conversion of methane and the production of hydrogen was observed, but no carbon monoxide was detected. This experiment shows that even on clean Ru dissociative carbon dioxide adsorption does not take place.

A regression analysis was carried for the transient responses of the reactants and products for all three catalysts based on the above mentioned reaction schemes. The modeling confirmed the different rate-determining steps for Ni and Ru/Rh. It also showed that the methane activation over Ni is slightly reversible in contrast to Ru. This was also observed by isotopic exchange experiments [4,5].

The above TAP observations for the three different catalysts, completed by data obtained on other reforming catalysts, give a direct evidence for common and/or specific features of the mechanisms proposed in the literature [2-5].

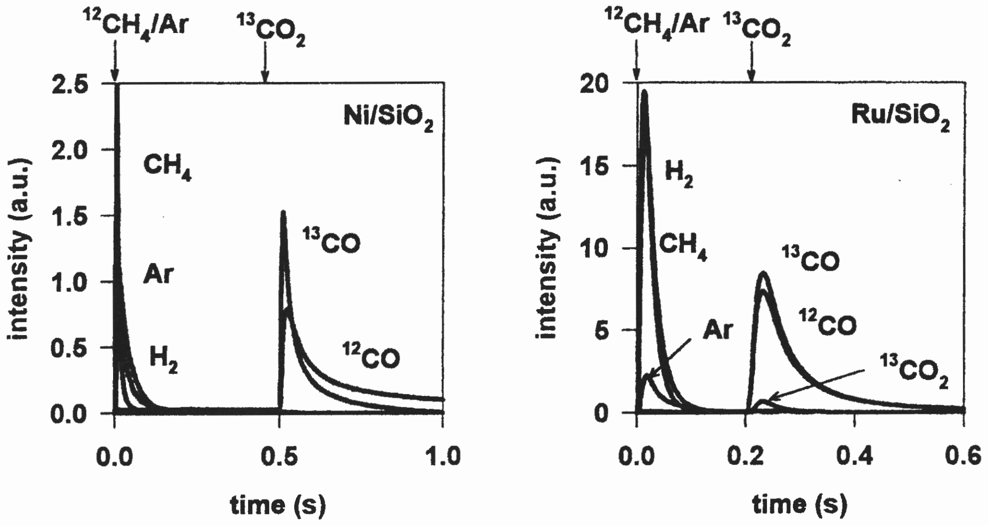


Figure 1. Transient responses from a mixture of CH_4/Ar and $^{13}CO_2$ over Ni/SiO_2 at 600°C and over Ru/SiO_2 at 550°C.

References

1 Rostrup-Nielsen, J. R., and Bak Hansen, J. H., J. Catal. 144 (1993) 38.
2 Mark, M. F., and Maier, W. F., J. Catal. 164 (1996) 122.
3 Kroll, V. C. H., Swaan, H. M., Lacombe S., and Mirodatos, C., J. Catal., 164 (1997) 387.
4 Schuurman, Y., Kroll, V. C. H., Ferreira-Aparicio, P. and Mirodatos, C., Catal. Today, in press
5 Zhang, Z.L., and Verykios, X.E., Appl. Catal., 138 (1996) 109; ibidem, Catal. Lett., 38 (1996) 175.
6 Gleaves, J.T., Ebner, J.R. and Kuechler, T.C., Catal. Rev.-Sci. Eng., 30 (1988) 49.

OP-5-6

PROPANE AMMOXIDATION ON AN Al-Sb-V-W-OXIDE CATALYST. A MECHANISTIC STUDY USING THE TAP-2 REACTOR SYSTEM

Andreas Hinz and Arne Anderson
Department of Chemical Engineering II, Lund University, Chemical Center, P.O. Box 124,
S-221 Lund, Sweden

Abstract

The ammoxidation of propane and especially the nitrogen insertion step and the active ammonia species on an Al-Sb-V-W-O catalyst were characterised with the TAP-2 reactor system. The TAP-2 reactor system provided high time resolution, enabling identification of the different intermediates in the reaction sequence from propane to acrylonitrile at 520 °C. Three different kinds of experiments were performed, namely pump-probe, TPD and multipulse experiments. Information about the reaction mechanism was collected from separate studies of the secondary reaction steps. These studies included the examination of the oxidation and ammoxidation of propylene, the oxidation of ammonia and the oxidation of propylene with O^{18}.

In pump-probe experiments a $=NH$ or $-NH_2$ was identified as being the active ammonia species. It was verified that this species not only was inserted producing acrylonitrile, but also was participating in the abstraction of hydrogen from the hydrocarbon. Furthermore, it was found that different types of oxygen species were responsible for the formation of the reaction products. The results showed different role for lattice oxygen and adsorbed oxygen, respectively. For the formation of carbon oxides both species are active, but for the formation of acrolein only lattice oxygen is inserted. From the product responses it was concluded that acrolein and carbon oxides are formed from propane both in a direct route and also via propene. Acrylonitrile was formed from adsorbed acrolein reacting with ammonia species.

The TPD experiments showed that ammonia decomposition occurs producing primarily N_2, which is partly oxidised to N_2O and NO. For propylene the TPD experiments showed that CO_2 is formed directly from C_3H_6 at low temperature and that at reaction temperature the formation proceeds via CO as an intermediate. Multipulse experiments with C_3H_6 feed showed that the catalyst surface has to be slightly reduced to obtain high selectivity to acrolein. This can be seen as a consequence of the requirement of both, adsorption sites and oxygen sites.

Kinetic Studies of Propylene Oxidation Over VPO Catalysts Using the TAP-2 Reactor System

Tom Brownscombe, Shell Chemical Company, 3333 Highway 6 South,
Houston, TX 77082

Shaorong Chen, J. T. Gleaves, Washington University, Department of Chemical
Engineering, One Brookings Drive, Box 1198, St. Louis, MO 63130

Heterogeneous selective oxidation of hydrocarbons requires catalytic materials that can activate a CH bond and add oxygen without completely oxidizing the alkane. One of the most important selective catalyst is vanadyl pyrophosphate $(VO)_2P_2O_7$ that is used in the oxidation of n-butane to maleic anhydride. Currently, the n-butane to maleic anhydride process is the only industrial process involving the heterogeneous selective oxidation of an alkane. Vanadium-phosphorus-oxides are also known to catalyze the selective oxidation of other hydrocarbons including C5 alkanes and alkenes. Consequently, gaining a fundamental understanding of how VPO catalysts function is an important step in developing new classes of catalytic materials for hydrocarbon oxidation.

Determining the nature and relative amounts of oxygen species at active sites and how they react is essential to understand how a VPO catalyst functions. Ideally, one would like to determine characteristics of the catalyst (e.g., the oxidation state of the catalyst surface) that influence the reaction selectivity and the reaction mechanism. Correlating changes in surface oxygen species with the evolution of reaction products can provide significant new insights into the nature of the active oxygen species that are responsible for CH bond activation and the addition of oxygen.

In this work the reaction selective oxidation of propene over VPO catalysts was studied using a TAP-2 reactor system. TAP transient response experiments were conducted by pulsing propene/argon mixtures over "reactor equilibrated" and "oxygen-treated" VPO catalysts. Results indicated that the major oxidation products are acrolein, benzene, CO, and CO_2. Figure 1 shows that the product distribution strongly depends on the catalyst oxidation state. As the catalyst changes from oxygen-rich to oxygen-lean, CO_2 production decreases, benzene production increases, acrolein production increases and reaches the maximum then decreases. Kinetic parameters for individual reaction step were determined using a combination of vacuum transient data and mathematical modeling. This study has provided more information to understand the nature of activation of CH bond and addition of oxygen.

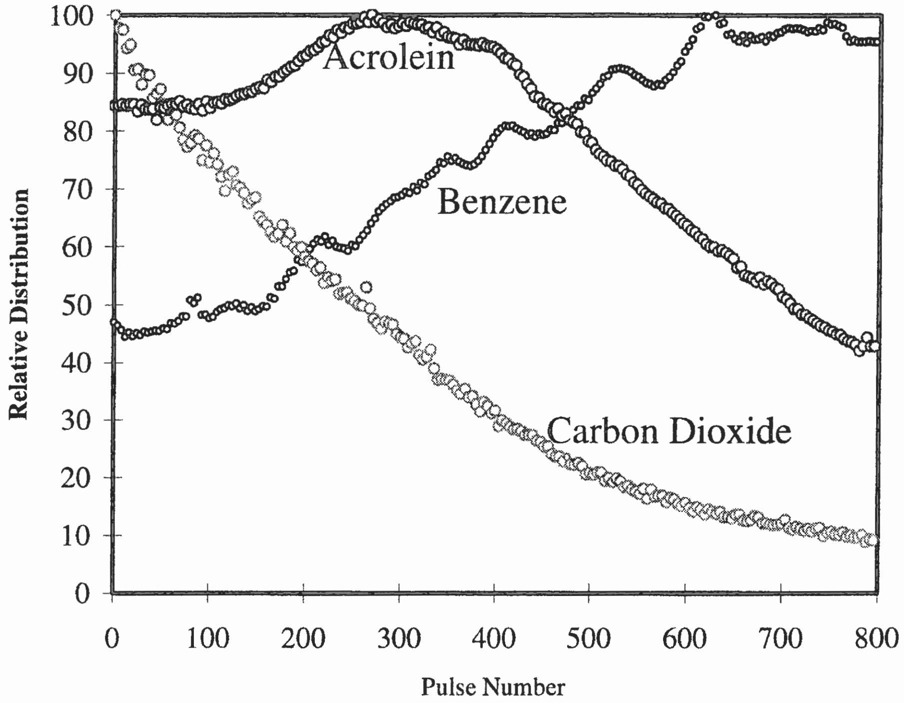


Figure 1. Relative distributions of oxidized product in propylene reaction with oxygen pretreated VPO catalysts

Section 6.

Dynamic Operation of Three Phase Reactors

PERIODIC OPERATION OF THREE-PHASE CATALYTIC REACTORS

P.L. Silveston

University of Waterloo
Waterloo, Ontario, Canada

J. Hanika
Institute of Chemical Technology
Prague, Czech Republic

Various modes of periodic operation of three phase reactors have been examined on a research scale. Enhancement of rates of reaction have been found so that this type of forcing strategy can increase either conversion at a fixed throughput or throughput at a fixed conversion. Of the modes that have been examined so far, periodic flow interruption and variation enhances reaction rates for concurrent trickle beds provided all reactant enter a reactor in the gas phase or that reactants in the liquid phase can be volatilized under bed operating conditions. Periodic flow variation is less effective than flow interruption, but the strategy can be used as periodic pulsing for hot spot prevention. Periodic variation of feed composition has been applied to concurrent trickle beds and fixed bed bubble columns. Temperature excursions in trickle beds can be effectively controlled by composition switching between an inert and a liquid phase reactant. The time average temperature of the bed can be increased so that the operation has no effect on throughput or even augments it slightly. Gas phase composition variation was not effective when employed for fixed bed bubble columns. Several approaches to increasing rate through faster mass transfer have been studied or are suggested by work in progress. Periodic switching of flow direction in airlift reactors increases gas hold up and thus rate through the influence of higher surface area on mass transfer. A quasi-periodic pulsing or slug flow regime can be imposed on a trickle bed reactor by use of a monolith with small diameter, parallel channels as structured packing. Investigations of regime transition and the mechanism of increased mass transfer in pulsing flow suggest periodic flow variation could be used to augment mass transfer in some conventional, randomly packed trickle beds. Periodic operation of three phase reactors appears to be fertile area for engineering research.

OP-6-2

Safe Operation and Control of Trickle Bed Reactor

Jiri Hanika
Institute of Chemical Technology, CZ-16628 Prague 6
e-mail: jiri.hanika@vscht.cz

Safe and profitable manufacturing opportunities in the chemical and petrochemical industry are no longer to be existed without the sophisticated rules for the reactor design and process operation. Gas-liquid-solid reaction systems are widely encountered, usually in continuous configuration using the packed bed of catalyst trickled by liquid reaction component with cocurrent flow of gas which represents the other reactant. Such trickle bed reactors are often applied in plant scale for strong exothermic reactions, a good example is hydrogenation of unsaturated hydrocarbons in pyrolysis gasoline *e.g. Hanika and Lederer, (1993*).

In reaction system containing besides the catalytic active solid phase the flowing reaction mixture in two phases the transport phenomena often come into play and influence the apparent reaction rate. The interaction of heat and mass transfer and strong exothermal reaction proceeding inside the catalyst pellet is so serious that at defined conditions and depending on properties of the reaction itself the multiple-steady states and partial or total phase change can appear. In such situation the reaction can proceed much more faster, can be controlled by a different mechanism or kinetics etc. Such a "pathological" state often results not only in a catalyst destruction in the hot spot inside the catalyst bed but from the safety of reactor operation point of view represents a considerable risk. In literature there are several papers devoted to this topic but it should be stressed the problems are current also in now-days, see e.g. *Goossens, van den Brink and Donker, (1997).*

The reaction mixture flow non-homogeneity in the trickle bed reactor is typical feature of the reaction system. The liquid maldistribution in the catalyst bed makes possible formation of dry unwetted zones. In case of the strong exothermal reaction, adiabatic regime and volatile reaction components the reaction rate in such zone is usually higher in comparison to the well wetted catalyst area. The higher reaction rate accelerate the heat production and thus the hot spot enlargement is often observed. The interaction between the exothermal reaction and the transfer phenomena is very serious event mainly near the boiling point of reaction mixture, see e.g. *Hanika et al., (1977).*

Experimental evidence illustrating on a laboratory scale the possibility of the prevention of the hot spot formation by a two level feed concentration control procedure has been shown recently by *Hanika et al., (1990)* and *Lange et al., (1994).* During the application of the control algorithm the trickle bed reactor operates under the non-steady state regime. Periodic concentration and temperature waves traverse down the catalyst bed. The necessary condition for the reactor control improvement and scale-up of the data consists in the dynamic modelling and in the successfull model parameter identification, see e.g. *Hanika and Lange (1996).*

The key effect for the control of trickle bed reactor play the following parameters:
- feed rate and its composition
- gas flow rate and pressure of operation
- inlet temperature and/or catalyst activity.

The experimental evidence of these effects on the behaviour of the laboratory trickle bed reactor during hydrogenation of unsaturated hydrocarbons will be demonstrated in the paper.

The elimination of a hot spot formation in the trickle bed reactor in the case of strong exothermal reaction is very important from its safe operation point of view. The safety of the reactor regime can be improved also by an application of control algorithm. Based on the monitoring of the axial temperature profile in catalyst bed the two-level control algorithm has been recently applied for the suppression of hot spot formation in trickle bed reactor. The control algorithm often results into the flow rate, concentration and temperature oscillations inside the catalyst bed which can be described using the limited Fourier's series after harmonic analysis of experimental data. The analysis enabled to identify the main factors influencing the dynamics of the trickle bed reactor. The optimization of reactor control parameters is aimed to improve the safety of the trickle bed reactor performance.

Literature

1. Goossens E., van den Brink F., Donker R.A., 1997, *1st Internat. Symp. Hydrotreatment and Hydrocracking of Oil Fractions,* Oostende, Belgium, Feb. 17-19, 1997.
2. Hanika J., Sporka K., Růžička V., Pištěk R.: Dynamic Behaviour of an Adiabatic Trickle Bed Reactor, 1977, *Chem. Eng. Sci.,* **32**, 525-528.
3. Hanika J., Staněk V.: Design and Operation of Trickle Bed Reactors, 1986, *Handbook of Heat and Mass Transfer Volume 2 (Mass Transfer and Reactor Design),* pp. 1029-1080, Gulf Publishing Co., Houston.
4. Hanika J., Lange R., Turek F.: Computer-Aided Control of a Laboratory Trickle Bed Reactor, 1990, *Chem. Eng. Process.* **28**, 23-27.
5. Hanika J., Lange R.: Dynamic Aspects of Adiabatic Trickle Bed Reactor Control Near the Boiling Point of Reaction Mixture, 1996, *Chem. Eng. Sci.,* **51**, 3145-3150.
6. Hanika J., Lederer J.: Simultaneous Hydrogenation of Dienes and Olefines using Palladium Catalyst in Plant Trickle Bed Reactor, *1st European Congress on Catalysis,* Montpellier, France, September 1993.

OP-6-3

Thermal Effects in the Periodic Operation of a Trickle Bed Reactor

Javier Ochoa, Leonardo Gabarain, Jorge Cechini and Patricia Haure
INTEMA. Facultad de Ingeniería. J.B. Justo 4302. 7600.
FAX 54 23 810046. Mar del Plata. Argentina.

The performance of a Trickle Bed Reactor (TBR) under cycling operation is extremely complex, specially for the gas-limited, liquid -volatile exothermic reaction system. In the wet cycles, reaction proceeds via liquid-solid catalyzed mechanism but in the non-wet cycles, if the liquid is volatile and significant effects are present, a gas-solid catalyzed reaction can occur on the dry catalyst, resulting in higher rates and temperatures.

Castellari & Haure (1995) studied the hydrogenation of alpha-methylstyrene in a TBR with periodic interruption of the liquid phase. Reaction rates were increased up to 400% with respect to the steady state results. Gabarain et al. (1997) proposed a phenomenological model that explains the events occurring during cycling. The overall reaction rate is an average between the diffusion-controlled liquid-phase reaction and the more rapid gas-phase catalytic route. The reactor operates at higher average temperatures compared to the steady-state, but is the change in reaction mechanism responsible of the results obtained. The increase in the local reaction rate and the temperature rise may be a feature of concern because it can lead to the formation of uncontrolled hot-spots and the subsequent sintering of the catalyst, runaway conditions and undesirable side reaction.

The objective of the present work is to predict the maximum temperature. Based on the model developed by Gabarain et al (1997), from mass and energy balances in the dry cycle, the following relationship is obtained :

$$\frac{P_B^V(T_O)}{P_B^V(T_{m\acute{a}x})} = \frac{k_O\, e^{\left[\frac{E_a}{R_g T_{m\acute{a}x}}\right]}}{k_g} \frac{T_O}{T_{m\acute{a}x}} \frac{\rho_s (1-\varepsilon_B) d_p}{6} \frac{(-\lambda_r + \lambda_v)}{-\lambda_r} < 1 \qquad (1)$$

Maximum temperature T_{max} depends on initial temperature T_0, liquid vapour pressure p_B, reaction and vaporization heats (λ_r and λ_v), particle diameter d_p and bed porosity ε_B. Gas-solid mass transfer coefficient k_g was evaluated according to Goto and Smith (1975). Kinetic constant k_0 was obtained following Cini & Harold (1991).

Experimental and predicted results are presented in Tables 1 and 2 for different conditions.

Table 1. Q_g : 900 cm^3/min

T_0 (°C)	T_{max}^{cal} (°C)	T_{max}^{exp} (°C)
33	62	50
41	77	71
55	92	100

Table 2. $T_0 = 41$ °C.

Q_g(cm^3/min)	T_{max}^{cal} (°C)	T_{max}^{exp} (°C)
400	60	65
900	77	71
1500	87	80

Experimental and theoretical results differ in less than 10 % in most cases, except at 33°C. The relationship obtained can also be applied to predict temperature excursions obtained during "steady-state" experiments at low liquid flowrates. In this situation, wetting is incomplete and if the liquid reactant is volatile and the reaction is exothermic a gas-solid catalyzed reaction may occur in the dry catalyst (Castellari et al. 1997). Results obtained by Sedricks and Kenney (1971) and Watson and Harold (1993) are reasonably predicted by eqn (1).

References

Castellari A.T., and P. Haure. AIChE J. 41, 6 (1995)

Castellari A.T., J.O. Cechini , L.J. Gabarain and P. Haure. AIChE J. 43, 7 (1997)

Cini P., and M. P. Harold. AIChE J., 37,7 (1991)

Gabarain L.J., A. T. Castellari, J. Cechini, A. Tobolski and P. M. Haure. AIChE J. 43, 1 (1997)

Goto S., and J. M. Smith. AIChE J. 21 (1975)

Sedricks W., and C.N. Kenney. Chem. Eng. Sci. 28, 559 (1993)

Watson P., and M.P. Harold. AIChE J. 39, 989 (1993)

OP-6-4

Induced Pulsing Flow in Trickle Bed Reactors

H.W. Piepers, J.G. Boelhouwer and A.A.H. Drinkenburg
Department of Chemical Engineering
Eindhoven University of Technology
PO Box 513, 5600 MB Eindhoven, The Netherlands
phone: +31 040 2472241; fax: +31 040 2446104; e-mail: tgtchp2@chem.tue.nl

Abstract

Transient operating reactors offer substantial possibilities to increase conversion and selectivity, mainly through just-in-time delivery and removal of the reactants and the products.

Trickle bed reactors are normally operated in the gas-continuous (or trickling) regime, where in fact both gas and liquid percolate cocurrently and in continuous phases through the bed. Beyond certain gas and liquid loads the bed shows naturally a dynamic flow regime in which gas/liquid discontinuities occur, the pulsing flow regime. Pulses are in fact waves of liquid-rich hold-up that regularly travel down the column. These pulses, liquid-continuous in character, sweep up all stagnant liquid at the front, mix it thoroughly with the dynamic hold-up and leave refreshed liquid at the tail. At high gas throughputs, where the linear gas velocity is higher than the pulse celerity, gas enters the pulses from behind and leaves in the front. It appears that this gas flow is discontinuous in nature in the form of very small bubbles. The pulses and the penetrating gas bubbles cause a number of beneficial features in the reactor: strong enlargement of heat and mass transport, reduced back mixing, renewal of interfacial areas, elimination of hot spots.

A disadvantage of natural pulsing beds is that fairly high flow rates are required to get pulsing, and that consequently the contact times between the phases are rather short. Another drawback is that the frequency of the pulses in the natural pulsing flow regime cannot be adjusted independently of the flow rate.

By explicitly controlling the time-dependent inlet flows of gas and liquid to the trickle bed it appears that the natural regime of pulsing flow can be expanded and that the pulse frequency can be forced upon the bed.

Experiments are carried out in a Plexiglas column inner diameter 0.11 m and of 1.30 m height. Two packing materials are used, fairly uniform glass spheres of 6 mm and Raschig rings (5x6x10 mm). Liquid and gas at room temperature and at atmospheric pressure are used in the experimental runs. Magnetic valves in the feed line, activated by electronic timers are used to vary the liquid and the gas feed to the bed as a function of time.

For the two packing materials the transition from trickling to pulsing flow is determined, the liquid hold-up and the pulse frequency at the transition velocity.

In the forced pulsing mode the characteristics of the induced pulses (frequency, velocity, length) are measured with a conductance technique.

From the experimental results it is found that it is indeed possible to expand the natural pulsing flow regime to lower average flow rates and that by pulsing the gas feed it is possible to predetermine the frequency of the induced pulses in the bed and therefore the time constant of the pulses.

A model is set up that indicates the influence of the pulse characteristics to the conversion and selectivity as a first entrance on design rules.

OP-6-5

ENHANCING PERFORMANCE OF THREE-PHASE PACKED-BED CATALYTIC REACTORS BY PULSING-FLOW REGIME

Raeann Wu, Mark J. McCready and Arvind Varma

Department of Chemical Engineering
University of Notre Dame
Notre Dame, IN 46556, USA

Gas-liquid reactions on packed-bed catalysts are common in the chemical and petroleum industries. In these systems, even with constant external feed rates, hydrodynamic instabilities can occur that lead to spatial and temporal fluctuations in the local heat and mass transfer rates, such as those exhibited in the pulsing-flow regime. These fluctuations can significantly affect reactor performance.

Our research is directed towards understanding the effects of these fluctuations on the reaction outcome and taking advantage of their existence by operating prudently in the pulsing-flow regime. This can be accomplished by "tuning" the frequency of the hydrodynamic fluctuations. Several important reaction mechanisms are studied theoretically, utilizing mass transfer fluctuations consistent with experiments. The results indicate that reactor performance is generally enhanced for the pulsing-flow regime over the trickling-flow regime, and that the performance is sensitive to the frequency and can vary significantly depending on its value. These results imply that more efficient processing could be achieved for many common industrial reactions if the reactors were operated properly.

In order to provide a link with theory, the effects of pulsing-flow regime on reaction outcome were investigated experimentally. Hydrogenation of phenylacetylene, dissolved in n-tetradecane over Pt/alumina catalyst was chosen as the experimental reaction system. This is a consecutive reaction, with styrene and ethylbenzene as the desired intermediate and final products, respectively. With properly designed experiments, the reactor performance in pulsing-flow and trickling-flow regimes was compared directly. The effects of process variables such as temperature, feed flow rates and reactant concentrations on the outcome of reaction were also studied. A model of the experimental system was developed, based on the intrinsic kinetics obtained in this work, and using the liquid-solid mass transfer coefficients evaluated from correlations reported in the literature. The simulation results predict all the qualitative experimental trends, and provide a reasonably good quantitative match, with the experimental results. Both experimental and simulation results show that the yield of styrene is higher in pulsing-flow regime than in trickling-flow regime, which confirms the beneficial effect of pulsing-flow regime predicted by the theoretical work.

The results of this work provide a general understanding that can be applied to a variety of gas-liquid-solid reacting systems.

OP-6-6

Mass transfer in Taylor-flow Monoliths:

Enhancement of the mass transfer rate as a result of the periodic character

T.A. Nijhuis, R.K. Edvinsson, P.J.M. Lebens,
F. Kapteijn, and J.A. Moulijn

Delft University of Technology
Department of Chemical Engineering, Section Industrial Catalysis
Julianalaan 136, 2628 BL Delft, The Netherlands
Tel: +31-15-2786458, Fax: +31-15-2784452, E-mail: t.a.nijhuis@stm.tudelft.nl

Introduction

Monolithic catalysts are an attractive alternative to both slurry and trickle bed catalytic reactors. The main advantage of a monolithic 'fixed bed' reactor are a low internal mass transfer resistance, a large external surface area, and a very low pressure drop. In the Taylor-flow regime (Figure 1a) the gas-liquid mixture flows through the narrow monolith channels as a bubble train, in which only a thin liquid film separates the gas-bubble from the wall (and the catalyst). Secondary recirculation in the liquid plugs enhances radial mass transfer and reduces axial dispersion. This paper discusses the development of a simplified model for the mass transfer of a gaseous component under conditions typical for a liquid-phase hydrogenation reaction, in which the hydrogen mass-transfer rate is limiting.

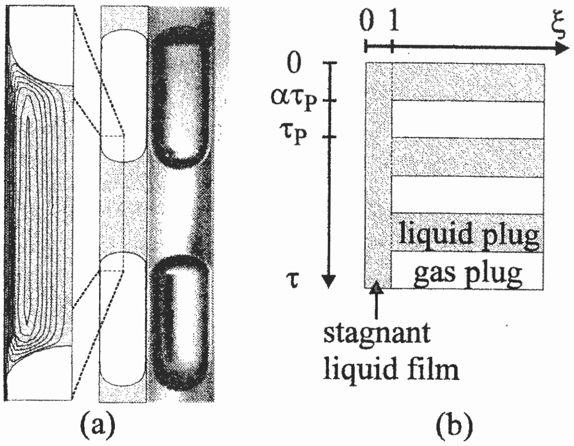


Figure 1. Taylor flow of gas and liquid in a narrow channel: a) calculated and observed (adapted from Edvinsson, 1994), b) simplified representation.

Modeling

The Taylor-flow bubble pattern is simplified as shown in Figure 1b. The assumptions necessary for the modeling are:

- The stagnant liquid film separating the gas and liquid plugs from the catalyst wall is thin, of uniform thickness, and stagnant.
- Reaction on the catalyst surface is first order and limited by the gas component.
- Gas transfer through the end caps of the plugs is neglected

- Liquid plugs contain no dissolved gas as they make contact with the stagnant liquid film.
- The gas and liquid plugs are of constant length and move with a constant velocity.

Using these model assumptions the partial differential equations with the appropriate boundary conditions can be drawn up. By numerically solving these equations the activity of the catalyst can be calculated as a function of for example the cycle time τ_p (the time it takes for one gas and liquid plug to pass) and the gas fraction α. An enhancement factor E can be defined as the increase in the catalytic activity as a result of the periodic nature of Taylor-flow regime in the monolith (*i.e.* activity in comparison to an infinite cycle time, $\tau_p=\infty$). The enhancement factor for a typical hydrogenation reaction, as a function of α and τ_p is shown in Figure 2.

In Figure 2 a clear rate enhancement as a result of the periodic nature of the Taylor flow in the monolith is visible, the rate enhancement being a result of the increased mass transfer rate. The same model also shows that for cycle times smaller than 0.1 s, the catalyst is at a virtual steady state. Furthermore, it was shown that also for reactions, which are not only mass-transfer controlled, the rate enhancement as a result of the periodic operation was significant.

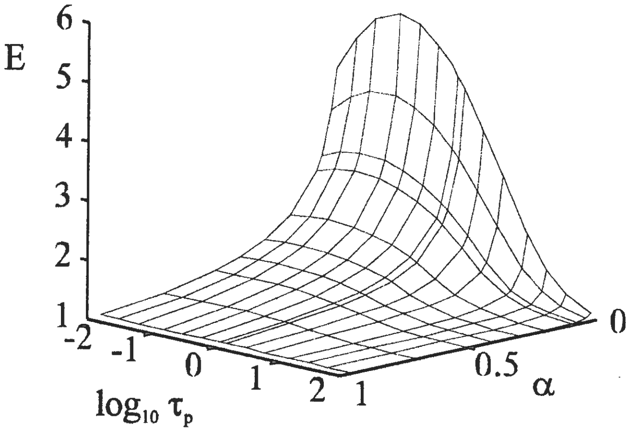


Figure 2. *Enhancement factor as a function of gas fraction (α) and cycle length (τ_p) for a fully mass-transfer controlled reaction.*

Conclusions

Based on the modeling of mass transfer in a Taylor-flow monolith, we conclude:

- At typical liquid-phase hydrogenation conditions in a monolithic catalyst, a significant contribution to the mass-transfer rate can be attributed to transient effects.
- The rate enhancing effect is highest at low gas-to-liquid ratios.
- Even a very thin liquid film on the monolithic catalyst walls is sufficient to dampen fluctuations in concentration, making the catalyst operate in a virtual almost steady-state.
- A monolithic reactor can provide a convenient way to carry out a transient process.

Reference

R. Edvinsson, 'Monolithic reactors in three-phase processes', Ph.D. Thesis, Göteborg (1994).

Section 7.

Nonlinear Phenopmena in Heterogeneous Catalytic Systems

Chemical waves on catalytic surfaces

R. Imbihl, Institut fuer Physikalische Chemie und Elektrochemie, Universitaet Hannover, Callinstr. 3-3a, D-30167 Hannover, Germany

Chemical waves arise to the coupling between an autocatalytic reaction and the diffusion of the reactants. These waves have first been studied in fluid phase reactions but they also occur in many catalytic reactions. In catalytic CO oxidation and NO reduction chemical wave patterns have been investigated on Pt and Rh single crystal surfaces employing various spatially resolving methods which cover different length scales and are based on different contrast mechanisms: photoemisssion electron microscopy (PEEM, 1μm resolution), low energy electron microscopy (LEEM, 0.1 μm resolution), field electron and field ion microscopy (FEM and FIM, 2 nm resolution). On solid surfaces one observes new types of patterns such as rectangularly shaped patterns or standing waves because new aspects come into play which are not present in fluid phase: diffusion anisotropy, global coupling via the gas phase and elastic strain between phases with different densities. Often the surface changes are not restricted to the adsorbate layer but involve a reaction-induced roughening of the catalytic surface. Complex new types of patterns often resembling biological structures can then be found. Chemical wave patterns are not only important for understanding the dynamical behavior of catalytic reactions but they also offer the potential for steering a catalytic reaction. Employing microlithography one can construct microstructured bimetallic surfaces. Turing-like patterns are found in which the adsorbate variations are linked to a spatially modulated composition of an alloyed surface By taking advantage of the dynamical coupling between regions of different catalytic activity one can use the composite surfaces to control the activity and selectivity of catalytic reactions.

OP-7-2

The surface specificity of the oscillating CO-oxidation on small Pd and Pt single crystal planes investigated by FEM

V.V.Gorodetskii[1], P.D.Cobden[2], B.E.Nieuwenhuys[2]

[1]*Boreskov Institute of Catalysis, Prospekt Lavrentieva 5, Novosibirsk, 630090 Russia*
[2] *Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands*

The kinetics and mechanism of CO catalytic oxidation on platinum group metals were the subjects of extensive research. Fascinating kinetic phenomena were discovered [1]: oscillations of the reaction rate and chemical waves moving over the metal surface. In the oscillating regime the reaction mixture variously affects the properties of the metal and can be accompanied by (i) surface phase transition {$CO+O_2$, Pt(100); 1x1 ↔ hex}; (ii) faceting of the surface {$CO+O_2$, Pt(210)}; (iii) formation of a subsurface oxygen layer {$CO+O_2$, Pd(110)}; (iv) «explosive» nature of adsorbed particles interaction {NO+CO, Pt(100)}. «Oxide» or «Carbon» models of kinetic oscillations become possible at high reactant pressures.

Knowledge of the surface specificity is necessary to gain a better insight into these phenomena. The surface of supported metal crystallites with a size of 100-300 Å is mainly formed by the most densely packed (111), (100), (110) faces which differ dramatically in adsorption and oscillation behavior. Therefore, the search of methods for detection of *nano*scale level surface structures active in the oscillative reaction is necessary to design metal catalysts with predeterminated properties. In this work the mechanism of movable waves generation in the oscillating $CO+O_2$ reaction has been studied on Pd and Pt tips by Field Electron Microscopy with a lateral resolution of 20 Å. This method is used for in *situ* study of real dynamic surface processes in which the different *nano*planes present on the emitter-tip are simultaneously exposed to the reacting gas.

The study of the Pd-tip surface has shown that the CO oxidation reaction is characterized by a sharp boundary between two spatially separated adlayers (CO_{ads} and O_{ads}) forming under oscillating conditions: $370 < T < 450$ K, $P_{CO} + P_{O2}$ (1:10) = 2.10^{-3} torr. The CO_{ads}- covered areas are formed only on the {100}planes, whereas O_{ads}- covered areas are formed only on the {110}, {310}and {210}planes. Chemical waves appear on the emitter surface and propagate in phase with self-sustained isothermal oscillations. The initiating role of a *subsurface* oxygen layer formation has been established for the generation of regular waves along certain crystallographic directions on the Pd-tip surface: (i) O_{ads} wave follows the path in the direction (110) → (210) → (100); (ii) CO_{ads} wave moves in the opposite direction.

The work function variation with coverage was used for determination of the isosteric heat of CO adsorption on the clean Pd surface: ~38 kcal/mole was found at low coverage. Probably, the presence of subsurface oxygen can produce a significant decrease in the CO adsorption energy. As a result of this oxidized surface local oscillations can be obtained.

For CO+O_2/Pt system, the experimental observations strongly suggest that the CO oxidation is a face-specific reaction; kinetic oscillations are observed for (100), (110) and (210) but not for (111), (112) planes. A study of the Pt-tip surface has shown that the CO oxidation reaction is characterized by a sharp boundary between movable waves of CO_{ads} and O_{ads}. A reaction zone with a width of 50 Å has been found between CO_{ads} and O_{ads} layers exhibiting the maximum activity in the CO_2 production. Two spatially separated adlayers (O_{ads} and CO_{ads}) are formed on the Pt-tip surface under oscillating conditions. The initiating role of a reversible *phase transition* Pt(100)-*hex* ⇔ *1x1* has been established for the generation of regular waves along the certain crystallographic directions on the Pt-tip surface: (i) CO_{ads} wave follows the path in the direction (111) → (113) → (100); (ii) O_{ads} wave moves from (100) → (210) → (110) faces. The Pt(100) surface in the *1x1* phase is catalytically active due to its ability to dissociate O_2 molecules; S_0 sticking probabilities are 0.3 and 10^{-3} for the 1x1 and hex phases, respectively.

In summary, it may be concluded that the character of the CO+O_2 oscillating reaction on Pt differs remarkably from that on Pd: (i) *subsurface oxygen mechanism* (Pd) and *phase transition mechanism hex ↔ 1×1* on Pt; (ii) oxygen front travelling in the reverse direction: on Pd starts from (110) moving to (100); on Pt starts from (100) moving to (110). The principal result of this work lies in the following: *the appearance of regular waves* under the reaction rate oscillations is an amazing example of *self-organization of a catalytic reaction* when the size of the active catalyst averages *some hundreds Å*.

References

1. G.Ertl. Adv. Catal. 37 (1990) 213

Acknowledgement This work is supported by RFBR Grant # 96-03-33211 and by Grant NWO.

OP-7-3

Unsteady behavior of CO oxidation over supported Pt catalysts and Pt single crystals: self-sustained rate oscillations in the Torr pressure range

G. Bonilla, T.D, Pletcher, G. Haas, and J. Lauterbach

School of Chemical Engineering,
Purdue University,
West Lafayette, IN 47907-1283
phone: (765) 494-4076
fax: (765) 494-0805
e-mail: jochen@ecn.purdue.edu

The CO oxidation on platinum single crystals has been studied very intensively regarding self-sustained rate oscillations and spatio-temporal pattern formation under vacuum conditions. A rich variety of fascinating non-linear phenomena has been reported. Experiments have also been carried out in the pressure regime of practical interest in which the oscillatory kinetics of supported catalysts are studied near atmospheric pressure. Therefore, a considerable pressure gap exists between model investigations of single crystals and studies of supported catalysts under more realistic conditions. There are very few studies of supported catalysts at low pressure conditions, which makes a comparison of the reaction behavior of single crystals and supported catalysts very difficult. Also, typically low-pressure oscillations on single crystal surfaces are explained with an adsorbate induced surface phase transition, while the oscillations observed at higher pressures on supported catalysts are more frequently rationalized in terms of a surface oxidation and reduction model, although there is no universally acknowledged mechanism.

In this paper, we report unsteady behavior of the CO oxidation over supported platinum catalysts (Pt / Al_2O_3 and Pt / SiO_2). Experiments were performed in two flow reactors. One is a reaction cell attached to an ultra high vacuum system. The sample holder can both house single crystals and thin pressed catalyst disks, therefore allowing a direct comparison of both catalyst types under the same flow conditions. Reaction rates are followed with a differentially pumped mass spectrometer. The second system is a small IR transmission cell, where we can perform time resolved FT-IR spectroscopy of admolecules on supported catalysts.

We have studied the CO oxidation systematically over a wide range of pressures from ~ 10^{-3} mbar to ~ 100 mbar, i.e., from strictly isothermal to slightly non-isothermal conditions. We also varied the flow in the reactor, thereby controlling the amount of gas-phase coupling. While for the supported catalyst, our measurements concentrated on the reaction rate as a function of control parameters pressure and temperature, we also used a novel technique, ellipsomicroscopy for surface imaging (EMSI), to follow spatio-temporal pattern formation on the Pt(100) and Pt(110) single crystal surfaces. Our goal here was to compare the parameter space (partial pressures of the reactants, catalyst temperature, pumping speed of the reactor) for unsteady behavior of the CO oxidation on the supported catalyst samples with the platinum single crystals in the same reactor under very similar conditions.

In general, the oscillatory range for supported catalysts is much broader with respect to the gas composition compared to the single crystals. The supported catalysts show a fascinating variety of oscillations over a very wide range of CO / O_2 rations. We believe that one key to the understanding of those rate oscillations is to take into account the gas-phase coupling mechanism, which can synchronize different active areas on the supported samples very effectively. Time-resoved FT-IR spectra will be shown correlating the concentration of adsorbed CO on the supported catalyst surface with the reaction rate.

Chaos, Synchronization and Phase Death Phenomena in Globally Coupled Kinetic Oscillators

M.M. Slinko, E.S. Kurkina, M.A. Liauw, N.I. Jaeger

Institute of Chemical Physics RAS, Kosygina str., 4, Moscow 117334, Russia
Department of CM&C, Moscow State University, Moscow 119899, Russia
Technische Chemie I, Universität Erlangen-Nürnberg,D-91058 Erlangen, Germany
Universität Bremen, FB 2, PF 330440, D-28334 Bremen, Germany

Various types of dynamic behaviour including periodic regular, self-similar mixed mode and chaotic oscillations have been observed during the CO oxidation over Pd zeolite catalysts [1,2]. One of the possible origins of complicated dynamic behavior in this system may be incomplete synchronization between reaction rate oscillations from various parts of the catalyst bed layer [2]. The goal of the present study is to model the dependence of the properties of the observed global oscillations of the reaction rate upon the strength of coupling of various parts of the catalyst bed through the gas phase.

A detailed mathematical model, describing the global coupling of various parts of the catalyst layer in CSTR via the gas phase was developed on the basis of a simple discrete model, described in [2]. The catalyst layer was divided in n (n>3) parts. Each part could produce oscillations, due to the periodic reduction-oxidation of Pd clusters and described by the subsurface oxygen model. The global coupling of all local oscillators was simulated, considering the gas-phase mass balance of the concentration of the deficient component, CO. The external parameters of the model corresponded to experimental conditions. The constants of the reaction mechanism were taken from the literature and were fitted to describe the regular periodic oscillations.

The strength of coupling between local oscillators is defined by the ratio of the amount CO consumed due to the reaction over each part of the layer to the amount of CO, introduced into the reactor with the reactant mixture. It depends on the activity of the Pd site, the value of the external surface of Pd and the flow rate.

The frequency of rate oscillations produced by the subsurface oxygen model is nearly completely defined by the ratio of constants responsible for the reduction and the oxidation of Pd subsurface layer, resp. By varying this ratio for various parts of the catalyst bed, it was possible to model the gas phase coupling of oscillators with widely different natural frequencies. The results of mathematical simulations demonstrated that the dynamic behavior of the global reaction rate depends greatly on the difference of frequencies of natural oscillators, their character and the degree of conversion, which is linked with the strength of coupling. Complete synchronization always occurs for oscillators with less distinct relaxation character when the degree of conversion exceeds 5-6%, even if the natural frequency of the local oscillators differed more than 500 times. These are the conditions of the strong coupling between oscillators under which only periodical synchronous oscillations may be obtained. Mixed mode oscillations were obtained in the case of widely different natural frequencies for only extremely relaxation character of local oscillators. These conditions were favourable also for the development of the oscillator death phenomena -regime of the stationary behavior, when local oscillators were linked together.

The chaotic regime and self-similar mixed mode oscillations were observed only under the conditions of a weak coupling, which correspond to the degree of conversion less than 1 %. It was demonstrated, that such conditions may be obtained by the increase of the flow rate, the decrease of the external surface of Pd and/or activity of each local oscillator. The chaotic time series were found under the conditions, when the parameters of one of the uncoupled oscillators are chosen in the neighbourhood of the Andronov-Hopf bifurcation. These are the conditions of the maximum sensitivity of the dynamic behavior of one oscillator to the other oscillators.

The comparison of the considered model with experimental data will be presented and the origin of chaotic oscillations in heterogeneous catalytic systems will be discussed.

Literature

[1] M.M. Slinko, N.I. Jaeger, P. Svensson "Mechanism of the Kinetic Oscillations in the Oxidation of CO on Palladium Dispersed within a Zeolite Matrix" J.Catalysis, 118, 1989, 349-359

[2] M. Liauw, P. Plath, N. Jaeger " Complex oscillations and global coupling during the catalytic oxidation of CO", J.Chem.Phys., 104 (16), 1996, 6375-6386

OP-7-5

The Mechanism of Kinetic Oscillations in the Catalytic N_2O Decomposition over Cu-ZSM-5

Thomas Ochs and Thomas Turek*
Institut für Chemische Verfahrenstechnik, Universität Karlsruhe (TH),
D-76128 Karlsruhe, Germany, *Tel.: +49 (0)721 608 4267, Fax: +49 (0)721 608 6118,
e-mail: thomas.turek@ciw.uni-karlsruhe.de

Introduction

Cu-ZSM-5 has now become a model catalyst for the study of several reactions of nitrogen oxides. It is still the most active catalyst for the decomposition of nitric oxide and also exhibits high activity with respect to the decomposition of nitrous oxide. When excessively exchanged Cu-ZSM-5 is used, kinetic oscillations during N_2O decomposition have been observed in a broad range of experimental conditions [1-3]. The explanation of this phenomenon allows to identify the active copper site and the role of adsorbed species during the above reactions.

Experimental

Cu-ZSM-5 catalysts with different copper content were prepared by ion-exchange of Na-ZSM-5 (Si/Al = 46) with copper acetate solutions at room temperature. Activity measurements in integral or gradientless reactors were carried out between 623 und 723 K, typically with 1000 ppm N_2O in He at reactor inlet. The exit concentrations were measured with a magnetomechanic oxygen analyzer, a series of infrared spectrometers, and a quadrupol mass spectrometer in multiple ion-detection mode. The amount of adsorbed species under reaction conditions was determined by different temperature-programmed and transient experiments [4] as well as by *in situ* FTIR measurements.

Results and Discussion

The variation of copper content showed that the N_2O decomposition activity exhibits maximum values at copper exchange levels between 100 und 200% (i.e. $0.5 < n_{Cu}/n_{Al} < 1.0$). Only above 100% exchange level, sustained kinetic oscillations are developed. During the oscillations, two different states of catalytic activity with respect to nitrogen formation and a characteristic desorption of O_2 and NO at each transition from low to high activity can be observed (Fig. 1). The development of the amount of adsorbed species, determined by transient desorption experiments at different stages of the oscillations, reveals that the catalyst is in the active state at the first exposure to nitrous oxide. The adsorption of atomic oxygen effects rapid initial deactivation. Results after pretreatment of the catalyst with different reducing agents clearly show that Cu^+ is the active form of copper in ZSM-5.

During the period of lower decomposition activity, nitrate is additionally formed in a slow side reaction. The development of this nitrate species can also be observed by *in situ* FTIR measurements. The oscillations emerge from the dynamic interaction between the adsorbed species, atomic oxygen and nitrate, which results in periods of different coverage of the active copper sites and thus different decomposition activity. It is believed that NO synchronizes the individual oscillators through the gas phase.

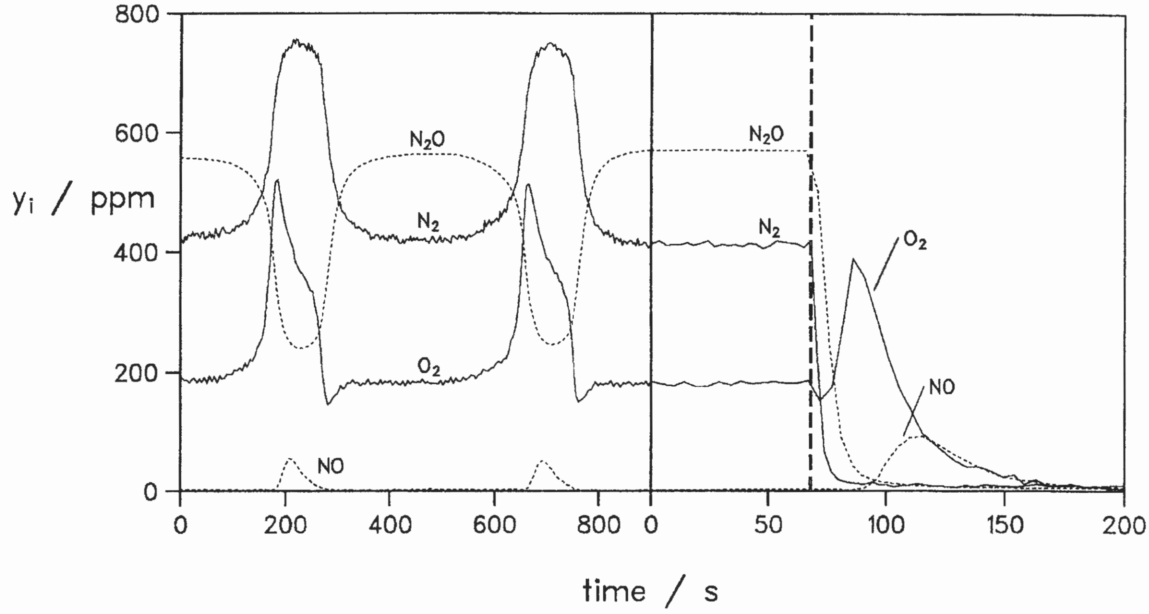


Fig. 1: Exit concentrations in the integral reactor versus time using Cu-ZSM-5(177%) at 698 K, 1000 ppm N_2O in He, GHSV = 60.000 h^{-1}. Left hand side: Sustained oscillations. Right hand side: Transient response at switching to pure He at reactor inlet.

With the aid of a simple reaction scheme consisting of five reactions it is possible to calculate the development of gas-phase and adsorbed species in the sustained oscillations as well as the concentrations during the transient desorption experiments. In both cases, good agreement between results from the mathematical model and the experimental observations is achieved.

References

[1] H.G. Lintz und T. Turek, *Catal. Lett.* 30 (1995) 313

[2] T. Turek, *Appl. Catal. B* 9 (1996) 201

[3] P. Ciambelli, E. Garufi, R. Pirone, G. Russo und F. Santagata, *Appl. Catal. B* 8 (1996) 333

[4] T. Turek, *J. Catal.* in press

OP-7-6

SPONTANEOUS ISOTHERMAL OSCILLATIONS IN N_2O DECOMPOSITION

P. Ciambelli[1], A. Di Benedetto[2], R. Pirone[3] and G. Russo[3]

[1]*Dipartimento di ingegneria chimica e alimentare, Università di Salerno, 84084 Fisciano (SA) Italy*
[2]*Dipartimento di ingegneria chimica, Università di Napoli "Federico II", 80125 Napoli Italy*
[3]*Istituto di ricerche sulla combustione, CNR, P.le Tecchio, 80 Napoli 80125 Italy*
Tel. [39] (81) 7682220 Fax [39] (81) 5936936. E-mail: pirone@irc.na.cnr.it

N_2O decomposition has been investigated on Cu over-exchanged ZSM5 zeolite. As we recently reported [1,2], when a gas mixture containing nitrous oxide (300 ppm) in He carrier is fed to the catalytic reactor, self-sustained isothermal oscillations of N_2O and O_2 outlet concentration are observed. Up to now, this is the only one example of isothermal oscillations reported in a monomolecular reaction [1-3], whereas many oscillating catalyzed bimolecular reactions have been discovered [4].

In our experiments the reactor isothermicity is assured by both the temperature control of the electrical furnace in which the microreactor is inserted and the negligible thermal effects due to the heat of reaction because of the very low reactant concentration involved. Moreover, it is worthwhile to point out that the reactor temperature axially measured along the catalytic bed is constant in the whole experiment (maximum fluctuations range within ± 0.1 °C).

We have found that the oscillations become unobservable with increasing the catalyst particles size. Fig. 1 reveals that when the intraparticle diffusion takes place (as noted from N_2O average conversion decrease), the amplitude of oscillations reduces. This occurrence demonstrates the essential role of chemical kinetics.

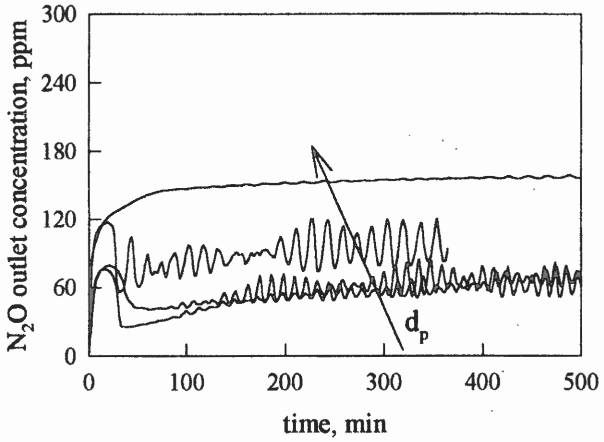


Figure 1. N_2O outlet concentration as a function of time in reaction tests carried out at 370°C with different catalyst particles size: d_p = 200-300, 300-400, 400-710 and 710-1000 μm. Feed: N_2O (300 ppm) and balance He. W/F = 0.038 g·s·Ncm^{-3}. Catalyst Cu content = 3.94 %-wt. Si/Al = 80.

Moreover, we have carried out a reaction test by adding a little amount of NO (100 ppm) to the feed containing N_2O (1000 ppm) and He (as a balance) in conditions at which the nitrous oxide average conversion is quite complete. Fig.2 shows that in such conditions, although the N_2O outlet concentration is very close to zero, the concentration of O_2 still oscillates around an average value, stoichiometrically in agreement with nitrous oxide consumption. It is worth

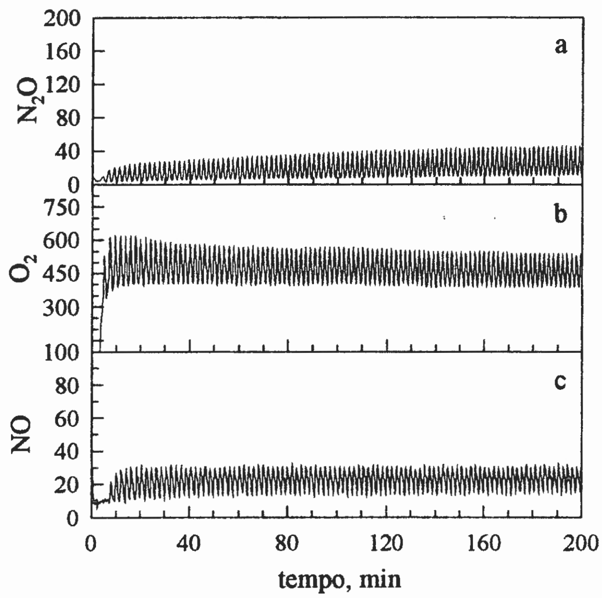


Figure 2. N_2O (a), O_2 (b) and NO (c) outlet concentrations as functions of time in a reaction test carried out at 425°C. Feed: N_2O (1000 ppm), NO (100 ppm) and balance He. W/F = 0.030 g·s·Ncm^{-3}. Catalyst Cu content = 2.03 %-wt. Si/Al = 25.

noting that NO decomposes too, since its outlet concentration oscillates around a value of about 25 ppm. The appearing of NO oscillations indicates that not only the decomposition rate of N_2O, but also that of NO is unstable, although NO oscillations do not appear in any experimental condition investigated when N_2O is absent in the feed. These results suggest that periodic transformations occur in the catalyst while decomposing N_2O. These modifications give rise to the oscillations of reactant as well as product outlet concentrations, but also to the oscillations of another possible reactant.

Consequently, we have developed a kinetic model for N_2O decomposition based on a reaction mechanism involving the redox chemistry of copper, which attributes gas phase oscillations to periodic changes of the state of oxidation of the catalyst. The reaction mechanism proposed is reported below:

$$N_2O + Cu^+ \rightarrow [N_2O^- \text{-} Cu^{+2}] \qquad (1)$$

$$[N_2O^- \text{-} Cu^{+2}] + Cu^+ \rightarrow N_2 + [Cu^{+2} \text{-} O^{-2} \text{-} Cu^{+2}] \qquad (2)$$

$$N_2O + [Cu^{+2} \text{-} O^{-2} \text{-} Cu^{+2}] \rightarrow N_2 + O_2 + 2\ Cu^+ \qquad (3)$$

$$[Cu^{+2} \text{-} O^{-2} \text{-} Cu^{+2}] \rightleftarrows O_{ads} + 2\ Cu^+ \rightleftarrows \frac{1}{2}\ O_2 + 2\ Cu^+ \qquad (4)$$

$$2\ O_{ads} \rightleftarrows O_2 \qquad (5)$$

Numerical simulations carried out to model the outlet composition from a plug flow reactor have shown that the reaction mechanism (1-5) may produce an oscillating kinetics. The model gives quite good quantitative description of the experimental data.

REFERENCES

1. Ciambelli P., Garufi E., Pirone R., Russo G. and Santagata F., *App.Catal. B*, **8** (1996) 333.
2. Ciambelli P., Di Benedetto A., Garufi E., Pirone R., and Russo G., *J. Catal.* (1998) *in press.*
3. T. Turek, *Appl. Catal. B*, **9** (1996) 201.
4. M.M. Slin'ko and N.I. Jaeger; *Oscillating heterogeneous catalytic systems*; Elsevier Science, Amsterdarm, 1994.

OP-7-7

SPATIOTEMPORAL PATTERNS IN A HOMOGENEOUS FIXED-BED REACTOR MODEL

Moshe Sheintuch and Olga Nekhamkina
Department of Chemical Engineering
Technion, Haifa, Israel 32000
Abstract submitted to USPC-3

Phone: 972-4-8292820
Fax: 972-4-8230476
e-mail: cermsll@tx.technion.ac.il or olgan@cestar.technion.ac.il

The dynamics of the homogeneous thermokinetic ($Le = 1$) reactor model has been investigated extensively (e.g. see Subramanian and Balakotaiah [1]). This model cannot account for catalytic oscillations due to the large heat capacity. Spatiotemporal pattern formation in a heterogeneous fixed-bed reactor were recently studied by Barto and Sheintuch [2] for the one-dimensional model with slow and reversible changes in activity. Sharp fronts emerge in this case due to the local multiplicity caused by bistability and transport resistance.

In the present work we study the spatiotemporal patterns in a homogeneous thermokinetic reactor model, i.e. when gradients between the solid and fluid phases are small, with slow activity changes. The three variable model accounts for temperature (θ), conversion (x) and activity (ϕ):

$$x_t - Pe_x \Delta x - \nabla x = Da\phi(1-x)exp(\frac{\gamma\theta}{\theta+\gamma}), \tag{1}$$

$$Le^*\theta_t - Pe_\theta \Delta\theta - \nabla\theta = BDa\phi(1-x)exp(\frac{\gamma\theta}{\theta+\gamma}) \tag{2}$$

$$\phi_t = K_\phi(\alpha - \phi - \beta\theta). \tag{3}$$

B and γ are the dimensionless adiabatic temperature and activation energy; Da and Pe are the Damkohler and Peclet numbers; the parameters in the Eq. 3 define the variation of the catalytic activity.

This model admits sharp fronts for high Pe and γ numbers: Shape preserving fronts are possible in infinitely-long bistable systems. Note that in the heterogeneous model the source term in the energy balance equation, which combines the kinetic source with interphase heat exchange term, may be multivalued. In the homogeneous model the source term is single-valued sigmoidal: The incorporation of the flow-terms, written in an appropriate cell model, may render it multivalued when dispersion is sufficiently strong. We can construct then phase diagrams in the plane (θ, ϕ). The dynamics of the cell-model can be analyzed and classified in terms of these models and the regions of pattern formation can be estimated.

A typical series of patterns is presented in Fig. 1. Varying a parameter leads first to bifurcation from a stationary front to an oscillatory periodic one. The oscillation period changes until eventually a fully extinguished solution is achieved. Since the temperature profile is monotonically increasing we expect that these are the only possible patterns.

We also studied patterns formation in a cooled reactor and in a cross-flow design with reactant feeding along the reactor. Here, the temperature profile can show one or several maxima, respectively, and exists a richer variety of patterns.

References

1. S.Subramanian and V.Balakotaiah, Chem. Eng. Sci., **51**, 401 (1996)
2. M.Barto and M.Sheintuch, AIChE J., **40**, 120 (1994)

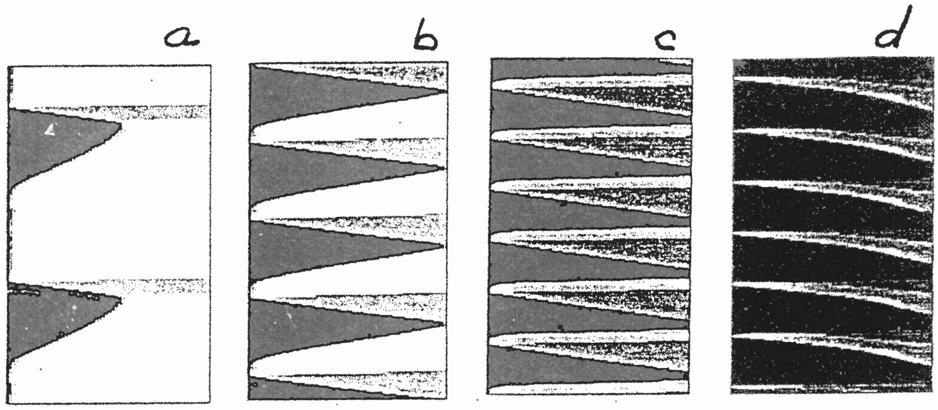


Fig. 1 The evolution of periodic patterns in a homogeneous reactor with changing β: β=0.09 (*a*), 0.10 (*b*), 0.15 (*c*), 0.5 (*d*). Pe_t=50, Pe_c=500, Da=0.06, B=30, γ=20.

OP-7-8

DYNAMICS OF CO OXIDATION OVER EUROPT-3: SUPPRESSION OF SELF-OSCILLATIONS BY PERIODIC OPERATION

Frank van Neer and Alfred Bliek

Department of Chemical Engineering, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands, tel. +31-20-5255265, fax +31-20-5255604, e-mail: bliek@chemeng.chem.uva.nl

Introduction

In the research into the use of forced oscillations in heterogeneous catalysis we investigated the mechanism underlying vibrational control. It has been shown in literature that forced oscillations can be used to suppress self-oscillations during CO oxidation (see for instance [1]). However, a mechanism is often lacking.

In order to fully understand the response on imposed transients, first the mechanism underlying self-oscillations must be elucidated. There are various mechanisms that may explain the oscillations which have been experimentally observed for CO oxidation on Pt, the reaction of our interest [2]. The Langmuir-Hinshelwood reaction between adsorbed CO and O atoms has been well established as the dominant mechanism for this reaction. The dissociative adsorption included in the model causes multiplicity of steady states which is a necessary condition for the occurrence of self-oscillations. Much debate in literature is devoted to the second characteristic; the feedback mechanism that drives the system from one steady state to the other. Depending on the catalyst, pretreatment of the catalyst, equipment properties etc. different results were obtained and consequently various mechanisms were proposed. Among them are sorbate induced restructuring, coverage dependent activation energy, catalyst deactivation by carbon deposition and the oxidation/reduction of Pt particles.

From the above a twofold objective for the present study is derived:

- elucidation of the feedback mechanism during self-oscillations on our catalyst
- finding out the mechanism of vibrational control

Experimental

EuroPt-3, a catalyst consisting of 0.3 wt.% Pt supported on Al_2O_3, was used in transient IR experiments conducted in a specially designed low volume flow cell as presented in [3]. The reaction intermediates present during the reaction on the catalyst were monitored by FTIR and gas phase composition was analysed by a mass spectrometer. Concentration programming was carried out using a 4-way valve. Results of forced oscillation as well as steady state (self-oscillation) experiments will be presented.

Results and conclusions

As an example the results of a (semi) steady state experiment are given in Figure 1. Upon introduction of a 0.25% CO / 5% O_2 in Helium mixture in the cell at 220°C the shown response is obtained. Initially one would conclude that the system is stable as becomes clear from the constant conversion during the first 100 minutes. However, accumulation of various species on the surface is observed and conversion decreases after some time. Interestingly, strong bands are found for CO on PtO. Calibration of the IR absorbances made us to conclude that after 400 minutes nearly all the Pt is oxidised and the relatively inactive species CO-PtO are formed. The formation of this unreactive species leads to oscillations at a certain point due to the decrease of the number of sites where reactions can occur. We observed that as long as the CO-PtO concentration is kept below a critical level (see Fig. 1), oscillations are absent. Oxidation of the catalyst with O_2 may promote the self-oscillations whereas reduction with H_2 removes all the oxidised species and stabilises the system. We will show that an oxidation/reduction mechanism is able to describe the observed oscillations.

Periodic operation is performed by periodically feeding a 0.25% CO / 5% O_2 / He mixture and 5% CO / He to the reactor. When a period of 1 min. is applied a cycle split of 80% is sufficient to keep the amount of CO-PtO below a critical level. We will demonstrate that the oscillations are suppressed and simultaneously the time-average reaction rate is increased.

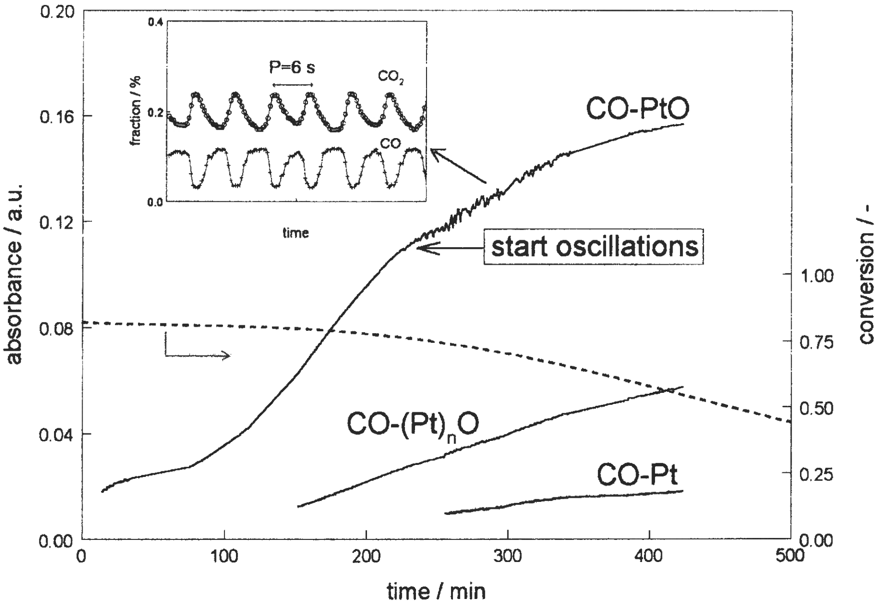


Figure 1. Response of reduced EuroPt-3 upon introduction of 0.25%CO / 5%O_2 at 220°C. IR absorbance of the main species as well as the conversion of CO is shown.

[1] F. Qin and E.E. Wolf, Chem. Eng. Sci., 50 (1995) 117.

[2] M.M. Slin'ko and N.I. Jaeger, Studies in Surface Science 86, Oscillating Heterogeneous Catalytic Systems (Elsevier, Amsterdam, 1994).

[3] F.J.R. van Neer, B. van der Linden and A. Bliek, Catal. Today, 38, 1 (1997) 315.

Section 8.

Dynamics of Automotive Converters

EFFECTS OF INTERNAL DIFFUSION LIMITATIONS IN CATALYTIC FIXED BED REACTORS WITH CYCLING OF THE FEED

J.H.B.J. Hoebink[1], A.J.L. Nievergeld[2] and G.B. Marin[3]

Eindhoven University of Technology,
Laboratorium voor Chemische Technologie
P.O. Box 513, 5600 MB Eindhoven, the Netherlands
phone + 31 40 2472850; fax + 31 40 2446653; E-mail TGTCJH2@CHEM. TUE.NL

The operation of chemical reactors under transient conditions, when compared to the traditional steady-state operation, is well-known for its potential to increase the reactor performance, e.g. conversion, selectivity, energy saving. A recent overview was presented shortly [1] One way of achieving better performance is perturbation of the reactor feed concentrations, an example being cycling of the feed as met in catalytic converters for automobile exhaust gas [2]. Improvements could be due to non-linear reaction kinetics [3,4]. Perturbations should be applied at a timescale which is comparable to the timescale of the reaction. As each elementary step in a kinetic model has a distinct timescale, a detailed knowledge of the kinetics on the level of elementary steps is a prerequisite for the successful design of a transient reactor. Transient kinetic studies, moreover, provide a lot of extra mechanistic and kinetic information, leading to a wider applicability of a kinetic model.

The current contribution addresses the effects of diffusion limitation in catalyst pellets under transient condition. In an industrial application this phenomenon might improve reactor conversion/selectivity when adsorption of one reactant in the outer shell of a pellet inhibits the reaction rate [5]. In a laboratory environment, however, when studying kinetics with transient methods, one wants to avoid transport limitation in order to obtain intrinsic data. The criteria for such an approach are well-developed only for steady-state reactors. For transient numeration an onset has been made only for step- and pulse-wise [7] operation. The problem seems even more relevant when high frequency perturbations are applied. In automobile exhaust gas converters oscillations at typical frequency of 1 Hz occur. Recently Zeron

---

[1] Corresponding author
[2] Current address: AspenTech Europe BV, P.O. Box 258, 5680 AG Best, the Netherlands
[3] Current address: Universiteit Gent, Laboratorium voor Petrochemische Technieh. Erijgslaan 281 S5, B-9000 Gent, Belgium

Altamira announced a commercial microreactor for fast-switching applications at frequencies as high as 5 Hz [8]. The present paper will report experimental data obtained with a reactor at Eindhoven University that allows cycling of the feed up to 10 Hz [9].

Besides a theoretical study was made to elucidate the operation conditions at which forced oscillations at the outer surface of a catalyst pellet may penetrate into the pellet in an undisturbed way e.g. without damping or phase shift. Emphasis was put on the oxidation of carbon monoxide in the framework of automotive exhaust gas treatment. Forced oscillations of carbon monoxide and oxygen in counterphase were applied. It will be shown that the amplitude and phase of the resulting carbon dioxide oscillations in the bulk gas are not affected by intrapellet diffusion at frequencies up to a few Herz and effective diffusivities in the catalyst pellets over 10^{-6} m^2s^{-1}. Surface coverages of adsorbed CO and O adatoms within the pellet are rather uniform and oscillate in phase with the corresponding gas phase concentrations. At 10 Hz the CO_2 oscillation shows damping and phase shift. Similar behaviour is seen for gas phase and surface coverage oscillations at different positions inside the pellet. At diffusivities of 10^{-7} m^2s^{-1} CO and CO_2 gas phase concentrations are severely damped while O_2 is not. Strong pellet profile in the surface coverages develop, adsorbed CO being dominant in the outer pellet region and O adatoms in the inner one. As a result, the carbon dioxide production rate increases with 50 % and is hardly affected by the cycling frequency. It is obvious that in a kinetic experiment such rate increase would disguise the real kinetics, although the potential for practical applications is truly interesting.

References:

1. Y.Sh. Matros, G.A. Bunimovich, V.O. Strots, Stud. Surf. Sc. Cat. 109 (1997) 141.
2. P.L. Silveston, Cat. Today 25 (1995) 175.
3, A.B.K. Lie, J.H.B.J. Hoebink. G.B. Marin, The Chem. Eng. J. 53 (1993) 47
4. A.J.L. Nievergeld, E.R. vSelow, J. Hoebink, G.B. Marin, Stud. Surf. Sc. Cat. 109 (1997) 449.
5. B.K. Cho. Ind. Eng. Chem. Fund. 22 (1983) 410.
6. F.H.M. Dekker, Ph.D. Thesis, University of Amsterdam, 1995.
7. J.P. Huinink, J.H.B.J. Hoebink, G.B. Marin, Can. J. Chem. Eng. 74 (1996) 580.
8. Altamira leaflet, 1997.
9. M.A.J. Campman, Ph.D. Thesis, Eindhoven University of Technology. 1996.

OP-8-2

Using transients in the catalytic treatment of car exhausts: - Improving light-off performance and NO_x reduction under lean conditions

Magnus Skoglundh*, Peter Thormählen, Erik Fridell, Faegheh Hajbolouri,

Edward Jobson, Gudmund Smedler

Competence Centre for Catalysis, Chalmers University of Technology, 412 96
Gettysburg, Sweden

Corresponding author, phone: +46-(0)31-772 2958, fax: +46-(0)31-772 29 67,
e-mail: skoglund@tk.chalmers.se

Abstract

The catalytic exhaust cleaning system on cars are by nature running under transient conditions since the driver is constantly changing the throttle to regulate the power delivered from the engine. This transient operation, by itself, also generates more emissions than if the engine was running under steady state conditions. To minimise the released emissions there is a regulating system, monitoring several parameters, controlling the ignition and fuel injection system of the engine to optimise the performance of the catalytic converter. This regulating system has until now mostly been working by keeping the exhaust composition fixed near the stoichiomertric point. Today, these advanced systems can however be used for much more advanced applications, to even further improve the performance of the catalytic system by using well controlled transient changes in the exhaust gas composition. There are two major areas of interest in this case. The first one is to improve the light-off performance of the catalyst after the start of a cold engine. The second one is to remove NO_x produced under the lean conditions in diesel and lean-burn petrol engines.

During the light-off period, after a cold start, almost 80% of the harmful emissions are released during a driving test cycle. The low activity of the catalyst when it is cold is

attributed to self poisoning of the catalytic surface by the different components in the exhaust. By making rapid changes in the air to fuel ratio, it is possible to create pulses in the exhaust with different compositions. These pulses may be able to remove some of the components that are blocking the catalyst surface which then leads to an improved light-off performance compared to the corresponding case with a feed of static composition. To study this, several light-off experiments have been made with pulses of different components, to determine how they affect the overall performance of the catalyst.

The oxygen excess in the exhaust from diesel and lean-burn petrol engines, makes it very difficult to reduce NO_x by the conventional three way catalyst systems used today. A way around this problem is to run the system in a repeated transient cycle. During the first phase of this cycle, NO_x is stored in the catalyst under lean conditions. During the other phase, the catalyst is regenerated under rich conditions and the stored NO_x is released and then reduced to harmless N_2.

In this paper we will present new results which show that it is possible to decrease the light-off temperature of commercial and model catalysts by using transients in the exhaust gas composition. We will also present results which show that transients in the exhaust gas composition may be used to reduce NO_x emissions under lean burn conditions.

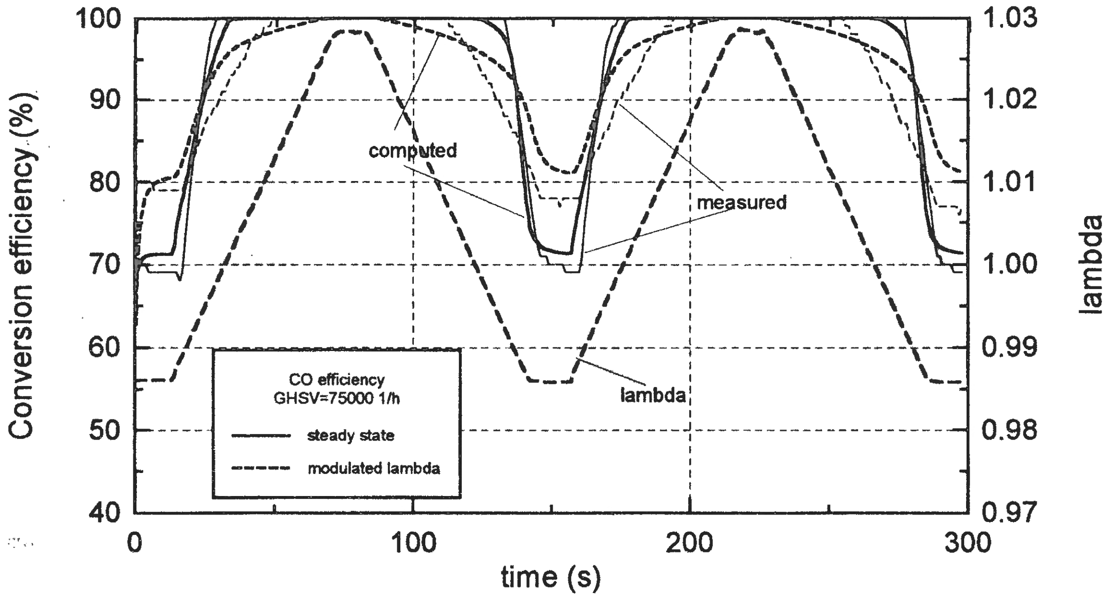
OP-8-3

Modelling Dynamic Phenomena in 3-Way Catalytic Converters

G. C. Koltsakis, I.P Kandylas and A. M. Stamatelos

Laboratory of Applied Thermodynamics, Aristotle University Thessaloniki, 540 06 Thessaloniki, Greece, Tel: +30-31-996066, Fax: +30-31-996019, e-mail: tassos@antiopi.meng.auth.gr

The advent of stricter U.S. and European exhaust emissions regulations has increased the need for reliable 3-way catalytic converter models supporting the design of demanding exhaust systems for low-emitting vehicles. Although a number of tunable models are already been employed in this direction, the full exploitation of their capabilities relies on the efficient modeling of dynamic 3-way catalytic converter behavior. That is, additional knowledge of dynamic processes on the catalyst surface should be aimed at, to understand and model the interplay of catalyst dynamics with heat and mass transfer and eventually support the design of catalytic converters with improved operation under the cycling A/F exhaust gas of the automobile. Improved catalyst behaviour under cycling A/F is mainly attributed to the ability of some washcoat components to be periodically oxidized and reduced depending on the exhaust gas redox environment. For example, the activity of the noble metals Pt, Pd and Rh depends on their oxidation state and is lowered for higher oxidation levels. Currently, 3-way catalytic converter models are employed in two main directions: (i) quasi steady-state models are tuned with input from static laboratory experiments, that is, with static synthetic exhaust gas composition, and produce predictions for the same type of tests, (ii) quasi steady-state models are tuned with input from real world engine tests, with dynamic A/F oscillation and used to predict real world operation. However, even in this case, the exhaust gas composition input to the models is sampled to the order of 1 Hz frequency, and thus it cannot really take into account the fast oscillation in exhaust composition. That is, the kinetic improvements by A/F oscillation are only lumped in the model tunable kinetics parameters. The only truly transient model that is known from the literature *(Nievergeld et al., 1994)*, works only with simple synthetic gas of CO/NO and O_2. This paper presents the details of specific improvements of the LAT/AUTh 3-way catalytic converter model *(Koltsakis et al., 1997)*, that allowed the prediction of automotive catalyst performance improvements under truly dynamic exhaust gas feed conditions. This has been possible by employing improved fully dynamic oxygen storage and release models, as well as an enhanced reaction scheme comprising the steam-reforming reaction. The advanced oxygen storage submodel presented is capable of accounting for the redox and temperature dependence of the oxygen availability under transient operation. The redox sensitivity of the reaction scheme allows to get clearer insight in the "lambda-window" behaviour of 3-way catalysts. It is concluded, that although the task of predicting emissions over random driving scenarios is quite demanding in both chemical kinetics and inlet conditions data, most optimisation applications may be successfully handled with existing kinetic expressions information. Study of the behavior of the 3-way catalytic converter under such dynamic conditions presents high practical interest, since catalyst efficiency may be significantly improved by an optimized feed gas modulation amplitude and frequency. A complete application case study is presented to illustrate the accuracy attainable by the model application to real world testing of catalytic converter operation. Demonstration of the model tuning accuracy is made by comparison of the tuned model predictions to the results of static and dynamic laboratory light-off and lambda sweep experiments (see for example Figure 1 below). In this Figure we show the results of the computation and measurement of a static lambda sweep test. Once the model is tuned to the results of the static tests, it is able to predict with good accuracy the improvements in lambda window with a 1 Hz dynamic test.



REFERENCES

Nievergeld A.J.L., Hoebink J.H.B.J., Marin G.B., *"The performance of a monolithic catalytic converter of automotive exhaust gas with oscillatory feeding of CO, NO and O_2: a modelling study"*, Catalysis and Automotive Pollution Control III, Elsevier Science Publ.B.V., 1994.

Koltsakis G.C., Konstantinidis P.A., Stamatelos A.M., *"Development and Application Range of Mathematical Models for Automotive Three-Way Catalytic Converters"*, Applied Catalysis B (Environmental), Vol. 12, Iss. 1, 1997.

REVERSE FLOW CONVERTER FOR AUTOMOTIVE APPLICATIONS

Yu.Sh. Matros, G.A. Bunimovich, V.O. Strots, E.A. Mirosh
(Matros Technologies, Inc., St. Louis, MO, USA)
(Alternative Fuel Systems, Calgary, Canada)

Fixed bed catalytic reactor with periodic flow reversal (RFR) have been discussed in a number of papers (see reviews [1,2]). In this reactor, the catalyst serves as a heat regeneration media. The high temperature reaction zone is trapped inside the catalyst bed at low temperature of inlet and exhaust gas. For reversible exothermic processes, theoretically optimal temperature profile can be attained in one catalyst bed without intermediate heat removal [1]. The RFRs have been used commercially for SO_2 oxidation in sulfuric acid production, and for complete oxidation of volatile organic compounds and NOx reduction from stationary industrial sources of polluted air. The present paper considers theoretical and experimental study of a new RFR application directed to the emission control after the automotive engines.

In its major part, the paper discusses the exhaust gas treatment after the dual fuel Diesel engines operated with the combination of natural gas and diesel fuels. Use of natural gas in Diesel engines provides for fuel economy, less green house gas emissions and reduced particulates and NOx emission compared with the dedicated diesel engines. However, dual fuel engines emit high amount of hydrocarbons (mostly methane) and carbon oxide during low torque driving operations. At those operations the exhaust gas temperature is below 200-300 °C that insufficient for igniting modern oxidation catalysts. Our study shows that the problem can be solved using the flow reversal reactor concept.

The study includes mathematical modeling and experimentation with the commercial prototype converters. The developed mathematical model of straight channel catalytic monolith [3] considers the essential factors for converter design such as heat and mass transfers between solid matrix and gas phase, heat accumulation in solid matrix, exothermic reactions of oxidation of methane and carbon oxide. The model analysis shows that the rate of heat transfer between the monolith solid matrix and gas stream is exceptionally high for typical square channel monolith structures. The converter efficiency is only limited by the activity and thermal stability of oxidation catalyst.

The converter behavior is characterized by standard automotive testing procedures. These procedures prescribe predetermined stepwise changes in engine load and speed. The exhaust gas temperature and composition follow changes of engine parameters. An example of a comparison between the experimental data and mathematical simulation for a 13th modes standard procedure is shown in Fig. 1. The model allows to predict the integrated parameters of the converter, such as average bed temperature and outlet methane concentration. The flow reversal converter (lines 1, 2, 5, Fig. 1) demonstrates superior performance at low temperature modes of operation compared to the conventional non-flow reversal system.

The paper also considers a new flow reversal reactor configuration which is applied for removal cold-start emissions after the conventional gasoline fueled and diesel fueled engines. The problem of cold start emission control has been emerged recently as a result of strengthening of environmental regulation standards. The converter comprises an adsorbent block placed between two catalytic monoliths. The adsorbent captures the hydrocarbons emitted during the first minutes after the engine cold start-up when exhaust gas has low temperature. Further while the engine warming up the exhaust temperature grows up. At these conditions, periodic flow reversal results in gradually increasing temperatures at both boundary layers of the catalytic monoliths while the adsorbent in the central part of the converter remains cold and retains the adsorbed hydrocarbons. When the adsorbent temperature eventually rises, it begins to release hydrocarbons to the gas flow, which transports them to one of the previously preheated portions of catalyst where they are destroyed, regardless flow direction

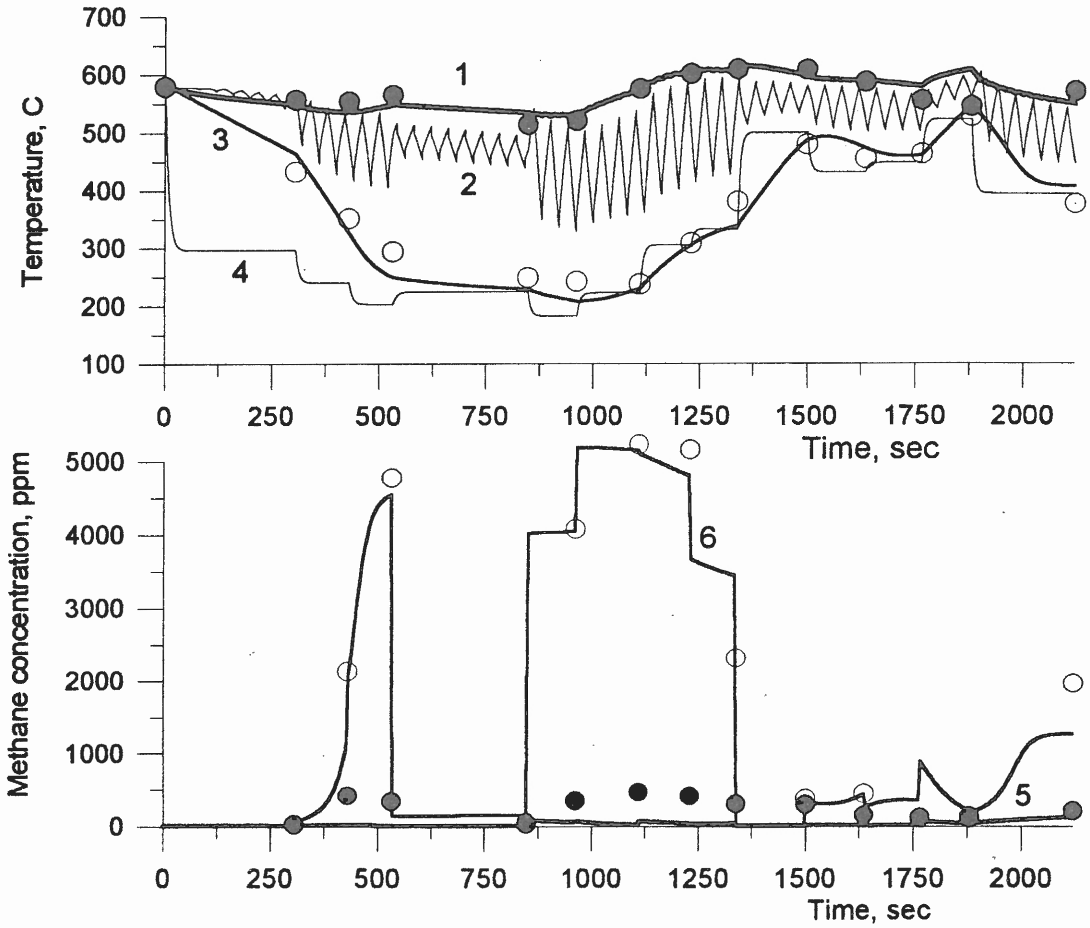


Fig. 1. Conventional and flow reversal converter operation during a standard 13 modes driving procedure. Points: experiment, lines: model. 1: average bed temperature in flow-reversal converter, 2: instantaneous temperature in one of the boundary in flow reversal converter, 3: average bed temperature in non-flow reversal converter, 4: inlet temperature, 5: methane concentration after flow reversal converter, 6: methane concentration after non-flow reversal converter.

Literature:

1. Matros Yu.Sh. Catalytic processes under Unsteady-State conditions, *Studies of Surface Science and Catalysis, Vol. 43.*, Elsevier: Amsterdam-Oxford-New York-Tokyo, 1989.
2. Matros Yu. Sh. and G.A. Bunimovich. Reverse Flow Operation in Fixed Bed Catalytic reactors, *Catal. Rev. - Sci. Eng.*, **38 (1), 1-68, 1996.**
3. Bunimovich G.A., V.O.Strots, Yu.Sh.Matros and E.E.Mirosh, A Reverse Flow Converter for Diesel Fuel Engine, 30th International Symposium on Automotive Technology and Automation. The Motor vehicles and the Environment. Florence, Italy, 1997, Ed. Automotive Automation LTD, p. 97-104.

POSTER SESSION

MECHANISTIC ASPECTS OF KINETIC MODELS FOR SIMULATION OF AN UNSTEADY-STATE BEHAVIOUR OF THE SCR REACTION

L.N.Bobrova, E.A.Paukshtis, L.G.Pinaeva
Boreskov Institute of Catalysis, SB RAS Novosibirsk, 630090, Russia,
***Fax:** (3832)357678, **E-mail:** bobr@reverse.nsk.su*

The selective catalytic reduction of nitrogen oxides by ammonia (SCR process) is the widely used technology for NO_x removal from stationary sources. The kinetic analyses of the process have generally been performed on the basis of empirical power-law rate equations under the assumption of the quasi-stationary state of the catalyst surface. Engineering of unsteady-state SCR technologies employing the dynamics of catalyst surface require an unsteady-state kinetic model for mathematical description of the process. In few papers [1-3] the Eley - Rideal mechanism was used as the basis for the unsteady-state kinetic model.

$NH_3 + [\ ] \leftrightarrow [NH_3]$

$NO_x + [NH_3] + O_2 \rightarrow N_2 + H_2O + [\ ]$

In the present work the mechanistic aspects of SCR reaction over vanadium-titanium monolayer catalyst are discussed with regard to the IR spectroscopy and the transient response technique studies. The most essential surface reaction transformation steps are analyzed to construct the kinetic schemes for simulating the SCR transient modes. Catalyst used in the studies was prepared by grafting technique. Titania of anatase modification with a surface area of 88 m^2/g was treated by three $VOCl_3$ supporting cycles. Surface ammonia species formed upon ammonia adsorption, their thermal stability and reactivities towards the nitrogen dioxide addition are highlighted by means of transmittance IR analyses. The transient response studies [4] of 0.25% NO + 0.25% NH_3 +He reaction in the presence and in the absence of 1.2% oxygen were carried out. The product gas were recorded by a quadrupole mass-spectrometer "SENSORLAB 200 D" coupled with IBM AT PC. The catalyst (0.152 g) was oxidized at 623 K in 3.6% O_2 +He for 15 min and subsequently cooled up to the reaction temperature.

The results show that surface species are clearly assigned to N-containing compounds or hydroxyl groups in accordance with the published literature. One of the most interesting results of the IR-studies within this work is that nitrogen dioxide preferably reacts with the strongly coordinated ammonia species. Then signal intensity of the weakly coordinated ammonia were seen to decrease. In contrast the strong signal due to Brønsted-bound ammonia indicated that new ammonium ions were formed with adding of nitrogen dioxide at first. The intensity passed a maximum and were found never to become extinct until coordinated ammonia disappeared.

Essentially all ammonia species can be involved in the reaction at the lack of ammonia in the gas phase.

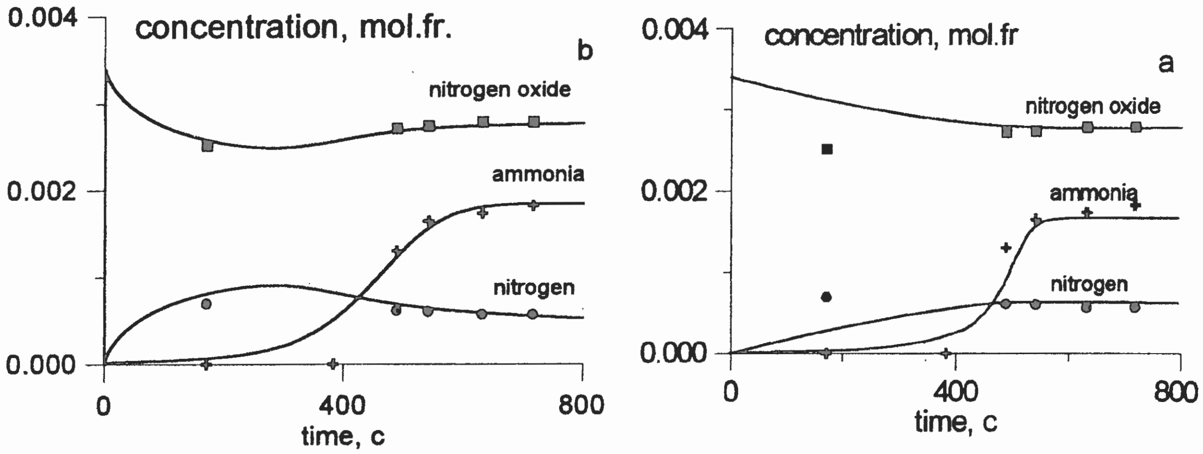


Fig.1. Concentration profiles as a function on time for the products of the SCR reaction: curves - modeling, points-experimental data; a- by two-step Eley-Rideal model, b -by model proposed with the buffer stage.

On the basis of the present studies the kinetic scheme reflecting the dynamics of catalyst surface in SCR reaction have been proposed. The catalytic cycle is initiated by ammonia adsorption on the strong Lewis sites. The formation of the ammonia storage capacity on the catalyst surface has been described by the buffer stage of ammonia adsorption on the sites of Brønsted type. Three ways of SCR reactions can be described: interaction of nitrogen oxide with ammonia at presence or absence of oxygen and the oxidation of ammonia by oxygen. The distinctive time of the unsteady-state behaviour of the SCR reaction over the vanadia-titania catalyst with contact time 0.1 c is about 10 min (see Figure). It is rather tangible magnitude for the unsteady-state technologies. Results of the comparison simulation of the reaction by the simple model of isothermal stirred tank reactor with the two-step Eley-Rideal model (a) and the kinetic scheme with the buffer stage (b) are shown on the Figure. One could see that the latest is valid to account adequately for the observed transient concentration of the species involved in the reaction, and in particular of nitrogen and nitrogen oxide.

References:

1. E.S.Borisova, A.S.Noskov, L.N.Bobrova, Catal. Today, 1(1997) 97.
2. D.W.Agar and W.Ruppel, Chem.Eng.Sci., 43 (1988) 2073.
3. E.Tronconi, G.Riccardi, P.Forzatti, A.Baldacci, S.Malloggi; G.Centi et al. (Editors), Environmental Catalysis 1995 SCI Pub: Rome (Italy), p.219.
4. L.G.Pinaeva, A.P.Suknev, A.A.Budneva, E.A.Paukshtis, B.S.Bal'zhinimaev, J.Mol.Catal.,112(1996) 115.

MODELING OF METHANOL SYNTHESIS REACTOR UNDER FLOW REVERSAL (I)

- -Identification of elementary step sequences on a copper-based Catalyst

Chen Xiaochun Rao Guoying and Li Chengyue
(Beijing University of Chemical Technology, Beijing 100029, P. R. China)

ABSTRACT

One of the most important advantages of flow reversal reactor is that a thermodynamically favorable axial temperature profiles for the reversible exothermic reactions, such as catalytic synthesis of methanol from either CO or CO_2 would be created[1~2]. To model the reactor which is operated under unsteady-state with flow reversal, it is essential to get the transient kinetics, and one must collect information about elementary step sequences first. As a part of modeling study of unsteady-state methanol synthesis in a flow reversal reactor, some in-situ studies of TPD, TPSR, and FTIR spectra to identify the elementary step sequences are reported in this paper.

The experimental set-up consists of one micro-reactor (with 6mm i.d. and 200mm length, packed with 0.5-1.0g MK-101 catalyst), one in-situ reactor cell for FTIR spectroscopy (approximately 6-10mg catalyst sample was placed in the sample holder of the cell). Figure 1 shows schematic diagram of the experimental set-up. The pressure of the experiment was controlled and measured by one PIC set placed at the entrance of the system, and the temperature of the catalyst bed in the reactor was exactly controlled by a multi-channel temperature controller. The flow rate of the reactant was measured by a mass-flow-meter. The surface reaction intermediates were identified with an in-situ FTIR spectroscopy. The tail-gas composition of the micro-reactor was analyzed by GC online.

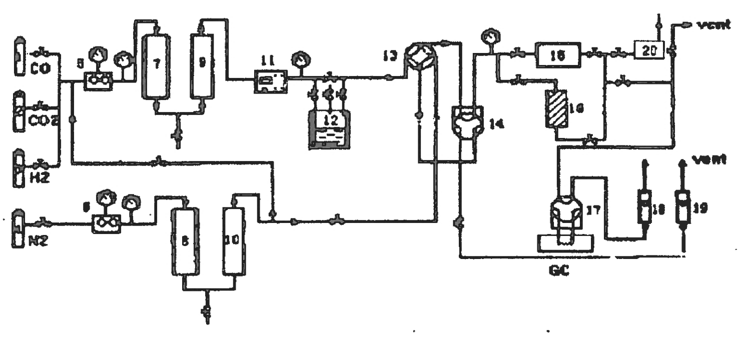


Fig. 1 Schematic diagram of the experiment set-up

The experimental conditions are summarized in Table 1

Table 1. Main experimental conditions

type of experiments	temperature °C	pressure MPa	space velocity h^{-1}
absorption	100-150	2.0	10,000
TPD	100-260	0.1	10,000
reaction	240-250	2.0	10,000

The TPD spectra of CO, CO_2, H_2 and CH_3OH on the active surface of copper-based catalyst packed in the micro-reactor were investigated. The results obtained are discussed. As a few of examples, some typical TPD spectra of CO and CO_2 and H_2 by micro-reactor are shown in figure 2. The in-situ FTIR-TPD spectra of CO and CO_2 are given in figure 3, and no dissociative chemisorption of H_2 on the catalyst surface was found during the experiment.

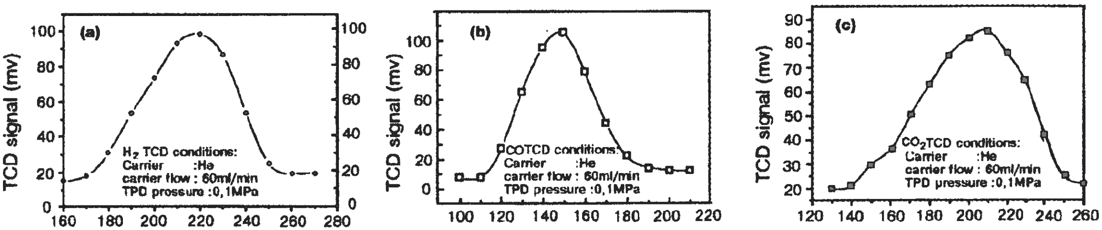


Figure 2 The TPD spectra of adsorbed H_2 (a), CO(b) and CO_2(c) on the surface

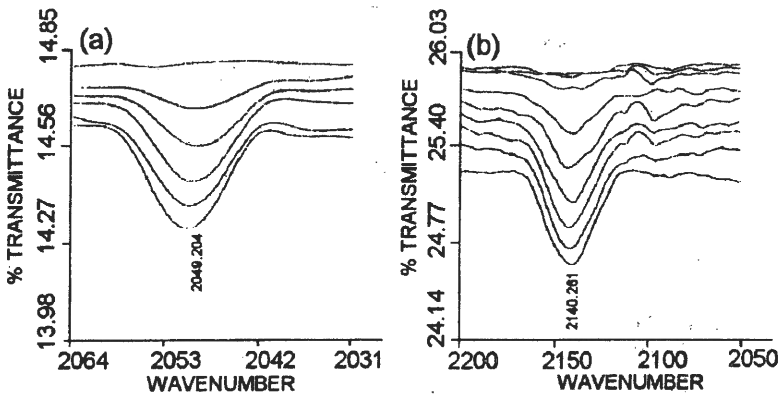


Figure 3. In-situ FTIR TPD performance of adsorbed CO (a) and CO_2 (b)

figure3-a: from top to bottom: 138, 126, 120, 107, 70, and 32 °C;

figure3-b: from top to bottom: 20mins at 240, 240, 220, 200, 180, 160, 140, 120, and 100 °C

Transient response experiment was used as a tool to understand the role of the observed species on the catalyst surface, by exposing the actived catalyst to concentration sudden increase of the reactant to be determined and following the time evolution of the adsorbed species under various conditions. Some dynamic information of adsorbed precursors were obtained. Figure 4 shows transient responses of surface intermediates for the methanol synthesis from CO and CO_2 respectively. The infrared bands at 1562cm^{-1}, 1447cm^{-1}, and 1644cm^{-1} in Figure 4 are assigned to the stretching and bending vibrations of the precursors of formate, formaldehyde and water adsorbed on the active surface, and at the same time, at 3700cm^{-1}, 2928cm^{-1} and 2857cm^{-1}, the stretching and bending vibration of M-OH, M-H_2O, M-CHOH, and M-OCH3 are also investigated.

The results show that methanol may be synthesized from CO and CO_2 solely, and the main inltermediates are M-COOH, M-CHOH, M-OH from CO_2, and M-CHO, M-OCH_3 from CO. The M-COOH and M-CHO may be transformed each other under special conditions, the reaction speed of WGSR or reverse WGSR is bigger than that of methanol synthesis reaction.

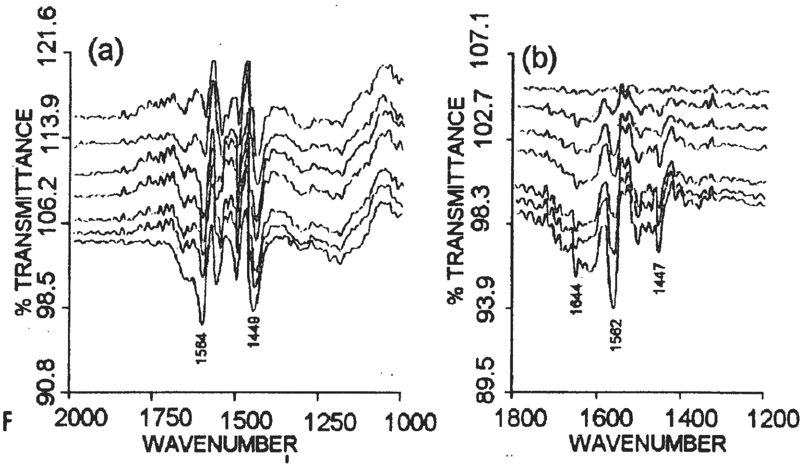


Figure 4 Transiet responses of surface intermediates:
a) for CO plus H_2; b) for CO_2 plus H_2

References:

1. Neophytides, S. G. and Froment, G. F. "A Bench Scale Study Ot Reversed Flow Methanol Synthesi", Ind. Eng. Chem. Res., 3l, 1583-1589, 1992
2. Vanden Bussche, K. M., S. M. Neophytides, I.A. Zolotalskii and G.F. Flometlt, "Modeling and simulation of the Revers-flow operation in a Fixed-Bed Reactor for Methanol Sytnthesis.", Chem. Eng. Sci., 48,3335-3345 (1993).

UNSTEADY STATE EFFECTS IN PROCESS OF MECHANO-CHEMICAL ACTIVATION OF CATALYSTS

P.E. Davydov, O.A. Dehtjar, N.N. Kuznetsova, V.V. Lunin

Moscow Lomonosov State University, Moscow, Russia

The given work is devoted to effects exhibited during mechano-chemical activation of catalysts based on the Pr-Co-Cu-H systems. The systems based on the intermetalic compounds $Pr(Co_xCu_{1-x})_5$ (x = 0; 0,6; 1) and $Pr(Co_xCu_{1-x})_2$ (x = 0; 0,2; 0,4; ... 1), and also appropriate hydrides were investigated. An active hydrogen absorption by the intermetalic compounds was observed during mechanical splitting in CO and H_2 environment. For $Pr(Co_xCu_{1-x})_5$ systems the formation of phases Co and Cu, and also hydride PrH_2 was shown. The mechanical activation of intermetalic compounds $Pr(Co_xCu_{1-x})_5$ and $Pr(Co_xCu_{1-x})_2$ in pure H_2 environment during 5÷8 hours resulted in formation of intermetalic hydrides with the contents of hydrogen reaching 3 atoms per molecule, that is equal to hydrides which were obtained by conventional method. During mechano-chemical CO conversion on $Pr(Co_xCu_{1-x})_5$ and $Pr(Co_xCu_{1-x})_2$ systems and their hydrides an only product was the methane. The systems based on $Pr(Co_xCu_{1-x})_2$ and their hydrides exhibited large stability of catalytic activity: the speed of methane formation remained constant within more than 8 hours against 3 hours for catalysts based on $Pr(Co_xCu_{1-x})_5$ and their hydrides. The oscillations of catalytic activity during mechano-chemical processing were observed for catalysts based on $Pr(Co_xCu_{1-x})_5$ and their hydrides.

PP-5

STUDY ON THE KINETICS OF FILAMENTARY CARBON FORMATION UNDER CONDITIONS OF A CATALYST DEACTIVATION

G.G. Kuvshinov, Yu.I. Mogilnykh, D.G. Kuvshinov

Boreskov Institute of Catalysis, Pr. Akad. Lavrentieva, 5, Novosibirsk 630090, Russia

In spite of the fact that catalytic filamentary carbon, produced on hydrocarbon decomposition over a highly loaded Ni-containing (> 88 wt.%) catalyst, has undoubtedly valuable features such as high purity (> 99 wt.%), [1], high degree of graphitization [2], unique adsorption properties [2], and possibility to be manufactured as solid granules [2,3], the kinetics of carbon deposition over such catalysts was not practically studied.

In the present report we show how the reaction medium influences the rate of catalytic filamentary carbon (CFC) formation and deactivation of a heavily loaded Ni-containing (88 wt.%) catalyst on methane decomposition. The preparation technique and composition of the catalyst were reported elsewhere [1,3].

The experimental data were obtained on methane decomposition in a flow microreactor with a fluidized catalyst bed in the temperature range 490-590°C, hydrogen concentration ranging from 0 to 40%.

The experimental results show that the maximal rate of CFC deposition decreases as the temperature decreases and H_2 concentration increases, which qualitatively agrees with the known literature data (see, e.g. [4]). However, the data obtained are significantly higher than that of [4]. We think (as was in [4]) that the catalyst deactivation does not affect the rate of CFC formation when the actual rate of CFC formation is equal to the maximal one. Assuming the conclusion [4,5] that hydrocarbon dissociative adsorption on the surface of growth sites (GS) is a limiting stage of the process, one can process the experimental results using the Langmuir-Hinshelwood dependence allowing for the H_2 dissociative adsorption.

In processing the experimental results, we have found that the activation energy “E” is 94.442 kJ/mol.

To describe the process of the catalyst deactivation, we used the mechanism of GS blocking with the CFC formed.

Analyzing the experimentally established dependences between the rate of CFC formation and time, one can conclude that the rate of decrease in the active site portion on the GS surface is proportional to the amount of the CFC formed in a unit catalyst weight and to the second power of the rate of the CFC formation.

As a result, we have obtained an equation for the rate of CFC formation under conditions of the catalyst deactivation and the maximal amount of CFC formed in a unit catalyst weight up to its complete deactivation.

$$\frac{dC}{dt} = r = (-4r_{max}^{2\frac{1}{7}} C^2 k^* + r_{max}^{\frac{8}{7}})^{\frac{7}{8}} \qquad (1)$$

$$C_{max\,b} = 1/2(r_{max} k^*)^{-\frac{1}{2}} \qquad (2)$$

where C is the amount of CFC formed, g/g_{cat}; C_{maxb} is the maximal amount of CFC formed, g/g_{cat}; k* is the constant of deactivation rate of catalyst active sites, $(g_{cat}\ h)/g$, r is the rate of CFC formation, $g/(g_{cat}\ h)$; r_{max} is the maximal rate of CFC formation, $g(g_{cat}\ h)$; and t is time, h.

The relations obtained agree with the experimental results with an accuracy of 10%.

Note that by modifying the obtained equations, one can determine the kinetic dependences for CFC formation from heavy hydrocarbons (propane and more heavy hydrocarbons).

This research was supported by Russian Foundation of Basic Research Grant № 98-03-32-329a.

References

1. Goncharova O.V., Avdeeva L.B., Fenelonov V.B. et al. //Kinet. Katal. 36, 1995, pp. 293 - 298.
2. Avdeeva L.B., Kuvshinov G.G., Goncharova O.V., Mogilnykh Yu.I. and Likholobov V.A. // 1st World Congress "Environmental Catalysis", Pisa (Italy), 1995, pp. 459 - 462.
3. Kuvshinov G.G., Avdeeva L.B., Goncharova O.V., Mogilnykh Yu.I. Peculiarities of the process of producing the granular carbon materials of fibrous structure by hydrocarbon decompositionin unstatic catalyst bed reactor. //ACHEMA`94. International Meeting on Chemical Engineering and Biotechnology. Thermal Process Engineering, 1994, 9.6.
4. Demicheli M.C., Pouzi E.N., Ferretti O.A. and Yermain A.A. // The Chem. Eng. J., 1991, V. 46, pp. 129 - 136.
5. Alstrup.I., Tavares M.T. // J. Catal., 1993, V.139, pp. 513 - 524.

PP-6

ADSORPTIONAL-CATALYTIC CONVERSION OF DIMETHYLFORMAMIDE

R.I.Kuz'mina, V.P.Sevostianov, T.G.Panina, N.N.Mel'nichenko
Saratov State University's Inst. of Chemistry
83 Astrakhanskaya Str., Bldg. 1, Saratov 410026 RUSSIA

Purification of gaseous wastes from pollutants, in particular, from organic solvents, is a vital problem for the last years. Any solution of it is associated with creation of high-effective catalysts and adsorbents and development of novel technologies of gas purification.

The present paper deals with adsorptional-catalytic conversion of dimethylformamide (DMFA) on a copper-containing catalyst made of wastes of galvanic production. On being used as a sorbent on which galvanic sewage is purified, a kind of disperse silica (opoka) with 0.12-2.5 wt% of copper contained was annealed at 300°C in air and tested at 250-450 °C and the volume rate of a gas-air mixture 1000—10000 h^{-1}. The catalyst activity was evaluated according to the oxidation degree of DMFA and the rate of CO_2 production. Besides, several samples of the non-modified opoka with the specific area 40-50 m^2/g were examined.

The opoka surface has been found to adsorb DMFA regardless of the temperature of the preliminary annealing (200-900 °C). In the range 150-200 °C the adsorption degree reaches a certain value and then remains constant. Within 350-450 °C some reduction of the adsorbed DMFA amount was observed, to be attested to desorption and catalytic conversion.

Our study of DMFA adsorptional-catalytic conversion on copper-modified opoka has shown a coupling of the two competing processes, namely, adsorption and catalytic ones on each of the examined samples. Copper modification has a slight influence on DMFA adsorption within 150-200 °C but significantly increases the contribution of DMFA deep oxidation to the purification process in the range 350-450 °C.

The degree of DMFA deep oxidation shows a sharp tendency to increase with the copper content, it reaches its minimum at the copper concentration 0.5 wt%.

The catalyst was examined with the aid of electronic microscopy, and the presence of the copper spinel structure on the surface was observed. This centers obviously contribute to the process of DMFA deep oxidation but suppress the adsorptional function of the catalyst. This factor is wholesome as enables nitrogen, instead of its oxides, to be obtained.

It follows from the above that used copper-contained natural sorbents of galvanic production are active at catalytic purification of gaseous wastes from DMFA, this process of purification being of adsorptional-catalytic nature.

STUDY OF THERMOCATALYTIC DECOMPOSITION OF POLYETHYLENE AND POLYVINYL ALCOHOL UNDER UNSTEADY STATE OF A Fe-CONTAINING CATALYST

Nadezhda I. Maksimova and Oleg P. Krivoruchko
Boreskov Institute of Catalysis, pr. Akademika Lavrentieva, 5
Novosibirsk 630090, Russia
E-mail: opkriv@catalysis.nsk.su, Fax: +7(383 2) 35 57 56
Tel: +7(383 2) 35 57 62

Utilization of polymer production wastes, such as polyethylene (PE) and polyvinyl alcohol (PVA), is an important ecological problem. Thermocatalytic decomposition of polymers is one of the most promising approaches to this problem. This method allows to control decomposition products (DP), and thus, to increase yields of valuable chemical compounds. The latter can be used for basic and fine organic synthesis and production of composite materials.

We have studied the influence of catalyst changes, which take place upon its iteraction with reaction medium, on the selectivity of processes of PE and PVA thermal decomposition. The catalyst precursor chosen for these processes was Iron hydroxide, since Fe-containing compounds are known to be active and lower cost catalysts for thermal decomposition of light hydrocarbons (1) and graphitization of amorphous carbon (2). Iron hydroxide was introduced into the polymer solution, then solvent was removed from suspension. The solid phase was crushed and loaded into a flow system quartz reactor for thermal treatment. The latter process was performed in nitrogen flow in temperature range of 25 - 600°C at average heating rate of 125°/h, with the sample being kept at intermediate temperatures 250, 400 and 600° C for 2h. The liquid reaction products were condensed in a trap cooled to 25°C and analyzed by chromatomass spectrometry. The solid carbonized residue was studied by X- ray phase analysis.

Overall combination of polymer thermal decomposition processes and changes of catalyst composition under influence of reaction medium can be given by equations (1) and (2):

$$\alpha-\mathrm{FeO(OH)}+\mathrm{PE}\xrightarrow{\geq 350^\circ C}\alpha-\mathrm{Fe_2O_3}+\mathrm{DP(PE)}_{liq}\xrightarrow{350-450^\circ C}$$

$$\mathrm{Fe_3O_4}+\mathrm{FeO}+\mathrm{DP(PE)}_{liq}\xrightarrow{\geq 450^\circ C}\mathrm{Fe_3O_4}+\mathrm{FeO(traces)}+\mathrm{DP(PE)}_{liq}+\mathrm{C}_{am.}\quad(1)$$

$$\xrightarrow{450-600^\circ C}\mathrm{Fe_3O_4}+\mathrm{FeO(traces)}+\mathrm{C}_{am.}$$

$$\alpha-\mathrm{FeO(OH)}+\mathrm{PVA}\xrightarrow{\geq 350^\circ C}\alpha-\mathrm{Fe_2O_3}+\mathrm{DP(PVA)}_{liq}\xrightarrow{350-450^\circ C}$$

$$\mathrm{Fe_3O_4}+\mathrm{FeO}+\mathrm{DP(PVA)}_{liq}\xrightarrow{\geq 450^\circ C}\mathrm{Fe_3O_4}+\mathrm{FeO}+\alpha-\mathrm{Fe}+\mathrm{DP(PVA)}_{liq}+\mathrm{C}_{am.}\quad(2)$$

$$\xrightarrow{450-550^\circ C}\alpha-\mathrm{Fe}+\mathrm{C}_{am.}\xrightarrow{\geq 600^\circ C}\mathrm{Fe_3C}+\alpha-\mathrm{Fe(traces)}+\mathrm{C}_{graphite}+\mathrm{C}_{am.}$$

It is evident that the catalyst is in the unsteady state within the whole temperature range of polymer decomposition. At T≥ 450°C the catalyst remains in the oxide state and leads predominantly processes of polymer decomposition, yielding gaseous and liquid products. At PE decomposition Fe-containing catalyst suppresses formation of paraffin hydrocarbon and shifts the selectivity towards formation of olefines, and also it narrows the distribution of number of carbon atoms in product hydrocarbons to 12-18. At PVA decomposition the catalyst widens the range of products and leads to formation of several new aromatic hydrocarbons with number of condensed nuclei from 1 to 4. In the range of 450-600°C, the reaction products can reduce the catalyst to FeO and α-Fe depending on the nature of polymer. Being reduced, the catalyst guides the process of polymer thermal decomposition and increases yield of solid carbonized product and its graphitization at relatively low temperatures (600°C).

The work was financially supported by Russian Foundation for Basic Researches (grant N 96-03-33890).

Reference.

1. Chesnokov V.V., Buyanov R.A., Afanasiev A.D.// Kinet. and Catal. 1983. V.24. N 5. P.1251-1254.
2. . Marsh H., Warburton A.B.// J. Appl. Chem. 1970. V.20. P.133.

PP-8

TRANSIENT RESPONSE STUDY OF THE FORMALDEHYDE OXIDATION TO FORMIC ACID ON V-Ti-O CATALYST: FTIR AND PULSES STUDY

G.Ya. Popova, T.V. Andrushkevich, Yu.A. Chesalov, E.S. Stoyanov

Boreskov Institute of Catalysis, Prosp. Akad. Lavrentieva 5, Novosibirsk 630090, Russia

Mechanism of the formaldehyde oxidation to formic acid on V-Ti-O catalyst has been investigated by pulses and spectrokinetic (FT-IR in situ) methods.

The catalyst consisted of V_2O_5 (20%) and TiO_2 (80%). Techniques of pulses experiments have been described in [1]. The transient dynamic experiments were performed in a differential flow IR cell-reactor on a Bomem BM-102 FTIR spectrometer allowed to analyze both gas phase products and adsorbed species under actual reaction conditions. Experiments were conducted at 343-383 K in the next mixtures (% vol.):
reaction (2.2 % CH_2O + 20% O_2 +77.8 %He) ($R+O_2$), reduction (2.2 % CH_2O + 97.8 %He) (R) and oxidation (20% O_2+80% He) (O_2).

At reaction temperatures investigated, the formic acid was the only product of reaction. The rate of the reaction of formaldehyde oxidation to formic acid in pulses ($R+O_2$) under steady-state of the catalyst was about 10 times higher than that of the catalyst surface reduction by formaldehyde in pulse R. This data indicate that formic acid is formed mainly via an associated mechanism. The transient experiments allowed to propose a possible role of lattice oxygen $(O^2)^-$ and molecularly adsorbed one in the individual reaction steps. The in situ FTIR results have shown that mono (SS1)-and bydentate (SS2) formates are generated on the oxidized catalyst surface after introduction of $R+O_2$ or R mixtures into the cell-reactor at 70-120°C. The only gas phase product of oxidation of CH_2O in both mixtures was HCOOH, however in the absence of oxygen HCOOH was obtained with very low yield.

Figures 1,2 shows the transient responses of CH_2O and HCOOH and surface coverage with (SS1) and (SS2) after the following switch: O_2 (250°C, 1h) → $R+O_2$ (100°C)→O_2 (100°C) (fig.1) and O_2 (250°C, 1h) → R (100°C)→He (100°C)→O_2 (100°C) (fig.2).

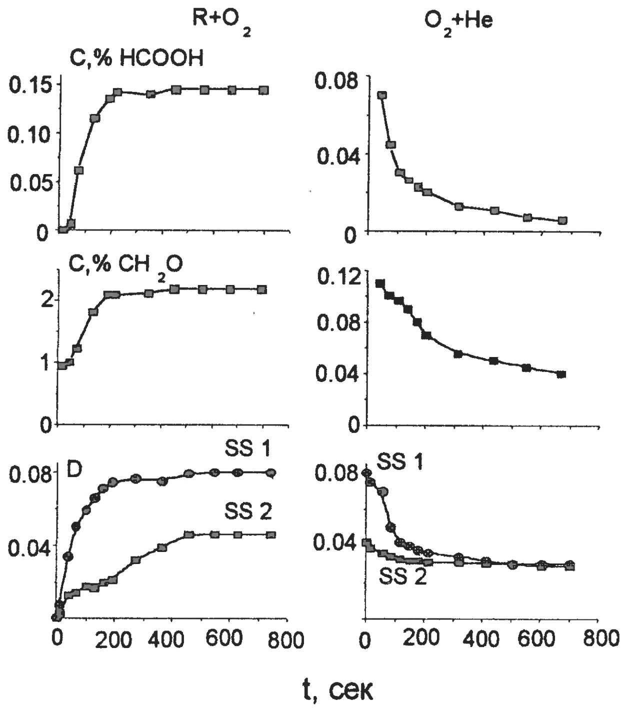


Fig.1. The responses of CH$_2$O and HCOOH and the surface coverage (SS1) and (SS2) after a step change from O$_2$ -→ R+O$_2$-→O$_2$.

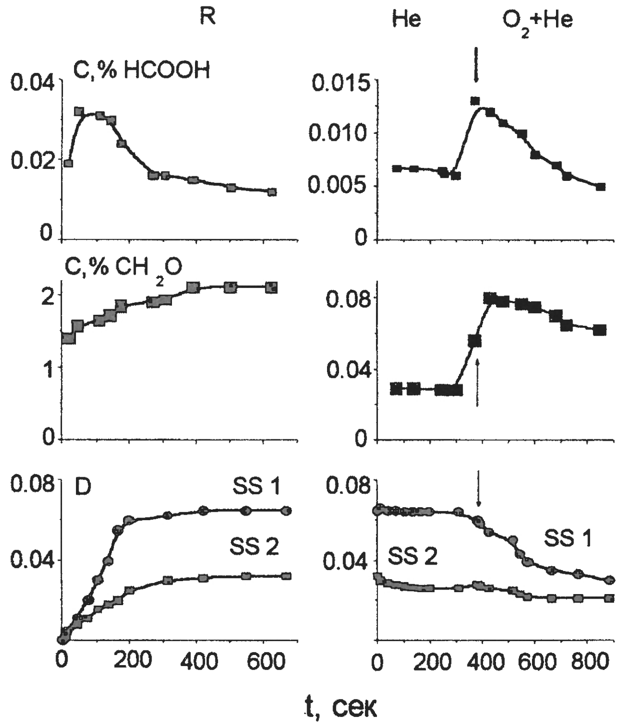


Fig.2. The responses of CH$_2$O and HCOOH and the surface coverage (SS1) and (SS2) after a step change from O$_2$ -→ R -→He -→O$_2$.

The same surface species are observed by adsorption CH_2O in the presence and absence of O_2. This indicated that catalyst lattice oxygen (O^{2-}) participate in the formation of oxidized surface species of CH_2O. Molecularly adsorbed O_2 participate in the decomposition step of this surface species. After a switch from $R+O_2$ to O_2 surface coverage (SS1) and (SS2) decreased and only HCOOH and CH_2O were detected in gas phase (fig.1). A similar experiment carried out in the He showed only a small decrease in the surface coverage (SS1) and (SS2) and the insignificant quantity of gas-phase products (fig.2).

A mechanistic scheme, including the participation of both the lattice oxide ions (O^{2-}) (via the formation of the oxidation surface species formaldehyde) and molecularly adsorbed O_2 (via the conjugation of desorption of the reaction products with surface reoxidation) seems quite relevant to explain the mechanism of oxygen incorporation.

Refferences.

1. G.Ya.Popova, T.V.Andrushkevich, V.M.Bondareva, I.I.Zakharov. Kinet. Katal., 1994, V.35, P.95.

Acknowledgement. This work was supported by Russian Foundation for Basic Research, Grant 96-03-33016.

PP-9

THE DYNAMIC BEHAVIOR OF HYDROCARBON -DeNO$_X$ CATALYSTS IN THE PRESENCE OF SULFURIC COMPOUNDS

V.A. Sazonov, Z.R. Ismagilov, S.R. Khairulin

Institute of Catalysis of the Siberian Branch of the Russian Academy of Science, Novosibirsk, Russia

The combustion of organic fuel containing sulfuric compound leads to simultaneous formation of nitrogen oxides and sulfur oxides. Sulfur dioxide is known to have negative effect on the catalysts performance in the process DeNO$_X$.

The aim of this work is the study of the influence of sulfuric compounds on activity of various catalytic system in HC - DeNO$_X$ process under unsteady-state condition and regeneration regimes.

The series of copper-containing ion-exchanged zeolite (ZSM-5) catalysts was prepared. Washcoated monolith honeycombs with ceramic matrix support have been studied.

The compositions of the catalysts manufactured are:

Cu / ZSM-5, Cu-Ce / ZSM-5
Cu / (Ti,Al+ZSM-5), Cu-Ce / (Ti,Al+ZSM-5)

The selective catalytic reduction (SCR) of NO by propane has been investigated in a flow setup at temperatures: 300, 400 and 500°C under continuos control of full composition of gas mixture components with accuracy - 1 ppm.

The dynamics of catalytic activity in DeNO$_X$ reaction under sulfuric compounds impact have been studied at variation of temperature both deactivation and regeneration processes.

The data obtained allow to make conclusion on catalysts performance under deactivation conditions and to develop optimal procedure of their regeneration.

PP-10

Mechanism of Nucleation and Growth of Surface Adsorption Structures in the Ethylene Reaction with Oxygen on Silver

A.N. Salanov, V.N. Bibin and O.V. Yapryntseva
Boreskov Institute of Catalysis, SB RAS, Novosibirsk 630090, Russia
E-mail: salanov@catalysis.nsk.su

Silver is the only known catalyst for the industrially important catalytic reaction of partial ethylene oxidation to ethylene oxide. This fact explains the high interest to investigations of the mechanisms of the O_2 and C_2H_4 adsorption and their interaction on silver. It is generally believed that the reaction direction to deep or partial oxidation is determined by the state of the silver surface and forms of adsorbed oxygen.

Several results of principle importance on the oxygen interaction with silver monocrystals have been lately obtained with the use of modern physical methods [1-2]. Data obtained by the molecular beam method [1] indicate two mechanisms of the dissociative oxygen chemisorption: "direct" one (without intermediate states) and "indirect" one (via a molecular chemisorbed state). According to scanning tunneling microscopy (STM) data [2], oxygen adsorption on Ag(110) surface is accompanied by the nucleation and quick growth of long chains (added rows) –Ag-O-Ag- in the (001) direction. These chains are formed due to the reaction of mobile surface silver atoms (supplied from the steps) with chemisorbing oxygen atoms. This results in the formation of a stable structure in which silver atoms are located in sites continuing the metal lattice whereas oxygen atoms occupy long bridge sites inside the row. These data made it possible to understand deeper the nature of the oxygen interaction with silver and open an absolutely new approach to the investigation of the mechanism of ethylene epoxidation on silver.

In the present study we tried to determine the mechanism of the nucleation and growth of surface adsorption structures during the chemisorption of O_2 and C_2H_4, and their interaction on Ag(poly) and Ag(110) surfaces, and state the role of the structures formed in the ethylene epoxidation reaction. Experimental results and data obtained by a Monte Carlo simulation of oxygen and ethylene chemisorption, and their interaction on Ag(poly) and Ag(110) were analyzed and compared in the frames of modern conceptions of the interaction of gases with metals: "direct" and "indirect" adsorption pathways, chemical reconstruction of the surface, lateral interactions in the adsorption layer, formation of surface adsorption phases and participation of intermediate adsorption states in reactions.

For analysis of the experimental data, a model based on the following key assumptions was considered:

1. The adsorption begins with a slow "direct" dissociative oxygen chemisorption – O_2 molecule interacts with chemisorbed Ag atoms to form fragments of adsorption chains (added rows) –Ag-O-Ag- (chains generation mechanism).
2. As –Ag-O-Ag- fragments accumulate, faster "indirect" oxygen adsorption begins to dominate – O_2 molecules interact with the adsorption chains –Ag-O-Ag-, are trapped into a precursor, and after migration over the adsorption chain chemisorb dissociatively at the ends of the chains (chain growth mechanism).
3. Ethylene adsorption begins after accumulation of –Ag-O-Ag- chains on the surface. C_2H_4 molecules adsorb on the silver surface only via the "indirect" mechanism. Interacting with the adsorption chains –Ag-O-Ag-, they are trapped into a precursor, and while migrating over the adsorption chain they may react with oxygen atoms of the chain resulting in the deep or partial oxidation of ethylene.

The experimental results obtained and their analysis with the application of the Monte Carlo simulations made it possible to determine the mechanism of the nucleation and growth of different adsorption structures on the silver surface during the chemisorption of O_2 and C_2H_4, and their interaction, and state the effect of the structures formed on the direction of the ethylene oxidation.

Acknowledgment. This work was supported by Russian Foundation for Basic Research, grant 96-03-32961.

References

1. D.A. Butler, A. Raukema and A.W. Kleyn, J. Chem.Soc., Faraday Trans., 92(1996)2319.
2. T. Hashizume, M. Taniguchi, K. Motai, H. Lu, K. Tanaka and T. Sakurai, Jpn. Appl. Phys. 30(1991)L1529; M. Taniguchi, K. Tanaka, T. Hashizume and T. Sakurai, Chem. Phys. Lett. 192(1992)117; Surf. Sci. 262(1992)L123; T. Hashizume, M. Taniguchi, K. Motai, H. Lu, K. Tanaka, and T. Sakurai, Surf. Sci., 266(1992)282

PP-11

INTELLECTUAL SYSTEM FOR TREATING OF NON-STATIONARY KINETIC EXPERIMENTAL DATA

V.N. Tomilov, A.N. Zagoruiko, P.A. Kuznetsov

Boreskov Institute of Catalysis SB RAS
Lavrentieva pr., 5, Novosibirsk, 630090, Russia
phone (383-) 2 354591, e-mail: vic@sirius.catalysis.nsk.su

Development of catalytic processes using unsteady state of catalyst surface is perspective path for creation of principally new high effective catalytic technologies. The main tool of such development is mathematical modeling based on unsteady kinetic model of chemical reactions (kinetic equations rate constants, activation energies, catalyst surface capacity, etc). The problem of searching of optimum non-stationary kinetic model and determination of its parameters is very complicated and its complexity grows with number of factors increase (the number of process stages, surface reactions etc.) and with taking into account influence of reaction mixture on the catalyst surface state.

Preliminary technological scheme of unsteady state catalytic processes development as a rule contains following steps:

- Experimental investigation of process unsteady kinetic
- Choosing of optimum non-stationary kinetic model, determination of kinetic parameters
- Construction of mathematical model and mathematical modeling of non-stationary regimes in catalyst pellet and in catalyst fixed bed
- Development of process technological scheme, determination of technological parameters, evaluation of economical efficiency

The most important and in the same time the most laborious part of work is a selection of optimal model and a discrimination of stadium kinetic parameters. This task is very crucial – its success is the main factor for correct completing of whole work and following modeling.

There are some problems during treating of non-stationary experimental data:

1. It is necessary to use optimized mathematical technique depending on the task type (experiment conditions, data range, complexity of model etc.).
2. It is important to evaluate task results correctly and constantly changing parameters of applied discrimination methods.
3. Full solving of such complex task requires the knowledge in various fields of chemical engineering, algebra and mathematical analysis as well as professional ability to create special software.

Authors of intellectual system have a goal to simplify the problem of treating of non-stationary kinetic experimental data. Software system created by authors contains all necessary optimized methods of searching, integration and optimization. Easy to use and powerful program user interface allows to prepare and solve tasks easily.

System capabilities:

- Easy to use and powerful program user interface (software created for Windows 95 and Windows NT)
- Fast and precise algorithms of integration and optimization, control of precision level of calculations
- The system can correct inner computational parameters using current results to achieve the optimal variant of calculations
- Improved method of exclusion allows to treat any errors in calculation process "in fly" correcting parameters range and parameters values. Errors are stored. This method allows avoiding the similar errors in the future.
- User can include new algorithms, models of reactors, data types in the system

- Using of data ranges separation enable to optimize the process of calculation
- Using of 32-bit programming significantly increases the speed and reliability of calculation
- Ability of work in multitasking environment allows calculation to be more effective and fast
- Using of "client-server" technology allows to calculate the process on several computers in network increasing the speed of calculation

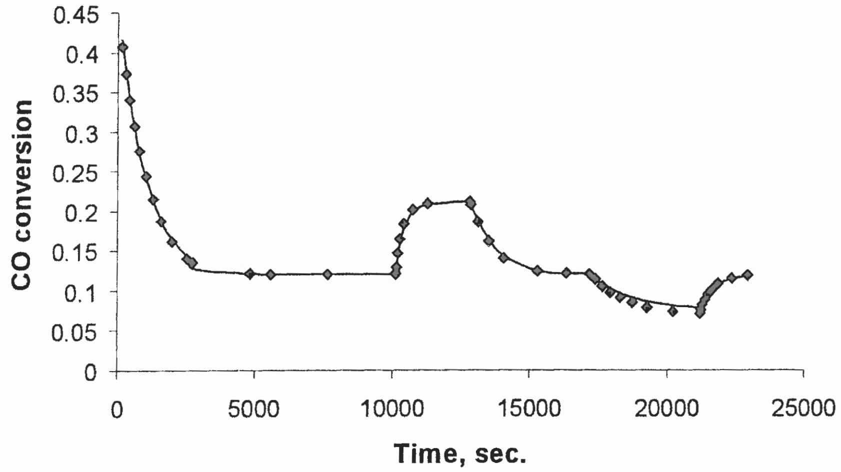


Fig. 1. CO oxidation on Fe-Sb-O catalyst. Comparison of experimental data and simulation results provided by intellectual system software (◆ - experimental data, curve – mathematical modeling data)

This intellectual system has been used for treating of experimental data of following processes: oxidation of carbon monoxide on Fe-Sb-O catalyst [1,2] (Fig. 1), partial oxidation of butene-1 to butadiene on Sn-Sb-O catalyst [2] (Fig. 2) and deep oxidation of styrene on Al-Mn-O catalyst.

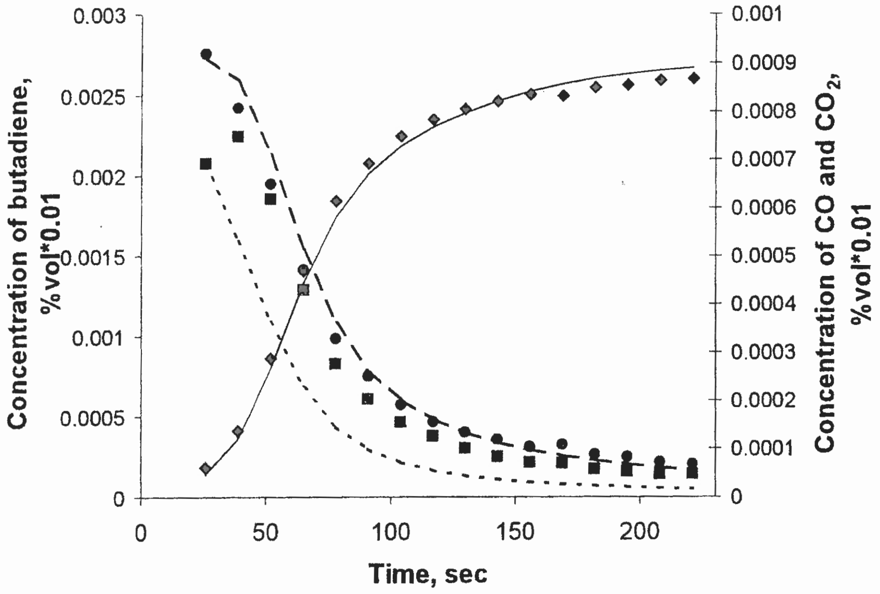


Fig. 2. Partial oxidation of butene-1 on Sn-Sb-O catalyst. Comparison of experimental data and simulation results provided by intellectual system software (■ ●◆ - experimental data: concentration of CO, CO_2 and butene-1 respectively, curves – mathematical modeling data: dotted line, dashed line and solid line - CO, CO_2 and butene-1 respectively)

1. V.N. Tomilov, A.N. Zagoruiko, S.A. Veniaminov "Kinetic investigation and mathematical modeling of oscillation regimes for oxidation of carbon monoxide on Fe-Sb-O catalyst", Chemreactor-XIII, June 1996,Vol. 2, 175-176.
2. V.N. Tomilov, A.N. Zagoruiko, S.A. Veniaminov "Kinetic investigation and mathematical modeling of oscillation regimes for oxidation of carbon monoxide and oxidative dehydrogenation of butene-1", CHISA-12, Prague, August 1996, 148.

PP-12

ALGORITHM AND SOFTWARE FOR PROBLEMS OF COMPLEX CATALYTIC REACTIONS MECHANISMS REDUCTION

Vaiman A.M., Spivak S.I., Galina G.K.

Institute of petrochemistry and catalysis of Academy of Science Bashkortostan, Ufa, Russia
Bashkir State University, Ufa, Russia

The problem of the derived equations system reduction to a smaller dimensions systems is one of the classical problems of mathematical modelling of complex chemical reactions. Various ways of solving this problem are known:

- straight exclusion of intermediate compounds including nonstationary chemical kinetic models [1].
- compounds gathering in group components (lumping) [2-3],
- reducing methods based on the theory of asymptotic proximity [4].

Algorithm allows to automize the process of selection of temporal scales and simplified subsystems appropriate to this scales, which can be solved analytically. It is essential, that in the given algorithm on a numerical solution is created a choice of the boundaries of temporal scales. Thus from a numerical solution the entry conditions for a solution of consequent systems imply. It allows to splice obtained solutions, that is also a labour-consuming stage in a method of an asymptotic approximation.

The aim of this work – software and mathematical providing creation. This work is based on reducing method, which was offered in [4].

Let any reaction scheme exists. It is described with the help of stoichiometric matrix G $(M \times N)$, where M – reactions quantity, N – quatnity of compounds, which take part in reactions. Then derived equations system is built:

$$\frac{dX_j}{dt} = \sum_{i=1}^{M} \gamma_{ij}\omega_i \qquad j=1..N$$

where $X=(X_1 \,..\, X_N)$ - compounds concentrations; $\omega=(\omega_1..\omega_M)$ – rates of the reactions; γ_{ij} – elements of matrix G.

Let us consider matrix with {N x (.M+1)} dimensions:

$$\mathrm{F(t)}=\left(\frac{X_j(t)}{t};\gamma_{ij}\omega_i\right), \quad i=1.M;\, j=1..N.$$

Here the first matrix column consists of absolute values of concentrations and time ratio, other columns – rate of elementary stages or zero, if any rate does not exist in equation.

After rows normalization F(t) in every moment t, we will have the matrix

$F^*(t) - I(t) * F(t)$, where $I(t) = 1/\max /F_{ij}(t)/$ if $i=j$ and $I(t)=0$ if $i<>j$; $i= 1..M$, $j=..N$;

By every *t*, matrix *F*(t)* determines significant level for corresponding members in derived equations system: the closer $f^*(t)$ to 1, the bigger the *j*-reaction investment in *i*-equation.
Algorithm of derived equations system simplification is built on assumption, that if f^*_{ij} is small in any time interval, then reduction of the corresponding member in derived equations system will have a small influence on it's solving in this time interval.
Significance matrix *F *(t)* is considering at the moment t and all members of original derived equations system are setting to the zero, if their corresponding components in *F*(t)* are less than value level. As a result, time intervals are assigned, and on every intervals the original system is approached by the system with smaller dimension. Time moments, when one subsystem changes to another, is determined as switch points.
This method was realized in the program for Windows 3.1/95.

Income data:

- rate constant of elementary stages.
- stoichiometric matrix,
- compounds concentrations values in time 0.
- time points of reaction start (t_ start) and finish (t_ finish)
- significance level.

Outcome data:

- reactions proceeding in a graphic form.
- values of compounds concentrations in every moment.
- form of reduced system on every interval.

References

1. Asadullin R.M., Spivak S.I. // Kinetika i Kataliz (rus), 1995, v.36, N6, p.926-929;
2. Lebedeva C.L., Ostrovskii N.M., Spivak S.I. // Kinetika i Kataliz (rus), 1993, v.34, N1, p.171-175;
3. Lebedeva C.I ., Spivak S.I., Iablonskii G.S. // Kinetika i Kataliz (rus), 1993, v.34, N6, p. 1102-1107,
4. Tropin A.V.,Maslennikov S.I., Spivak S.I. // Kinetika i Kataliz (rus), 1995, v.36, N5, p. 658-664.

PP-13

ABOUT NEW FUNDAMENTAL REASONS OF THE FORMATION OF NON-STATIONARY CONDITIONS IN THE INDUSTRIAL REACTORS

N.K. Valitov

Bashkirian State University, Chemical Faculty, Ufa, Russia

There was elaborated by the author the chromatographical method of the investigation of mechanisms of chemisorption and catalytic reactions for more than 40 industrial heterogeneous and homogeneous catalysts, in the presence of which there were investigated more than 60 individual components of the raw materials of the industrial processes of heterogeneous and homogeneous cracking, oxygenation, isomerization, reforming, hydrogenation, alkylation, dealkylation, hydrocracking, hydrocarbon conversion, of the oil products, etc.

Chromatographical method of the investigational of the natural non stationary conditions in the industrial catalytic reactors differs from the famous methods of chromatographical deviding to the individual components by the factor that there was used as a nozzle of chromatographical column the reactors with an extent of a catalyst from 0,2 grams up to 90 grams and with the length of the reactor not more than 10 cm. After the introduction into reactor of the investigated components of the raw materials and the desorption of its isothermally desorbed form of the chemisorption the temperature was rosen continuously with a speed 5-10 gradus/minute with a help of programming equipment for the desorption of the remained thermodesorbed products. Chromatographical column of the standart chromatographs of the division of gases and liquids to the individual components of the length of 300 cm was used only for carrying out of the analysis of the products of the catalytic reaction and products of the desorption. So, the length of such reactor (10 cm) and the time of contact of the travelling phase in the conditions of the continuous rise of the temperature in the medium of the continuously passing through the reactor of the gas-carrier, for instance, helium, it is absolutely insufficiently for the separate receiving of the chromatographical peaks of the isothermally desorbed component of the raw materials and the surplus reagent, which is not chemisorbed by catalyst. So the last ones formate one general peak, the content in which of the isothermally desorbed component is determined by the graphical dependence of the time of the retaining on the quantity of the time of the introduced sample.

With a use of this method it is established, that in spite of the generally accepted idea, thermodesorbed reagents are chemically reactable.

With a help of this method there was established by ourselves, that the natural reasons of non-stationary conditions in the industrial catalytical reactors can be any changes of the chemical composition of the raw materials, the temperature in the reactors the chemical composition of the heterogeneous and homogeneous catalysts as a result of chemisorption, the change of the dispersion and the quantity (the size) of granules of the catalysts, the change of the quantity and chemical composition of the adsorbed and chemisorbed products, etc. There was established experimentally by ourselves, that between 60 individual components of the raw materials of the many processes, 40 catalysts, the chemisorption is practically absent with its equal size (the quantity) of energy of their connection with catalysts and the equal time of the retaining.

Let's notice, that by the other methods of the investigation it is not practically possible to receive these enumerated quantitative conditions of the natural non-stationarity.

These investigations of the industrial reactors are published by author in more than 120 scientific articles, more than 70 of which are published in the magazines of the Academy of Science of the former USSR, Russia, Chekoslovakia, etc., where patents were received, there were inculcated into the industry more than ten methods.

PP-14

UNSTEADY - STATE PHENOMENA IN THE COURSE OF ETHYLENE GLYCOL OXIDATION INTO GLYOXAL ON SILVER CATALYST

O. V. Vodyankina, G. A. Izatulina, L.N. Kurina

Russia, Tomsk State University, 634050, Tomsk, Lenina str.,36,
phone (3822)424257, fax (3822)415579, e-mail galanov@xf.tsu.tomsk.su

Processes of the alcohol's into aldehyde oxidation on silver catalysts were carried out at high temperatures (600 - 700°C) when the probability of the reaction transition from the catalyst surface to the volume became higher [1].

The temperature oscillations in the range 580 - 640 °C during the study of ethylene glycol oxidation to glyoxal are observed at the variation of Ag catalysts grains dimensions. Effects of the ethylene glycol oxidation process parameters (ratio of O_2/EG and ethylene glycol concentration in water solution) on the generation, character and the field of existence of the oscillation phenomena are investigated.

It is shown that the amplitude and the period of oscillations change as the oxygen and ethylene glycol content in the reaction mixture increase. At the initial ethylene glycol concentration of 40% the generation of the oscillations on the larger silver grains (1.0 - 1.5 mm.) is observed at O_2/EG =0.8, the oscillations development at O_2/EG =0.9, the stable ones - at O_2/EG =1.0. The decrease of water content in the system (C_{EG}=60%) removes the boundary of field of the oscillations generation to the lower values of the O_2/EG ratio.

According to the obtained experimental data we can assume that the observed critical phenomena in the ethylene glycol oxidation process are connected with the development of volume stages between the grains of the silver catalyst. Necessity of the rapid cooling of the reaction products after the catalytic layer both at the alcohol and ethylene glycol oxidation is the confirmation of the homogeneous continuation of the process.

The analysis of the effect of water content in the reaction mixture on catalytic process parameters permits to suppose that glyoxal is mainly formed on the Ag surface by the heterogeneous path. This was confirmed by the thermodesorption researches [2]. The observed critical phenomena in the ethylene glycol oxidation on Ag catalyst are the result of CO oxidation to CO_2 as well as of the total oxidation of the products in the free volume between the grains of the silver catalyst, what is approved by the experimental data.

The temperature oscillations on the smaller Ag grains (0.25 - 0.5 mm.) at high contents of oxygen and ethylene glycol in the system are observed. Under such conditions development of the homogeneous processes beside the layer of the catalyst is possible.

On the basis of the experimental data obtained under variation of free volume between the Ag catalyst grains the glyoxal formation at the ethylene glycol oxidation is shown to take place by the heterogeneous path predominantly. The observed oscillation phenomena are generated by the heterogeneous - homogeneous oxidation of CO and reaction products to CO_2 in free volume between the catalyst grains. The investigated process of the catalytic oxidation of ethylene glycol to glyoxal on silver has a heterogeneous - homogeneous character.

1. Gorokhovatskii Y. B., Kornienko T. P., Shalya V. V. Heterogeneous - homogeneous reactions. Kiev: Technique, 1972, 204.

2. Vodyankina O. V., Kurina L. N., Sudakova N. N., Izatulina G. A. // Abs. VIII Internat. Conf.“ Theory and practice of adsorption processes“, Moscow, 1996, p. 161.

PP-15

DYNAMICS OF ACTIVITY OF OXIDE CATALYSTS IN THE PROCESS OF NITROGEN OXIDES DECOMPOSITION

Xu Yunlong, A.S. Savenkov, M.A. Sibirtseva

Kharkiv State Polytechnic University, Kharkiv, Ukraine

Catalytic decomposition of nitrogen oxides is most simple, thermodynamically feasible and economically profitable method. Fulfilment of nitrogen oxides catalytic decomposition in non-stationary-regenerative regime is most real way. However now the suitable catalyst with high activity in oxidative medium is absent. Oxygen, containing in exhaust gases or forming as a result of NO_X decomposition, competes with NO_X on adsorption sites and reduces catalyst activity.

The experiments on making more precise the composition of catalysts for NO_X decomposition in oxidative medium and influence of technological parameters on the process were carried out.

The properties of contacts on iron, aluminum and copper oxides base as well as their systems in the regime of NO_X decomposition and next reduction of the surface with ammonia-air mixture were investigated. The samples of catalyst prepared by commercial technique were tested in the mixture with initial NO_X content ca. 1 vol. % and oxygen ca. 6 vol. %. Ammonia with 0,8-18 vol. % concentration in the mixture with air or elementary nitrogen was used as a gas-reducer for catalyst regeneration. Temperature of tests was 400-550 °C, decomposition time - 12-16 hours, regeneration time - 0,5-3 hours. In our tests gas composition over catalyst layer was changed, but temperature in the layer was fixed.

The investigations showed that on elaborated catalysts in oxidative medium high decomposition degree (α=75-80%) could be obtained without external diffusion braking. However catalysts activity abruptly decreases after 8-12 hours but after 16 hours, becomes stable and equal 20-30%.

Activity recovery was carried out by means of catalyst treatment directly after decomposition regime at the same temperatures (see Fig. 1). Ammonia-air mixtures are more effective for this process compared with nitrogen mixtures because of nitrogen adsorption by iron oxides. Besides, the application of ammonia-air mixtures with high ammonia content 10-12 vol. % promotes chemical bonding of surface oxygen and its desorption in gas phase as a product of the reaction of elementary nitrogen formation, and complete catalyst activity recovery. However after 16 hours the reduction cycle must be repeated. 9 cycles of decomposition-regeneration were accomplished. In so doing catalyst doesn't lost initial activity.

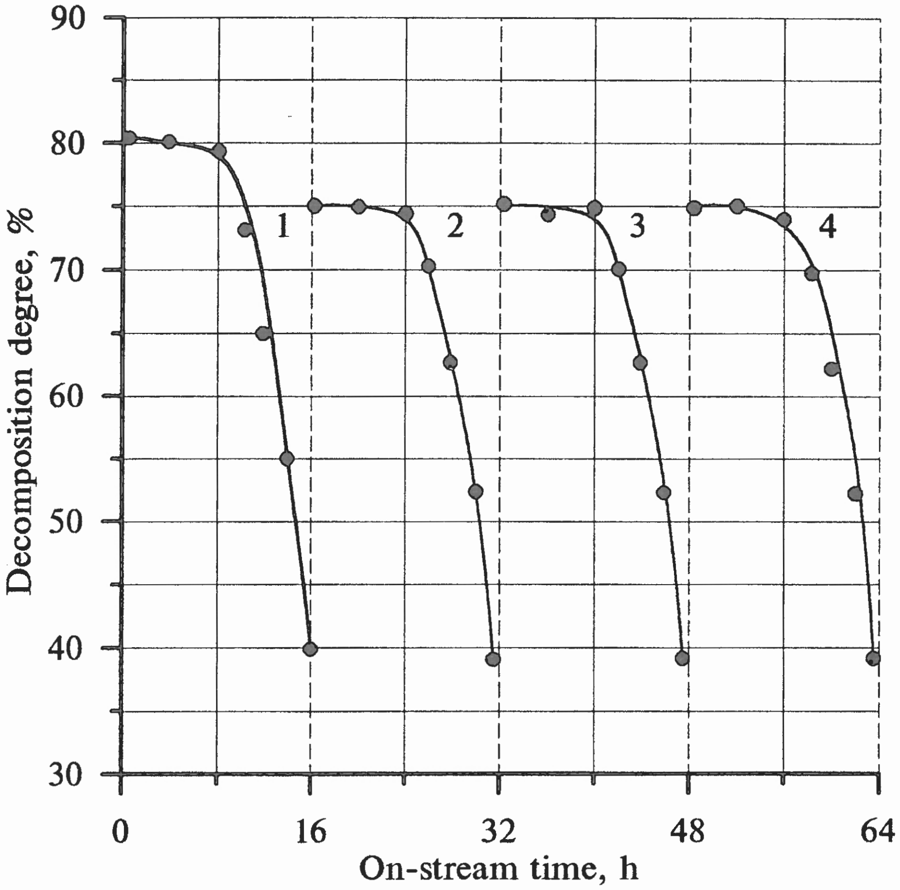


Figure 1 - NO_X decomposition degree dependency on catalyst on-stream time.

t=400 °C; $d_з$=0,25-0,5 mm; $\overline{w}$=1250 h^{-1}.

1 - new catalyst; 2, 3, 4 - catalyst after regeneration with ammonia-air mixture.

Elaborated catalysts and non-stationary regimes of their operation allows to carry out commercial realization of exhaust gases cleaning of nitrogen oxides.

There are some ways for its commercial realization: moving catalyst layer with intermediate regeneration; organized «boiling» layer with regeneration of a part of catalyst and impulse regime of ammonia inlet into direct flow installation operating with honeycomb catalyst.

PP-16

CATALYTIC REACTOR WITH CONTROLLED STRUCTURE OF ACTIVITY

V.V.Andreev
Chuvash State University, 428015, Cheboksary, Moskovskii pr., 15
E-mail: main@chgu.chuvashia.su

Chemical reactor with controlled structure of activity is investigated in the given work. This reactor represents the device, assembled from thin direct and parallel pipes. The catalyst is fixed on internal surfaces of these pipes. The reaction mixture flows through these pipes. It is supposed, that the catalytic reaction proceeds in an unsteady-state conditions and structure of activity on internal surfaces of pipes can also change in time.

For simplification of the analysis it is supposed, that conditions of quasistationarity are fulfilled [1,2]. Under such assumption the analysis of process in pipes is carried out on the basis of steady-state quasi-homogeneous model [3].

On the basis of these assumptions the basic laws of the given process realization are analyzed. Conditions are found, at which average for period productivity of reactor with varied in time structure of activity at realization of the catalytic reaction under the unsteady-state conditions is higher in comparison with the steady-state conditions. The equations for the determination of an optimal structure of activity in pipes in every moment of time are also obtained. The obtained results make a theoretical basis for management of a structure of activity on internal surfaces of pipes in dependence of changing in time reagents concentrations and temperature at the entrance of reactor.

1.V.V.Andreev, N.I.Koltsov, A.F.Ivanova and N.V.Konstantinova, Mendeleev Communications, 1995, 152.
2. V.V.Andreev, Mendeleev Communications, 1997, 35.
3. R. Aris, The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts, Clarendon Press, Oxford, 1975.

SIMULATION OF ETHYLENE OXYCHLORINATION PROCESS IN CATALYTIC FLUIDIZED BED

A.V.Balaev, M.M.Zalimova, Ju.K.Dmitriev, Ya.M.Abdrashidov

Institute of Petrochemistry and Catalysis of Bashkortostan Republic
Academy of Science (IP&C AS RB), AO "Kaustic"
450075, Ufa, pr.Octyabrya, 141, IP&C AS RB
Phone: 347 2 31 22 36
Fax: 347 2 31 27 50
E-mail: root@ink.ufanet.ru

The catalytic process of ethylene oxychlorination has been widely applied in the industry, since the major reaction product of 1,2-di-chloroethane is an intermediate one for vinyl chloride manufacturing.

All experiments on studying process kinetics were carried out in a pilot plant at a research department AO “Kaustic”. In the course of the latter an initial component ratio C_2H_4:HCl:air, a volumetric flow rate of fluidized gas and temperature were varied.

Quantitative analysis data permit to isolate 16 major components: ethylene, hydrogen chloride, oxygen, 1,2-dichloroethane, 1,2-dichloroethene, 1,1,2-trichloroethane, 1,1,2-trichloroethene, tetrachloroethane, vinyl chloride, ethyl chloride, chloroform, carbon tetrachloride, carbon dioxide, water and nitrogen.

1,2-dichloroethane yield was found to be 88...92% in dependence of experimental conditions. The major side reaction products were shown to be 1,1,2-trichloroethane and carbon dioxide. The other side products are presented in a reaction mixture in small quantities and were not considered.

A material balance was summarized as follows: a quantity of 1,2-di-chloroethene formed was added to a quantity of 1,2-dichloroethane, and 1,1,2-trichloroethene and tetrachloroethane to 1,1,2-trichloroethane.

Then reaction scheme may be presented as follows:

$$\begin{aligned} &C_2H_4 + 2\,HCl + 0.5\,O_2 = C_2H_4Cl_2 + H_2O \\ &C_2H_4Cl_2 + HCl + 0.5\,O_2 = C_2H_3Cl_3 + H_2O \qquad (1) \\ &C_2H_4 + 3O_2 = 2CO_2 + 2H_2O \end{aligned}$$

PP-17

The kinetic equations of the sum chemical reaction rates are interpreted by a Langmuir-Hinshelwood mechanism and taken from literature.

An ethylene oxychlorination process was shown to proceed with a significant decrease of reaction volume (moles number of a reaction mixture) according to stoichiometric equations (1). Hence, velocity of fluidizing gas, void fraction and other hydrodynamic characteristics are considered to be variable along the reactor height.

A transient two-phase model of fluidized bed reactor was developed for process simulation. Heat and mass transfers in a dense phase at the expense of longitudinal diffusion, transfers in a dense phase and bubble phase by convective flows, and also Stephan's flow arising due to a reaction volume change are taken into account in the model. A calculation of hydrodynamic and thermophysical parameters was carried out with empirical criteria expressions.

The complete non-stationary model is described in a paper. The abstract presents a stationary system of material balance equation for kinetic parameters.

$$\begin{aligned}
&qU\, dy_i/dl = f(\beta + \mu)(x_i - y_i) + f\Sigma(\nu_{ij} - \delta_j y_i)W_j, \quad \delta_j = \Sigma\nu_{ij}\\
&\beta(1 - q)U\, dx_i/dl = f\beta\,(y_i - x_i)\\
&dU/dl = f\Sigma\delta_j W_j \qquad (2)\\
&\mu = -(1 - q)\,\Sigma\delta_j W_j - e_o/[e(1-e)]\, U/e\, de/dl\\
&l=0:\ y_i = y_i;\ x_i = x_i;\ U=U_o
\end{aligned}$$

where y_i and x_i -component concentrations in a dense phase and bubble phase; W_j - reaction rates; U - superficial velocity of fluidizing gas; q - flow share in a dense phase; f - value reverse to factor of expansion of a layer; μ - speed of Stephan's flow; β - coefficient of mass change; e and e_o - void fractions of fixed and fluidized beds; l - axial coordinate; ν_{ij} - stoichiometric coefficients (scheme 1).

Kinetic and adsorption parameters were determined with the help of the equation (2). The complete system of non-stationary equations of heat and material balances was used for process simulation at various values of operation parameters.

PP-18

THE DYNAMIC OF INTERMEDIATE PROCESSES IN RUNNING REACTOR WITH FIXED BED OF CATALYST

Balakaeva G.T., Zhapbasbaev U.K.

Kazak State University, Almaty, 480090, Universitetskaya st., h. 30, app. 76

ph. (3272) 64-59-69

Dynamic of intermediate processes characterizes initiation of catalytic reaction on the catalyst grain, formation of the front of concentration and thermal wave and its extension through the catalytic bed, influence of regime parameters to set definite regime of running macroscopical phenomena, the standing of reactor to the stationary regime etc. This problem always is in the center of attraction of investigators.

In most researches the filtration stream velocity is taken as constant across reactor section and ignored real aerodynamic surrounding in reactor. Some attempts to account of stream distribution nonuniformity is based on the integral approach with setted amplitude of pressure. Experimental research show the possibility of local overheats appearance in catalyst bed, existence of "hot" spots and consequently the existence of some stationary running processes regimes. This fact requires to make engineering method of intermediate processes dynamic calculation in reactor with fixed catalyst bed on the base of 2-dimensional and 3-dimensional models of movement and heatmass transfer with existence of chemical reactions.

Let us consider the nonstationary process of initiation in catalyst bed, which is porous insertion in plane channel with axial symmetry, on onestage chemical reaction with observing velocity.

Mathematical model is a set of hydrodynamic and heat exchange equations, which are soluble by numerical methods.

The heat emission in the granular bed does not take significant qualitative reconstruction of apparatus aerodynamic in adiabatic regime at constant value of porosity through the section of the channel.

Heat expansion of gases in active zone a few increases the local filtration velocity, and corresponding to that, the bed resistance even grow through section of the channel. So, as in the case of free-running reactor work (without catalytic process), as the stream before insertion will brake, cross component of velocity with positive sign appears, stream lines decline from center to channel walls, velocity profiles become more full. Inside the bed stream lines change weakly. But behind the insertion stream lines decline to the center of the channel, cross velocity has negative sign and profile of longitudinal velocity begins to deform to acquiring parabolic form again.

Stream lines deformations accompanied by characterize vortex creation in the stream which can cause the appearance of macrononuniformities in velocity like popular "ears" behind insertion.

Thus, our mathematical model of aerochemical process has big potentialities for research of intermediate phenomena dynamic, it is reliable theoretical base for engineering calculations when managing of work process in apparatus with fixed catalyst bed.

ESTIMATION OF QUASI-STEADY STATE OF THE CATALYST IN A FLUIDIZED BED REACTOR

V.P.Gaevoi and S.I.Reshetnikov

Boreskov Institute of Catalysis, Prospekt Ak. Lavrentieva, 5

E-mail: resh@catalysis.nsk. su

In a fluidized bed reactor, catalyst particles move continuously along a reactor height in the reaction medium with varying composition of reagents. Under the influence of reaction mixture each particle permanently changes its properties being in unsteady state with respect to the surrounding reagents. The rate of this changes depends not only on kinetic of reactions but concentration gradients and mode of catalyst particle motion as well.

To analyze the processes in the bed it is necessary to create the complex mathematical model, which takes into account the chaotically catalyst particle motion as well as the changing of catalyst state. In this connection it is important to estimate the influence of different factors on the unsteady state of the catalyst. In case, when the unsteady state of the catalyst have not influence essentially on a process in a bed, the quasi-state approach of model can be used.

The aim of this work is obtaining of the analytical estimations of quasi-steady state of catalyst in fluidized bed reactor.

In this work the model reaction $A \rightarrow B$ is considered, which corresponds to the following reaction mechanism:

$$A + Z \rightarrow ZI, \qquad r_1 = k_1 C\,(1-\theta),$$
$$ZI \rightarrow Z + B, \qquad r_2 = k_2 C\,\theta.$$

Here C is the molar fraction of reagent A in the mixture; θ is the fraction of sites Z on the catalyst surface.

The mathematical model taking into account the unsteady steady of the catalyst [1] is used. Model is based on the assumptions of diffusional mixing of particles. When the axial diffusion coefficient of particles $D \rightarrow 0$, this model transfers to the well known plug flow one.

We can assume that the process in the bed will be quasi-steady if the difference between steady state $C^s(l)$ and unsteady state solution $C(l)$ less then accuracy ε:

$$| C(l) - C^s(l) | / \mathrm{Co} \leq \varepsilon$$

Using analytical correlation [1] and method of the asymptotic series the following estimation of quasi-steady state was obtained:

$$| C(l) - C^s(l) | / C_0 \leq [2D\tau/h^2] [k_1 C_0/(k_1 C_0 + k_2] \leq \varepsilon$$

Here $h = u_g (k_1 C_0 + k_2)/(a k_1 k_2)$ is characteristic height of the bed where input concentration C_0 decrease by e times; $\tau = 1/k_2$ is the maximum value of the relaxation time of chemical steps; a is the dimensionless coefficient characterizing the ratio between the number of the catalyst active sites and the molar amount of the gas in unit volume; u_g is gas velocity (m/s).

In the variables of k_1, k_2 the range of the quasi-steady state Ω (ε) will be follow:

at $k_2 \leq K_2$, $0 \leq k_1 \leq \infty$,

at $k_2 \geq K_2$, $0 \leq f(k_2) = K_2^{1/3}/[C_0(k_2^{1/3} - K_2^{1/3})]$.

here $K_2 = \varepsilon u_g^2 C_0/(2D a^2)$.

From resulted above inequalities follows that at the rate constant of the second step less than K_2 the process is quasi-steady state at any values of a rate constant of the first step, and at $k_2 \geq K_2$ a reaction is quasi-steady only in area of $k_1, \leq f k_2)$. Hence, even at a large both constants of the rate of steps there is the range of k_1, k_2 in which the process will not be quasi-steady.

Acknowledgment

This research was supported by the Siberian Branch RAS.

Reference

1. Gaevoi V.P. In: Mathematical Modeling of Catalytic Reactors. Novosibirsk, Nauka, 75-84 (1989).

PP-20

METHOD FOR INVETIGATION OF DYNAMIC PROCESSES ON CATALYST SURFACE

Prof. Dr.-Ing. habil V.V.Kafarov[1], Prof. Dr.Sc. V.N.Pisarenko[2]

1. Universidad Industrial de Santander, Bucaramanga, Colombia, tel. (57)-76-344746, FAX (57)-76-350540, e-mail <kafarov@uis.edu.co>
2. Russian University of Chemical Technology "D.I.Mendeleyev", Moscow, Russia

Detailed information on models for the porous structure of a catalyst pellet and numerical values of the model parameters are necessary for the synthesis of effective designs for a reactor and its control. However, the traditional methods, such as BET, porosimetry under pressure, and X-ray analysis, do not yield adequate information regarding the porous structure of a catalyst, and, hence, supplemental adsorption experiments must be performed.

A yield of constructive status is possible only when sequentially planned, dynamic experiments are performed, which are capable of ensuring a substantial increase of information with respect to the constants of the catalyst models. Such an approach to the study of adsorbents and catalysts made possible the production of models for adsorbents and catalysts with the necessary predictive possibilities and the evaluation of the constants there in with an acceptable accuracy.

Now consider the specific problems in creating a new strategy of catalytic investigation.

First problem of experimental design.

For a given overall time of conducting the experiment T, the vector of control variables $\boldsymbol{u}$ and the input times of the impulses of indicator t, Δt ... $N\Delta t = T$ determine the sequence of volumes of impulses which are inputted $v^{(1)}$ $v^{(2)}$,... $v^{(N)}$, which ensure maximization of a certain functional the information matrix $M(\in)$ with $\in = v$. The solution to this problem in this framework is achieved by nonlinear programming methods.

Synthesis of the optimal testing signal in determination of a model for the porous structure of catalyst can reduce the dispersion in the adsorption-desorption equilibrium constants by a factor of 10, in the effective diffusity D_{af} by a factor of 3, and in the adsorption rate-constant by a factor of 1.8 in comparison with an unplanned single-step indicator-signal. The solution to the problem of experimental planning (or else to the problem of constructing an optimal single-point experimental plan in which the components of the vector u of control variables are not varied) and its subsequent implementation still do not guarantee the production of estimates of the macrokinetic and adsorption constants with sufficient accuracy. This occurs most often in investigations of rapidly occurring adsorption over adsorbents and catalysts with low porosity and a small, specific, internal surface area. In such situations, a multistep experimental plan must be employed for evaluation of the constants. In this connection, the second problem in planning a catalytic experiment is formulated.

Second problem of experimental design.

For a given overall time of conducting a single-point experiment T and times for inputting impulses of *indicator* T=0, Δt,...,kΔt,...,Δt *N=T,* an optimal experimental plan must be constructed, in which the condition for performance of each individual *u*-th experiment are determinated by the vector $\omega_u = [U_u, V_u]$, where the subvector U_u, V_u, u = 1 ... N, also fix in the u-the experiment the values of the respective components in the subvector of control variables and in the subvector of impulse volumes which are inputted.

It now appears possible to construct an initial plan for carrying out an experiment. This initial experimental plan is dependent upon both the specific type of mathematical model for the process and the numerical values of its parameters. Experimental verification of the algorithms for this latter planning of catalytic experiments has shown that their conduct, comprising a certain experiment plant, depends, to a large extent, upon the type of mathematical model and, to a lesser extent, upon the specific numerical values of the model parameters. Consequently, an initial plan of experiments is effective in that stage of research, even when a priori information on point estimates of the parameters is extremely approximate.

Such a strategy for carrying out catalytic research will be extremely effective, and allows in comparison with the first problem of experimental planning, an increase in the magnitude of the determinant for the information matrix of the plan, with a significant reduction in the amount of dispersion in all of the constants of a model of a pellet of a catalyst.

The methods presented above for planning of a dynamic experiment can also be used for evaluation of the parameters in reactor models. Since few additional difficulties arise in the conduct of the experiment and the evaluation of the parameters there in, they will not be considered any further.

MATHEMATICAL METHOD FOR ANALYSIS OF DYNAMIC PROCESSES IN CATALIST PELLET AND CHEMICAL REACTORS

Prof. PhD. A. Ramirez[1], Prof. Dr.-Ing. habil V.V.Kafarov[1], Prof. Dr.Sc. V.N.Pisarenko[2], Prof. Ph.D. B. Mayorga[1]

[1]Universidad Industrial de Santander, Bucaramanga, Colombia, tel. (57)-76-344746, FAX (57)-76-350540, e-mail <kafarov@uis.edu.co>
[2]Russian University of Chemical Technology "D. I .Mendeleyev", Moscow, Russia

The catalyst bed can be represented as a complex heterogeneous system, wherein the immobile and randomly packed catalyst-particles interact with the gaseous stream flowing through the bed. The chemical conversion occurs on the internal surface of the catalyst and is accompanied by heat mass transfer, both inside the phases and between the phases, which leads to the formation of gradients in concentration and temperature in the longitudinal and radial directions. Moreover, the emergence of gradients in individual catalyst-granules is also possible.

Various dynamic models been developed in order to describe the complex processes occurring in a fixed of catalyst.

The multitude of dynamic models developed can be divided two classes: quasi homogeneous and multiphase models. The fundamental catalyst processes in the petrochemical and chemical industries are characterized by a multistage set of the specific chemical transformations with a significant chemical transformations with a significant number of the reactants participating therein. One result is complications of the mathematical model , into with a large number of equations, beginning with heat and material balances, enter. Practical use of these dynamic models is laborious, since large amounts of machine time on a digital computer are required in order to obtain the field of concentration and temperature for the reactants.

This has led in many practical situations to extremely complicated procedures for structural and parametric identification and to the impossibility of scientifically based selections of the mathematical model for a catalytic process, reflecting the results of industrial experimentation over a wide range of variation of the technological parameters.

These difficulties can be successful overcome if the dimensionality of the model equations is sharply curtailed by the use of invariants of the physicochemical (reactor) systems which are derived a priori. The latter also allows preliminary estimation of the parameters for the model and a check of the bases for selection of the boundary conditions.

The invariants proposed for catalyst pellet and reactor systems are represented by nonlinear algebraic or integral algebraic equations, containing the macrokinetic parameters of the models. The invariants relationships differ substantially from one another when the boundary conditions for the differential equations of the models are changed. Hence, it follows directly that the latter allows, from limited experimental information and by using traditional statistical Methods for the planning and analysis of precision and discriminatory experiments, the evaluation of the macrokinetic constants of interest to the investigator and the establishment or the basis for selection of the boundary conditions and mathematical model for the catalyst pellet and chemical reactor.

The practical use of this procedure opens new possibilities to investigators by substantially simplifying in many cases the construction of dynamic models for catalytic processes.

REFERENCES

KAFAROV V.V. Methoden zur Entwicklung von industriellen katalyschen Prozessen (238 p.). Verlag des Vereine Deutscher Ingenieur, Düsseldorf, 1993.

KAFAROV V.V., PISARENKO V.N. “Problems of Industrial Catalysis in a Fixed Bed”. International Chemical Engineering, Vol. 31 (1991), N° 2, p. 213-263.

CHERNIH I.S., KAFAROV V.V., PISARENKO V.N. “New Method o Analysis of the Diffusion Process on Catalyst Pellet”. Journal of Physical Chemistry, 1988, N° 6, p. 1520-1526.

DAMKÖLER G. Der Chemieingenieur, N° 3, 359 p. (1937). English translation in Intern. Chem. Engng., **28** (1988), N° 1, p. 132-198.

ZELDOVICH Y.B. Acta Phys. Chim URSS, **10** (1939).

THIELE E.W. Ind. Eng. Chem. **31** (1939).

WAKAO N., SMITH J.N. Chem. Eng. Sci. **17** (1962).

WHEELER A. Adv. Catalysis, **3** (1951).

LUSS D. Chem. Eng. J. **1** (1970).

ARIS R. The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts. Vol. 1: “The Theory of the Steady State”, 501 p.; Vol. 2: “The Questions of Uniqueness, Stability and Transient Behavior”, 423 p. Clarendon Press, Oxford, 1975.

ARIS R. Chem. Eng. Sci., **6** (1957).

KASAOKA S., SAKATA Y. Kagaku Kogaku, **30** (1966).

KASAOKA S., SAKATA Y. Kagaku Kogaku, **31** (1967).

KINETICS OF RAPID HETEROGENEOUS REACTIONS ON THE SMALL CATALYST PARTICLES ON A SUPPORT: A MONTE CARLO MODELLING

[a)] Myshlyavtsev A.V., [a,b)] Myshlyavtseva M.D.

[a)] Tuvinian Interdisciplinary Institute of SB RAS, 667007, Internatsional'naya 117a, Kyzyl, Tuva, Russia, 8-(39422)-35835, e-mail: root@tko.tuva.su

[b)] Tuvinian State University, 667000, Lenina 34, Kyzyl, Tuva, Russia

Kinetics simulations in heterogeneous catalysis are usually carried out for essentially infinite systems. These simulations correspond to the single crystal catalysts. However the real catalysts are well known frequently to consist of active nanometer-sized particles on more or less inactive supports.

In the present communication we analyze only the role of the spillover effect, consisting generally of adsorption on the support followed by diffusion from the support to the catalyst particle or vice versa. As usual the support is assumed to be catalytically inactive.

We consider below the $2A + B_2 \rightarrow 2AB$ reaction occuring via the standard Langmuir-Hinshelwood (LH) mechanism. We mimic CO oxidation on the noble metal catalysts together with rapid CO diffusion occurring via jumps to nearest-neighbour vacant sites. Oxygen diffusion is neglected. The reaction between nearest-neighbour reactants are considered to be instantaneous. This corresponds mathematically to $k_{dif}^{B} << k_{dif}^{A} << k_r$, where k_{dif}^{B}, k_{dif}^{A}, k_r are the rate constants for B-diffusion; A-diffusion and reaction, respectively.

We have considered the support as a simple square lattice $L_S \times L_S$ with periodic boundary conditions. The catalyst particle was represented as a square $L_M \times L_M$ placed on the support.

To simulate the reaction we use the following assumptions:

(i) The A-adsorption is irreversible and adsorption rate constant for support is equal to one for catalyst particle. (ii) The B-adsorption is irreversible and dissociative. The B-adsorption on the support is prohibited. (iii) The A-diffusion rate constant for support is equal to one for catalyst particle.

The Monte Carlo algorithm is as follows

(i) The arriving molecule is chosen to be A with a probability p and B_2 with the probability *(1-p)*. (ii) If the arriving molecule is A a site on the lattice is chosen at random. If that site is occupied, the trial ends. Otherwise, A adsorbs. Further, an adjacent site is randomly chosen, and if this site is occupied by a B particle then these particles are removed from the lattice. Otherwise, a new adjacent site is randomly chosen and so on, as while as all of adjacent sites will be considered. (iii) If the arriving molecule is B_2, two adjacent sites are chosen at random. If either site is occupied or belongs to support, the trial ends. Otherwise, B_2 dissociates and adsorbs on the chosen sites. Further, all of the six adjacent sites are randomly considered as well as in the previous paragraph. (iv) The A-diffusion are considered as an alternative process. If randomly chosen site is A-occupied an adjacent site is chosen at random. If adjacent site is occupied, the trial ends. Otherwise, the A-particle is moved from previous site to adjacent site. Further, all of the new adjacent sites are randomly considered as well as described above. The number of the diffusion steps accorded to one adsorption step is marked as N.

The preliminary results of our simulations are shown in Fig. 1. The continuous kinetic phase transition which takes place for infinite catalyst particle is easily seen to be lacked. The first-order kinetic phase transition is shifted to less value of probability p. It should be noticed that (a) the shape of the B-coverage curves is close to straight line for a rapid A-diffusion, (b) the maximum magnitude of the reaction rate increases and becomes more than one for infinite catalyst particle.

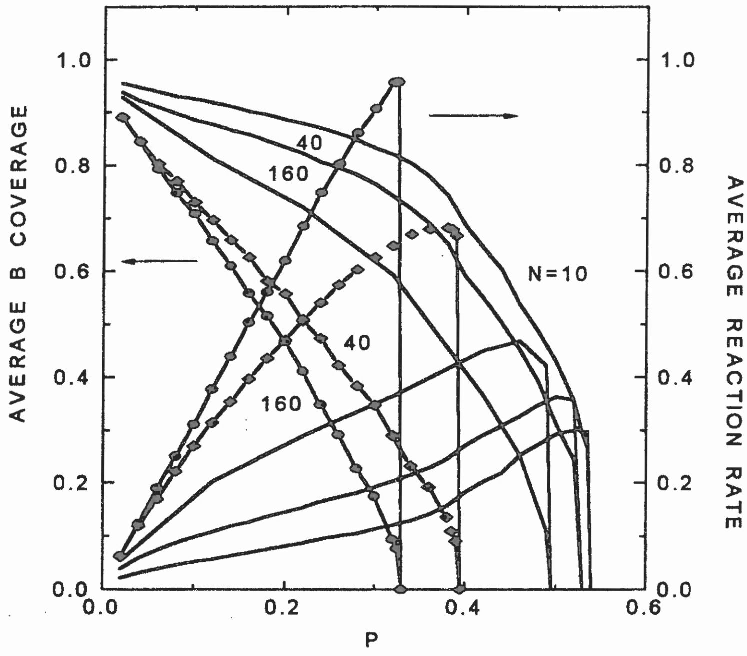


Fig.1

Average reaction rate and B coverage. Solid lines and lines with symbols correspond to 100×100 and 50×50 lattices with $L_S / L_M = 2$, respectively. The number of the diffusion steps is shown in figure.

CATALYTIC REACTION DYNAMICS IN THE PRESENCE OF CAPILLARY CONDENSATION

N.M. Ostrovskii and N.M. Bukhavtsova

Boreskov Institute of Catalysis, Omsk Department, Omsk, 644040, Russia

Tel: (007) 3812 66-44-74, Fax: (007) 3812 64-61-56, E-mail: ostr@incat.omsk.net.ru

The analysis of possible consequences of the capillary condensation for the reaction rate has been carried out in our previous publications [1-3]. The main purpose of this work was to demonstrate how the capillary condensation can affect not only the global reaction rate, but also the reaction kinetics and dynamics in transitional regimes.

Experiments. The model catalysts Pt/SiO_2 with approximately the same characteristics (except porous structure) were used. Two modifications of support SiO_2 were used (KCK-1 with relatively large pores ca. 10 nm, and KCM-5 with small pores ca. 3 nm). The model reaction of p-xylene hydrogenation provides the mild conditions of the experiments in both gas and liquid phases, and avoids the influence of side reaction and catalyst deactivation. The recycle type gradientless reactor were used. This permits us to eliminate the influence of mass and heat transport, and provides uniform temperature and concentration profiles within all the catalyst packing. The radius of pores (r_C), in which the capillary condensation is possible at initial partial pressure of p-xylene P_x^0 were calculated using Kelvin equation.

Reaction kinetics. Under conditions excluding the capillary condensation, the reaction kinetics has a Langmuir type equation: $w_G = k_G\, bP_X\, P_H^o/(1+bP_X)$. The deviation from this dependency was observed when the capillary condensation occurs. At low P_x the reaction rate is closed to that of eq. above. Further the fraction of Pt (acting in liquid phase) increases with increasing P_x that results in a decrease of the reaction rate. The reaction kinetics in liquid follows equation $w_L = k_L P_H\, x$, where x is molar fraction of p-xylene in liquid. At 60 °C and $P_x = 0.045$ atm the ratio $w_G/w_L \approx 20$.

Reaction dynamics. The effect of capillary condensation on the reaction rate in transitions has been studied by variations of the feedstock flow and temperature.

Flow rate variation. In experiments on Pt/KCK-1 the capillary condensation does not influence the reaction rate. Therefore, its relaxation to a steady-state value (after the switching of flow rate) proceeds rapidly. In contrast, when the capillary condensation embraces a considerable part of pores, then not only steady-state kinetics is changed, but also the reaction rate relaxation becomes slow. In Fig. 1a the relaxation dependency for Pt/KCM-5 at 80 °C and $P_x^o = 0.134$ atm are shown. The sequence of reaction rate measurements is marked by figures, and the direction of movement along the dynamic curve is shown by arrows.

The dynamic experiments start at high flow rate of feedstock. Therefore, the p-xylene conversion is small and its partial pressure is closed to the initial value ($P_x \approx P_x^o = 0.134$ atm). The fraction of pores filled with liquid reaches 90-95 %, and the fraction of Pt in these pores accounts for ~ 60 %. After switching to the lower flow rate the conversion increases, P_x decreases and the reaction rate falls sharply. However, the vaporization of liquid begins because of phase equilibrium shift in pores. This leads to the empting of some pores and the reaction rate grows slowly (0.5-1 hour) to a new steady-state value.

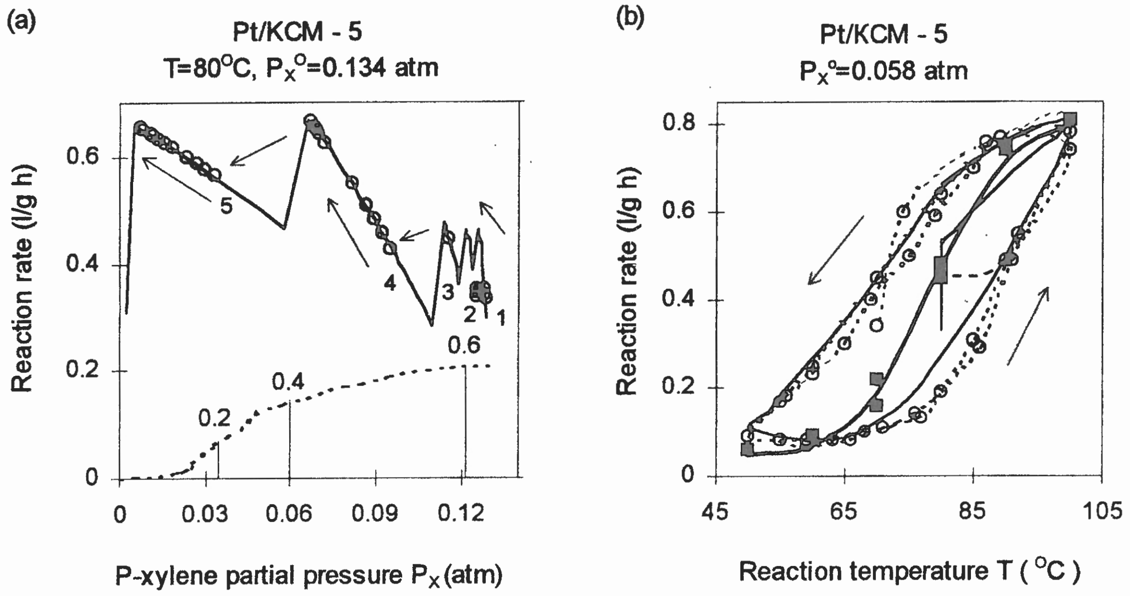


Fig. 1. Experimental (points) and predicted by model (solid lines) reaction rates in steady state (■) and dynamic (o) mode of operation:
The fraction of Pt in liquid is shown by figures and dotted line (a).
Arrows show the direction of moving along the dynamic curves.

Variation of temperature. The experiments were carried out at constant flow rate in two stages. At first, the steady-state dependency having S-form was obtained using slow operation of temperature (■ - in Fig. 1b). Minimal temperature (50-55 °C) provides the filling of all pores with liquid and permits a more exact determination of the kinetic parameters in liquid.

At the second stage rapid temperature variation was used (1-3 °C/min). The results of dynamic experiments (o - in Fig. 1b) were reproduced many times when the cycles of heating and cooling were repeated. The initial and end points of the hysteresis coincide with steady-state values of the reaction rate, because the catalyst pores in these points are filled entirely with either liquid or gas. In a heating period there is not enough time to empty all the pores with radius $r_p > r_C$ at current temperature. Therefore, the reaction rate becomes lower than the steady-state value. In a cooling period, on the contrary, there is not enough time for the capillary condensation to fill the pores. Since the fraction of pores filled with liquid is smaller than in steady-state, the reaction rate proves to be higher than the steady-state value.

Mathematical modeling. Using model [4], the mathematical simulation of steady-state and dynamic experiments was carried out. The calculation results are represented in Fig. 1. It is easily seen that the model demonstrates a good agreement with experiments in both steady-state and dynamic regimes. This confirms the interpretation of the experiments as the influence of capillary condensation on kinetics and dynamics of catalytic reaction.

1. N.M. Ostrovskii, N.M. Bukhavtsova, V.K. Duplyakin: *React. Kinet. Catal. Lett.*, 53, 253 (1994).
2. N.M. Ostrovskii, N.M. Bukhavtsova: *React. Kinet. Catal. Lett.*, 56, 391 (1995).
3. N.M. Ostrovskii: *Khimicheskaya Promishlennost*, 1, 13 (1995).
4. N.M. Bukhavtsova, N.M. Ostrovskii: *React. Kinet. Catal. Lett.* (1998).- In Press.

MATHEMATICAL SIMULATION OF ETHANE OXIDATION IN CHEMICAL REACTOR

I.S.Verzhbitzka, P.G.Itskova, A.T.Lukyanov
Kazakh State University, Almaty
Republic of Kazakhstan

The catalyst oxidation of gas mixture in a wall cooled fixed bed reactor was investigated. Non-uniform distribution of porosity of catalyst layer, absence of the diffusion in the spherical particles of catalyst, heat and mass transfer characterized by effective coefficients of diffusion and heat conduction, accordingly, were assumed.

The calculations were executed on the basis of few mathematical models and then obtained results were compared with each other and with available from literature sources experimental data /1,2/. In all mathematical models the process is described by two-dimensional pseudohomogeneous model of energy and mass transfer. In the first model is assumed uniform flow distribution within the bed. The reality however is different. Due to a change of the average porosity near the wall $\varepsilon = 1$ at the wall - the flow velocity increases close to the wall and is reduced again because of the friction condition. So in the second mathematical model the governing equations of energy and mass conservation are solved including these profiles. The artificial flow profile is described by the Brinkman equation which contains the wall friction and the Ergun pressure loss term /2/. In the third mathematical model is taken into consideration velocity radial and axial distribution and besides it dependencies of viscosity and density of gas mixture from temperature.

By means of the first Liapunov's method on the basis of zero-dimensional models, obtained from corresponding initial models, parametric regions of non-unity and auto-oscillation regimes on the plane "inlet temperature" - "inlet concentration" were obtained for the experimental data of ethane oxidation /1/. Comparing of obtained experimental /1/ and calculated regions of non-unity showed, that they covers. The agreement between available experimental data and theoretical results is improved under the assumption of flow non-uniformity and viscosity and density of gas mixture change with temperatures.

By means of corresponding two-dimensional models regime predicted for the experimental data on the basis of zero-dimensional models was realized. The comparison of temperature profiles, calculated on the basis of different mathematical models with experimental one /1/ showed that third mathematical model based on realistic flow conditions reveals best results, improving agreement between calculated and measured flow profiles.

Further calculations were executed on the basis of third mathematical model. Impact non-uniform radial distribution of porosity and flow velocity, size of catalyst particles, gradient of pressure, heat exchange conditions, inlet temperature and concentration on the parametric regions and dynamic regimes are investigated.

Impact of external periodical disturbances of pressure gradient on the performance of chemical reaction is investigated. The amplitude-frequency characteristic is obtained. The resonance phenomena were investigated.

Literature

1. Kalthoff O., Vortmeyer D.//Chem.Engng Sci.1979.V.35.P.49.
2. Vortmeyer D., Winter R.P. //Chem.React.Eng., 7-th Int. Symp., Boston.1981.p.49.

PP-26

MATHEMATICAL MODELING OF UNSTEADY STATE OPERATION ON THE CATALYST PELLET TAKING INTO ACCOUNT ADSORPTION AND CHEMISORPTION PROCESSES

N.V.Vernikovskaya, A.N.Zagoruiko, N.A.Chumakova, A.S.Noskov
Boreskov Institute of Catalysis SB RAS, Pr.Akad. Lavrentieva 5, Novosibirsk 630090, Russia, phone: +7(3832)350178, fax: +7(3832)357678, e-mail: nady@reverse.nsk.su

The hydrocarbons oxidation dynamics allowing for physical adsorption and chemisorption processes on the catalyst pellet in the mixed flow reactor was studied. The reaction of isopropyl benzene oxidation on the copperchromium catalyst was considered as an example. The reaction mechanism can be given in the next form [1]:

$$A + [O] \Leftrightarrow [AO] \qquad (1)$$

$$[AO] \Rightarrow [P] \qquad (2)$$

$$[P] + O_2 \Rightarrow CO_2 + H_2O + [O] \qquad (3)$$

here A - the molecule of starting organic compound; [AO] - compound A being reversibly adsorbed on the catalyst surface; [P] - unreversibly chemisorbed on the catalyst surface compound. We assume that the catalyst pellet is non-isothermal. Transient equations for temperature and gaseous compounds in the reactor were used in simulation. We apply the pseudo-homogeneous model with unsteady diffusion equations of gaseous compounds to describe the processes on the catalyst pellet. Transient equations for surface compounds on the catalyst pellet were used as well.

The method of orthogonal collocation was used to approximate the profiles with respect to pellet space coordinate in the equations of temperature and gaseous compound concentrations. The resulting system of nonlinear ODEs was solved by using a Rozenbroke's algorithm of the second order with automatical choice of integration step.

Two processes were studied:

1. Physical adsorption and chemisorption processes. The feed to the reactor was oxygen with starting hydrocarbon at low temperature (20°C). Under this conditions the rate

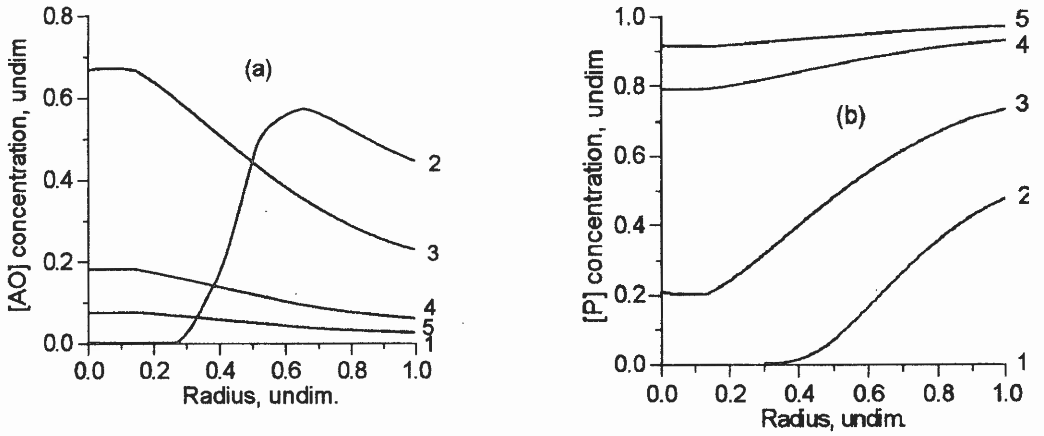


Fig.1. The process of physical adsorption and chemisorption. [AO] and [P] intrapellet concentration profiles. Lines 1-5 correspond to various time moments after regime beginning: 1-0, 2-31.3, 3-62.5, 4-125, 5-166.5 (hours). Pellet radius-2.5 mm.

of the third step is practically equal zero, oxygen intrapellet concentration is equal to input value, carbon dioxide is not produced and catalyst pellet is practically isothermal. Starting hydrocarbon penetrates into the catalyst pellet little by little, physically adsorbs (stage 1) and then chemisorbs (stage 2) (Fig.1a and 1b). The process is stopped when the hydrocarbon concentration at the reactor output is equal to input one with accuracy ε. Intrapellet profiles obtained in this regime are the initial ones for the next regime.

2. Burning process. The feed to the reactor was air without mixture of hydrocarbons at 300°C. Under this conditions at first, the hydrocarbon intrapellet concentration increases due to hydrocarbon desorption (Fig.2, curves 1,2).

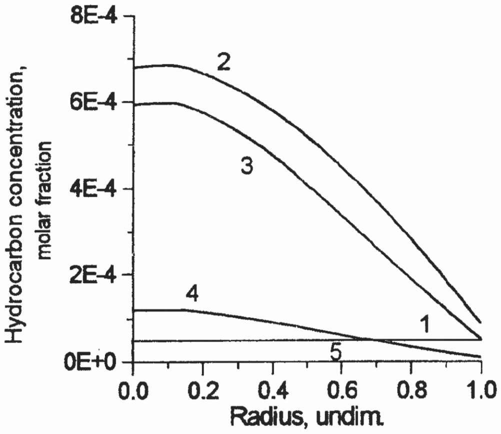


Fig.2. The burning process. Hydrocarbon intrapellet concentration profiles. Lines 1-5 correspond to various time moments: 1-0, 2-300, 3-600, 4-900, 5-1200 (c). Pellet radius-2.5 mm.

At the same time stages 2 and 3 occur. When chemisorbed compound oxidation occurs, the temperature of catalytic system gradually attains 270°C and then sharply increases up to 600°C (Fig.3a). This ignition behavior is due to sharp increase of the rate of chemisorbed compound oxidation. In Fig.3b the sharp increase of CO_2 concentration is presented. The values of the temperature jump and ignition temperature are in a good agreement with experimental results [2].

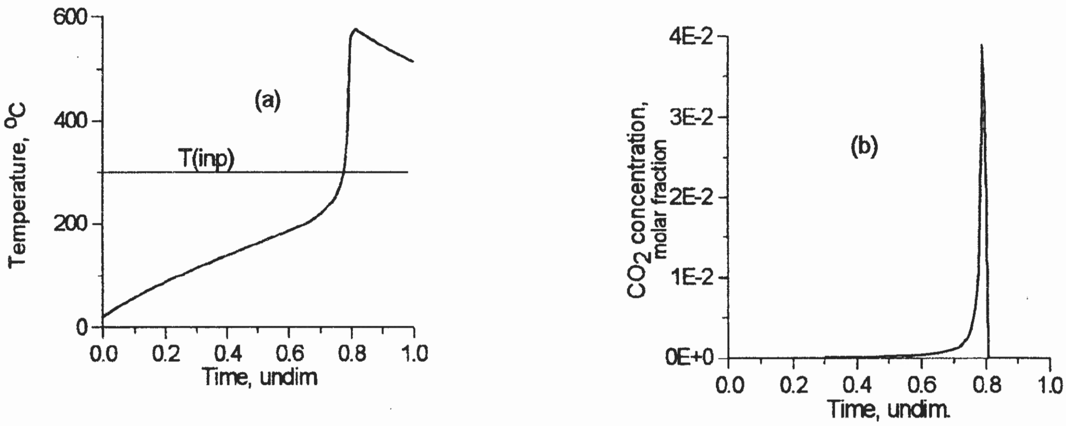


Fig.3. Dynamics of output reactor temperature (a) and CO_2 concentration (b) in burning process. Pellet radius-2.5 mm; T(inp)-the input gas temperature;

References

1. A.N.Zagoruiko. Nonstationary kinetic model of deep oxidation of aromatic hydrocarbons on oxide catalysts. - React.Kinet.Catal. Lett., in press.

2. Yu.A.Kachurovskii. The deep oxidation of aromatic hydrocarbons impurities in air on Cu/Cr/Al-oxide catalyst ICT-12-8. Thesis. Novosibirsk. 1988.

THE EFFICIENCY OF CLAUS CATALYST IN TECHNOLOGY OF SULFIDE METALLURGICAL OFF-GASES UTILIZATION

V.N. Galantsev, A.I. Oruzheinikov, O.I. Platonov, A.V. Severilov and S.P. Yatsenko

Mining-Metallurgical Research Center (GMOITS), Norilsk
663316, box 69, Russia

Instability of technological gas performance and fluctuations of it's components content are the main features of metallurgical off-gases, which can lead to decreasing of their utilization efficiency. As applied to elemental sulfur recovery from sulfide roaster gases the actual efficiency of Claus catalyst unit at Norilsk Copper smelter plant was investigated. The data set of a large-scale (35000 nm^3/h to feed gas) pilot catalytic converter survey that was performed during routine manufacturing of elemental sulfur in operation periods of 1993-1995 was used.

Using the obtained experimental data we have constructed an empirical model of the catalysis conversion efficiency as a function of catalyst temperature or technological feed gas composition.

The results of measurements and their analysis show, that the activity of the traditional alumina based Claus catalyst DR with grain size above 5 mm towards the recovery of elemental sulfur using in technology of metallurgical off-gas utilization is low in comparison with one under traditional steady-state conditions. Besides, the experimental data show that elemental sulfur yield (about 75 rel.%) is maximum at temperatures 250-280 °C, whereas in line with equilibrium model the largest yield is supposed to achieve almost 100% at lower temperatures. The characteristic difference between the equilibrium model forecast and experimental data with temperatures below 280 °C allows to identify the principal route and limitation mechanism of the process.

The main reason for impairing of the activity towards the recovery of elemental sulfur from both hydrogen sulfide and sulfur dioxide is the catalyst aging by sulfation, that occurs mainly because of stoppages. Using data sets on catalyst converter survey we have found that catalyst activity increases from 0 to 90% of maximum activity during 10 hours of continuous operating on line. This fact can be interpreted as an evidence of the catalyst regeneration in the reduced sulfide gas environment.

The available statistical data on mulfunctions make it possible to estimate the elemental sulfur yield losses because of catalyst sulfation. It was found that in practice the mean yield of elemental sulfur in real metallurgical off-gas utilization process is one-third or one-fourth less then in nonstopped one.

Another significant result of our investigation is that when the real catalyst is employed the effect of the reducing agents to oxidants ratio in feed gas on conversion coefficients of H_2S, CO, COS, H_2, SO_2 is negligible in comparison with the usual opinion. This fact from our point of view is the result of kinetic limiting conditions due to the low activity of the real catalyst.

The spectral power density of fluctuations of concentrations for the main components of technological gas in the frequency range 10^{-5}-10^{-2} c/s was measured by using the method of the varying intervals between sampling times. Basing on spectral density measurements and our empirical model for conversion coefficients as functions of technological gas composition we arrived to a conclusion that there is no need in designing and using a special monitor and adjustment system to control the feed gas (metallurgical off-gas) composition.

Generally the results of large-scale pilot catalytic converter survey show that the catalytic activity is diminishes greatly under unsteady operating conditions, for example, in the studied case of metallurgical off-gases utilization technology.

THE INCREASE OF ACTIVITY AND SELECTIVITY DURING THE OXIDATIVE COUPLING OF METHANE UNDER NON-STEADY STATE OPERATION

E.S.Kurkina[1], M.M.Slinko[2], D.Wolf[3], M.Baerns[3]

[1] Department of Computational Mathematics and Cybernetics,
Moscow State University, RU 119899 Moscow
[2] Institute of Chemical Physics, Academy of Science of Russia,
Kosygina ul. 4, RU 117334 Moscow
[3] Institut für Angewandte Chemie Berlin-Adlershof e. V.,
Rudower Chausseé 5, D-12484 Berlin

Periodic operation of heterogeneous catalytic reactors may lead to the enhancement of the reaction rate and selectivity [1]. The reason of the reaction rate and selectivity increase may be connected with the creation of the optimal conditions on the catalyst surface, which cannot be obtained under the steady state conditions. The goal of the present study is to analyse the possibility of the reaction rate and selectivity increase during the oxidative coupling of methane over a CaO/CeO_2 catalyst under non-steady state conditions.

The experimental results, concerning the study of the oxidative coupling of methane over CaO(20 mol-%)/CeO_2 catalyst and the kinetic model developed on the basis of this experimental results are presented in [2,3]. The characteristic feature of the process is the decrease of the C_{2+} yield with the increase of oxygen partial pressure. This trend was described, assuming that two types of oxygen species: (atomic and molecular forms) were present on the catalyst surface. Molecular oxygen was assumed to be a precursor for the stronger bonded atomic oxygen which played the role of the active site in methane dissociation. The kinetic parameters of the proposed reaction mechanism were obtained by the experimental data fitting procedure using a numerical strategy developed in [4].

The improvement of C_2 yield was investigated with the help of the computer experiment by optimisation of process conditions, i. e., temperature and ratio of $p(O_2)/p(CH_4)$. The results of the mathematical modelling demonstrated that the optimal conditions for reaction rate and selectivity depend greatly upon the concentrations of atomic and molecular oxygen on the catalyst surface. Atomic oxygen was shown to be important surface specie in the mechanism of C_2H_6 formation, while the molecular oxygen is responsible for consecutive ethane oxidation and the selectivity decrease.

Basing on these results the strategy of the non-steady-state operation was developed. The first step consists in the oxidation of the catalyst. The heavily oxidised surface, covered by only atomic oxygen may be obtained after 100 s. after the introduction of the oxygen pressure. However the results of mathematical modelling demonstrated that there is an optimal partial pressure of oxygen, 20 kPa, producing the surface, containing 90% of atomic oxygen in only 3,8 s. The response to single step change from oxygen to methane after this time is characterised by the large transient increase of the reaction rate and the selectivity followed by its decline due to the decrease of the atomic oxygen concentration. The transient growth of the reaction rate increases with the increase of the methane concentration in the feed. The step change from oxygen to CH_4/O_2 mixtures leads to the smaller reaction rate and the selectivity enhancement. The causes of this trend is connected with the appearance of the larger amounts of molecular oxygen on the surface, producing the formation of the side products from ethane.

On the basis of the obtained results it was demonstrated, that the reaction rate and the selectivity improvement are largest if the periodic introduction of oxygen and methane into the reactor would be used. The chosen cycle periods and reactants pressure allow to obtain unsteady state conditions, where the surface is nearly completely covered by atomic oxygen, while the concentration of the molecular oxygen is very small. As the reaction rate and the selectivity are controlled by the composition of the catalyst surface, the large increase of the reaction rate and the selectivity is achieved by the optimum periodic introduction of the individual reactants to a gradientless reactor.

Literature

[1] Renken, A, “Unsteady state operation of continuous reactors”
Int. Chem.,Engng., 24, 1984, 202-213
[2] Zhang, Z., Baerns, M., J. Catal. 135, 1992, 317
[3] Wolf, D., Catal. Lett. 27, 1994, 207
[4] Wolf, D., Moros, R., Chem. Eng. Sci. 57, 1997, 1182

MODELING OF PERIODIC FILAMENTARY CARBON PRODUCTION IN A FLUIDIZED BED REACTOR

G.G. Kuvshinov, Yu.I. Mogilnykh, D.G. Kuvshinov
Boreskov Institute of Catalysis, Pr. Akad. Lavrentieva, 5,
Novosibirsk 630090, Russia

Nowadays, the process of catalytic filamentary carbon (CFC) formation on hydrocarbon decomposition is considered as a nontraditional way to produce new carbon materials [1,2]. The necessity of CFC commercial production is determined by its unique properties of a catalyst [3], a catalyst support [4], an adsorbent [5,6], and a material for electrode manufacturing.

Estimating the cost of CFC production, one easily sees that the catalyst cost makes the main contribution to the cost of production. Therefore, it is necessary to attain the maximal proficiency in the use of a catalyst as the process goes upon continuous catalyst deactivation. A periodic CFC production in a fluidized catalyst bed reactor is favored from the standpoint of efficient catalyst operation. The process is proposed to arrange in the following way: a fluidized bed reactor is preliminary loaded with particles of the non-activated CFC and a catalyst. The process of CFC production will go at a constant temperature up to complete catalyst deactivation. Then a part of CFC is unloaded and a fresh catalyst portion is added into reactor. Note that the whole process of CFC production (the volume of CFC granules increases hundred-fold) in the fluidized catalyst bed should be accompanied by a variation of the fluidizing component flow rate (hydrocarbon-containing gas) with time.

The goal of the present work is to analyze various regimes of the periodic CFC production in a fluidized bed catalyst reactor.

For a mathematical modeling of the CFC formation in a fluidized nickel bed reactor, we assume that

(1) reaction is described by equation $CH_4 \leftrightarrow C + 2H_2$

(2) CFC formation follows the kinetic equation [3] allowing for the catalyst deactivation

(3) reactor operates under the unsteady-state isothermal regime, and the catalyst is continuously deactivated

(4) dependence of reaction gaseous component concentrations versus the height of the fluidized catalyst bed is described by a two-phase model of the fluidized bed:

(a) ideal gas forcing in the dense and bubble phases of the bed

(b) solid particles of the fluidized bed are ideally mixed with/along the height of its dense phase

(c) the rate of bubble winding/propagation/elevation in the fluidized bed is calculated using a dependence which accounts for the hydrodynamic interaction of bubbles [4].

Introducing the function of particle distribution with respect to CFC concentration, one may derive a CFC equation for the conditions above:

$$\partial C / \partial t = r(C) \qquad (1)$$

where C is the weight of CFC formed in a unit catalyst weight, g/g_{cat}; r is the rate of CFC formation averaged over a fluidized bed height, g/(g_{cat} h); t is the time of process performance.

Adding the unsteady-state equations for the methane balance in the dense and bubble phases of the fluidized bed, dependences for calculations the rate of bubble propagation in the fluidized bed, bubble portion in the fluidized bed, gas flow rate as a function of methane conversion, rates of methane conversion and the necessary boundary conditions to eq. (1), we have described the process of CFC formation which corresponds to the assumptions above.

This mathematical model permitted us to analyze various regimes for periodic CFC productions in the fluidized catalyst bed when the gas flow rate changed discretely/stepwise with time. Analyzing the calculated data, one can choose optimal parameters for the reactor and operation regimes from the standpoint of the catalyst efficient use. As was found, a discrete decrease in the gas flow rate (during the process performance) provides an increase in the efficiency of catalyst use and conversion of hydrocarbon-containing gas. The analysis indicates that this regime in combination with a number of measures intended to prevent formation of stagnation zones in the reactor meet all the criteria above.

REFERENCES

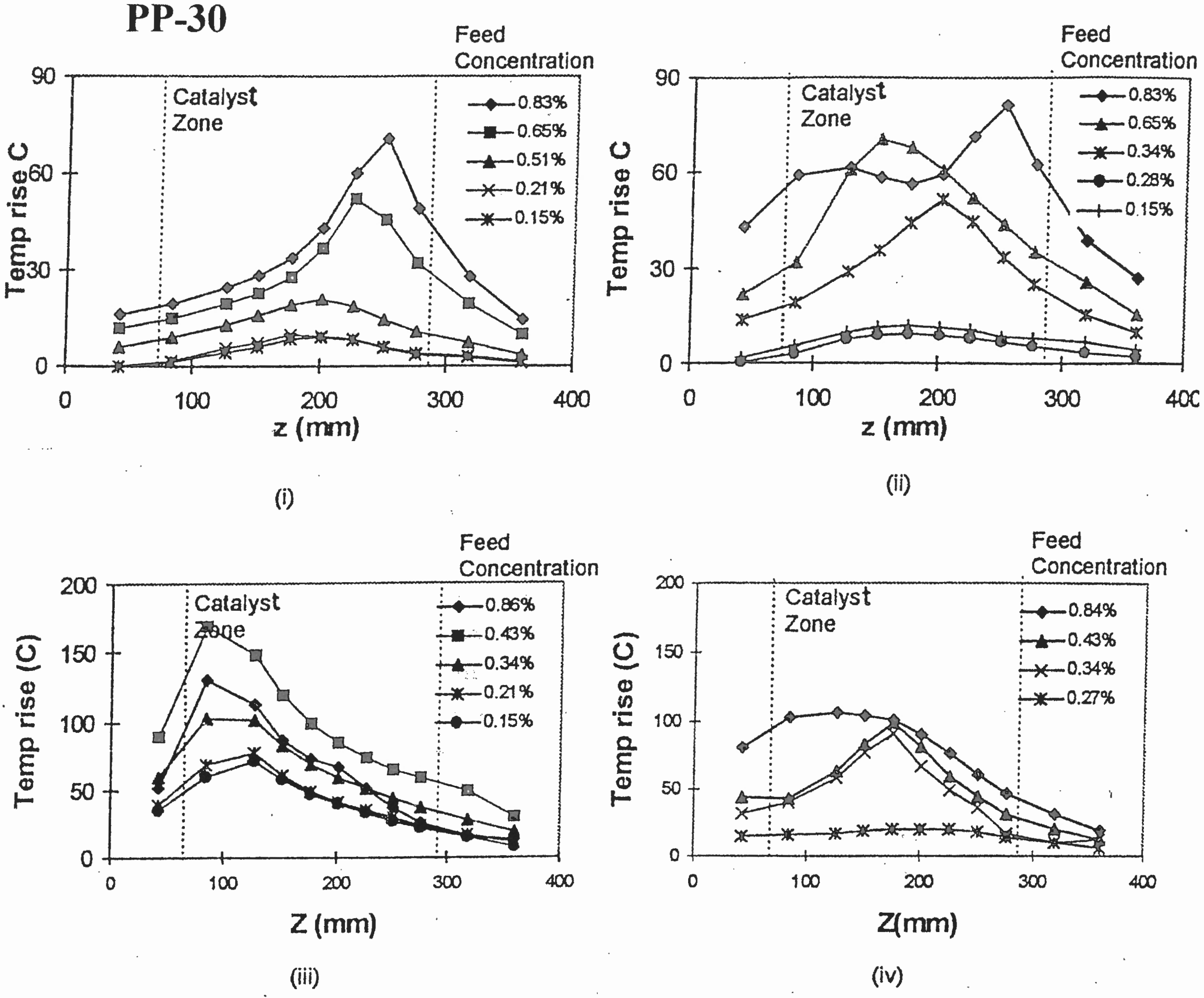
1. Baker R.T.K. // Carbon, 1989, V. 27, pp. 315.
2. Likholobov V. A., Fenelonov V.B., Okkel' L.G. et al. //React. Kinet. Catal. Lett. 1995, V 54, No. 2, pp. 381.
3. Kuvshinov G.G., Mogilnykh Yu.I., Kuvshinov D.G. // Catalysis Today (in press).
4. Kuvshinov G.G., Mogilnykh Yu.I.// Izv. Sib. Otd. Akad. Nauk SSSR, ser. Tekhn. Nauk, 1989, vyp. 4, p. 88.

COMPARISON OF FLOW-REVERSAL AND INNER-RECIRCULATION NONADIABATIC REACTORS

Moshe Ben-Tullilah and Moshe Sheintuch
Dept. of Chemical Engineerig
Technion, Haifa, Israel 32000
email:cermsll@tx.technion.ac.il; phone 972-4-8292820; fax-..-8230476

The advantage of reactors with periodic flow-reversal over simple operation and over reactors with indirect heat exchange has been demonstrated in numerous studies of adiabatic units. Adiabatic conditions cannot always be achieved, and that is especially true for laboratory-scale units. In this study we compare the behavior of a packed-bed reactor operating in reverse-flow or internal-recirculation modes, using ethylene oxidation on Pt/Al_2O_3 as a model reaction. The reactor was built from two concentric tubes (with 28.5 and 42.5 mm in diameter), both packed with a 20-cm section of catalytic bed and 5-cm alumina-pellets sections on each side. An adjustable opening between the tubes allowed for an internal recycle mode and the whole system could be operated with periodic flow-reversal. The reactor can be employed then either as a simple once-through bed in the inner tube (mode i), or as a bed with flow reversal in the inner tube (ii) or as bed with inner recirculation flowing from the inner to the outer tube (iii), or in the opposite direction, as well as an inner-recirculation reactor with flow reversal (iv). The center reactor temperature was monitored with a sliding thermocouple, while the wall temperature was monitored at certain points. The reactor was equipped with a heating-element wrapped around the external tube and covered with insulation. Jacket temperature implies the center temperature in the absence of reaction.

Comparison of the (center) temperature profiles, in the four modes at various feed concentrations, is presented in Fig 1. Fig. 1(i) presents characteristic profiles of a nonadiabatic reactor. Comparison of these profiles with the reverse-flow mode (Fig. 1ii), both operating with a jacket temperature of 55^0C, show larger hot domains and somewhat higher conversions (not reported) in the latter . Modes (iii) and (iv), which operated without external heating, exhibit higher temperature rises and in these cases the simple inner-outer internal-recycle reactor operated better than that with flow reversal, and much better than the outer-inner reactor (not shown). By lowering the feed concentration we determined the extinction point for each mode (Table 1) highlighting again the conclusions drawn above that inner-recycle operation may be superior to flow-reversal in nonadiabatic units.



(i)

(ii)

(iii)

(iv)

Fig. 1. Typical temperature profiles in the four modes of operation.

Operation modes	Jacket Temperature (C)	Ethylene Feed Concentration (%)
Simple Mode		
Periodic	50-60	0.32
One way	50-60	0.55
Complex Mode		
Internal one way	25	< 0.15
Periodic	25	0.34
External one way	50-60	0.43

Table 1. Extinction points.

THE UNSTEDY STATE CATALYTIC APPARATUS "KART"

Yu.V.Ostrovski, G.M.Zabortsev, A.A.Shpak

Novosibirsk Design and Research Institute VNIPIET
Phone: (3832) 76-96-35, E-mail ost@ pri.sib.ru

One of the most effective methods of cleanup of volatile organic compounds (VOCs) from exhaust gases of many productions is their catalytic incineration.

The degree of VOSc removal by this method is close to 100 %, but the realization of the process at small adiabatic heating (low VOCs concentration) requires considerable costs of consumed electric power for exhaust gas heating. Application of various heat recuperators reduces the costs, but the minimum concentration of organic substances for realization of autothermal process is nevertheless great for ventilation gases: 3-5 g/m^3.

Alternative method of organization of VOCs catalytic incineration is the unsteady state process, based on a periodic reverse of a flow of gas stream through a catalyst bed which simultaneously executes functions of catalyst and regenerative heat exchanger [1].

The replacement of a part of catalyst by an inert material allows to save catalyst and reduce pressure drop across the bed, with no significant change in the degree of VOCs removal. The autothermal purification of ventilation gases under unsteady state conditions is possible at lower VOCs concentration: 1-3g/m^3 (adiabatic heating 20-100 K) [2].

The drawback of the use of inert materials, such as ceramic rings, as heat exchangers, is decrease of the degree of VOCs removal due to the desorption of organic substances from the surface of an inert material and the slip of the untreated air from undercontact space.

A catalytic apparatus with regenerative heat exchangers with a capacity of 720 m^3/ hour (KART-720) (photo 1) is developed and designed by our Institute in collaboration with the Laboratory of Mathematical Modeling of Boreskov Institute of Catalysis. The distinctive features of the apparatus are the use of flap-type metal regenerative heat exchangers (photo 2) with a specific surface of 1500 m^2/m^3 located at the outer butt-ends of the catalyst bed divided into two parts and realization of the flow reverse at intervals of no more than 600 s (sliding mode [3]).

The method of mathematical modeling was used to determine main parameters of the apparatus: length, optimum structure and thickness of plates, inlet and outlet gas temperature, temperature profile along the length of the regenerator, period of the flow reverse, power necessary for start-up of the apparatus and for its stable autothermal operation.

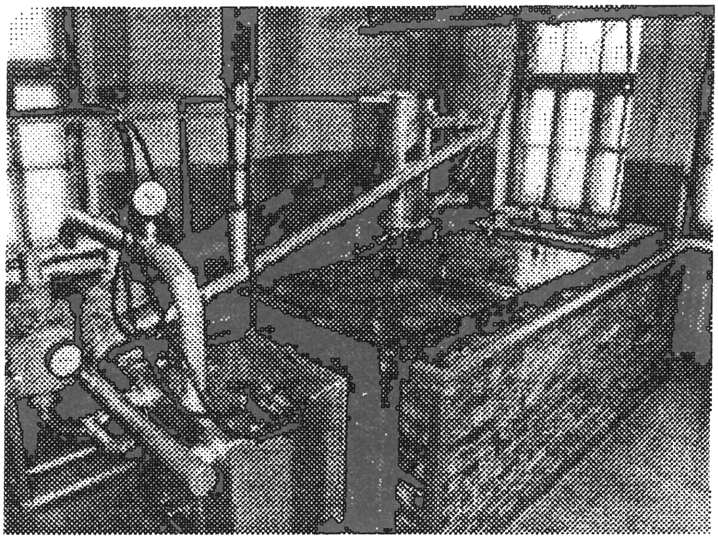


Photo 1. Apparatus KART-720

The tests of the apparatus KART-720, conducted under industrial conditions at the enterprise “SEVER” (Novosibirsk) confirmed the possibility of realization under a short cycle operational mode (T_{fr} no more than 600 s) of an autothermal incineration of VOCs at low concentration (1.0-1.5 g/m^3) over oxide catalysts IC-12-1 and IC-12-8.

At lower VOCs concentrations, in order to exclude a high cost of electric power for heating of the gas, a liquid or gaseous fuel (in our case industrial waste) is supplied into the catalyst bed [4]. It was shown that such technique is more optimum than the fuel supply into the gas stream at the inlet of the apparatus - it increases the degree of VOCs incineration by 2 - 3 %.

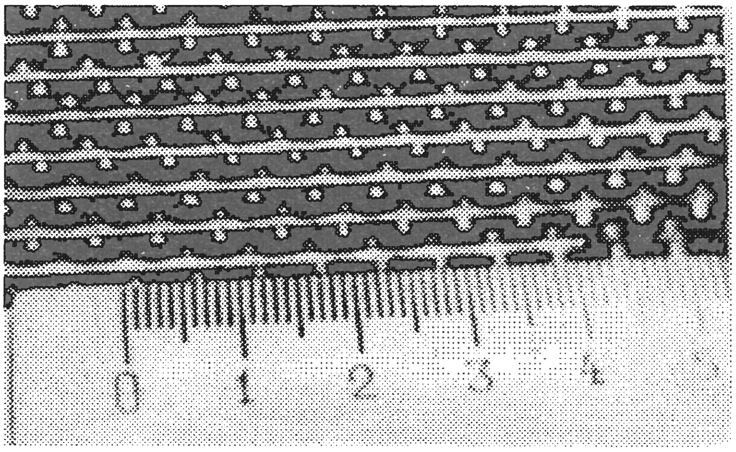


Photo 2. Apparatus KART-720
(model)

Table 1 compares main parameters of the apparatus KART-720 with those calculated by mathematical modeling showing good concurrence of theoretical predictions with the results of the tests.

Table 1

Parameters of the apparatus KART -720

Parameters	KART -720	KART -720 (model)
Gas flow rate, m^3/ h	720	720
Adiabatic heating, K.	20-30	10
Temperature at the inlet of the catalyst bed, ^{0}C		
Temperature at the outlet of the apparatus	450	400-450
(T_{fr}=100 sec), ^{0}C		
Power for the start-up, kW	50	50
Length of the heat exchanger, mm	15	35
	1920	2000

The further increase of VOCs removal efficiency by 2-3 % is possible with the application of apparatuses where the undercontact space is purged during continuous operation [5].

This work was carried out in 1985 - 1986.

References

1. Matros Yu. Sh., Chumachenko V. A., Zudilina L.Yu. An unstedy state method of catalytic purification of exhaust gases of industrial productions from organic substances and carbon monoxide, The inf. review "Protection of the environment and rational use of natural resources ". M.: NIITEKhIM, 1983.- vol. 4 (47).
2. Matros Yu. Sh. and other. An unstedy state method for removal of organic vapors and CO. Catalytic purification of gases, Materials of the 3rd All-Union Conference, Part1., Novosibirsk, IK SB AN USSR, 1981., S. 72.
3. Matros Yu. Sh., Catalytic processes under unsteady state conditions. - Novosibirsk: Nauka, 1987.
4. USSR Certificate of Authorship No 1418957 USSR, B01 Д53/36. A method of purification of oxygen contaning gases from admixture of organic substances / Zabortsev G.M., Ostrovski Yu.V., Popovski V.V., Sazonov V.A., Smirnov A.A., Shpak A.A. - Appl. No 4118204/23-26; date of application 15. 09. 86.
5. USSR Certificate of Authorship No 1832533 USSR, B01 J 8/04. The catalytic reactor / Govor V.V., Zabortsev G.M., Ostrovski Yu.V., Pigalov I.P. and Shpak A.A. - Appl. No 4841837/ 26; date of application 08. 05. 90.

PP-32

ANALYSIS OF A PARTIAL OXIDATION REACTION IN A FLOW REVERSAL REACTOR

Rosa M. Quinta Ferreira[1], Casimiro S. Santos and Ana C. Almeida-Costa
Department of Chemical Engineering, University of Coimbra, 3000 Coimbra, Portugal

Since recently Matros and Boreskov pointed out the increase in the efficiency of a catalytic reactor for the oxidation of sulfur dioxide into sulfur trioxide when submitted to a periodic reversal of the feed flow direction, several works studied the behavior of such cyclic operations in different adiabatic systems. The present study involves the analysis of a non-adiabatic exothermic process, the selective oxidation of o-xylene to phthalic anhydride, with flow reversal operation. Heterogeneous unidimensional models accounting for axial dispersion were used; the predictions of two models in what concerns the reactant transport inside the catalyst particles: diffusion and convection (model HT_{dc}) and only diffusion (model Ht_d) were compared. An irreversible first order reaction was considered.

Figures 1 represent the dynamic response of the system, temperature and concentration gradients in the bulk phase, after reversing the direction of the feed flow: being the system running stationary with the feed entering at the left edge of the reactor (curves *A*), the fluid was fed at the right end, in the reference time $t=0$. Due to the high thermal capacity of the catalytic bed, the velocity of the concentration wave is about 4800 times higher than the one of the thermal wave. So, in the first times the process is isothermal and only the concentration wave travels along the catalytic bed, curves *B* to *E*. The high bed temperatures near the reactor left end where the fluid now gets out come from the heating of that zone before the flow reversal. Since the reaction occurs now essentially near the right edge of the reactor where the reversed flow is entering, a hot spot is developed there and the previous hot spots will decrease, curves *F* to *I*. Therefore, a more uniform distribution of the temperature is obtained. However, if the fluid keeps on entering in this right side a final hot spot will be developed in this region which will be equal to the one of curve *A*, i.e., one will get a steady-state profile which will be symmetric to the previous steady-state situation since in both cases the operating conditions are the same and only the feed is entering in opposite ends of the reactor tube. The solution for keeping a more uniform thermal gradient along the catalytic bed will be to reverse again the flow direction. Therefore, a periodic reversal of the flow will be required in order to prevent high hot spots either at left or at right. We will have then a cyclic operation. This is illustrated in Figs. 2, where the initial steady-state before reversal (curve *A* in Fig. 1) is represented by curve *0* and the temperature profile obtained after *120* s of operation (curve *I* in Fig.1) is shown as curve *1*. Reversing again the direction of the flow by feeding the reactor at the left edge as initially, transient profiles will be developed until the one represented by curve *2* also obtained after *120 s*. Keeping on reversing the fluid direction each *120 s* (reversal time $t_p=120$ *s*) one gets thermal profiles with hot spots either at right for unpair reversals (n_i *=1, 3, 5, 7, ...*) or at left for pair reversals (n_i *=2, 4, 6, 8,...)* corresponding, respectively, to the entrance of the fluid at the right and at the left edge of the tubular reactor. In this case after *7* and *8* reversals of the flow, represented by dashed lines, one gets the so-called cyclic steady-state. Afterwards and keep on reversing the feed flow each *120 s* the process inside the reactor will not have further changes. In Fig. 2 (b) one can observe the increase of the global efficiency of the system by performing a periodic flow reversal operation.

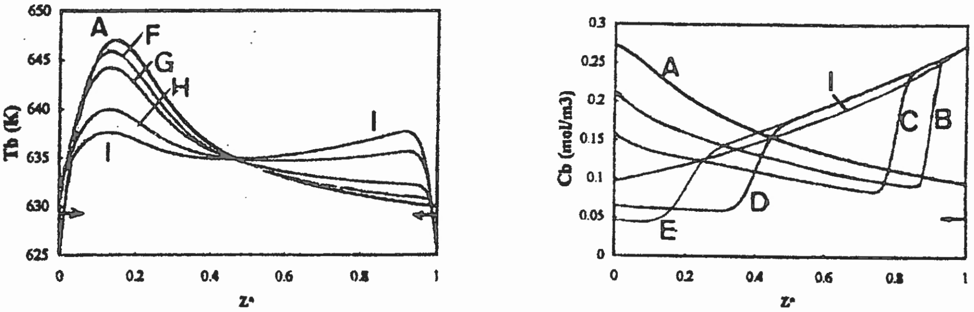


Figure 1. (a) Temperature profiles and (b) concentration profiles after flow reversal for different times (*s*): ***A*** - 0 ; ***B*** - 0.055; ***C*** - 0.11; ***D*** - 0.33; ***E*** - 0.44 ; ***F*** - 11 ; ***G*** - 28; ***H*** - 83 ; ***I*** - 120.

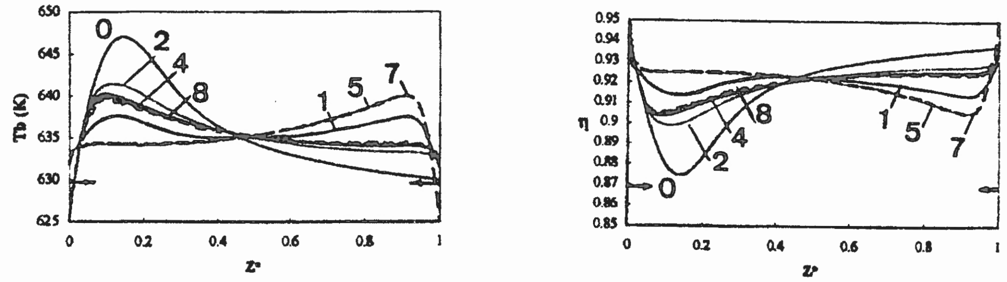


Figure 2. Reversal time t_p=*120s.* (a) Temperature0 profiles and (b) efficiency profiles for different number of reversals: n_i =*0 , 1 , 2 , 4 , 5 , 8.*

Decreasing the reversal time one can then observe that the reduction of the final cyclic hot spots are more pronounced, Fig. 3 for t_p=*60 s.* Conversely for higher reversal times the hot spots corresponding to the cyclic steady-states are higher, approaching those obtained without flow reversal, as can be observed in Fig. 4 where t_p=*240 s.* Moreover, the time needed for reaching those cyclic steady-states also increases with the time interval imposed between two cycles: 780s, 960s and 2160s for t_p=*60, 120* and *240s*, respectively. The behavior of the system when the model Ht_d was used is about the same. However lower conversions are achieved in this case since the reactant transport inside the catalyst particles is done only by diffusion instead of the two convective and difusive transport mecanisms considered in the model Ht_{dc}. In both cases the temperature along the reactor is more uniform with lower hot spots than when the conventional steady-state operation is undertaken without flow reversal.

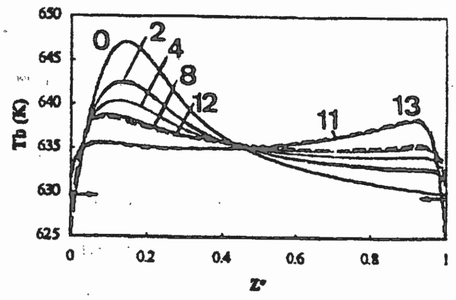


Figure 3. Reversal time t_p = *60 s.* Temperature profiles for different number of reversals: n_i =*0 , 2 , 4 , 8 , 11 , 12 , 130.*

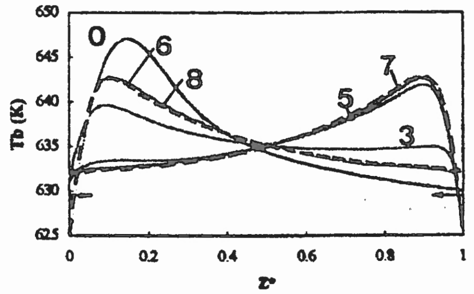


Figure 4. Reversal time t_p = *240 s.* Temperature profiles for different number of reversals: n_i =*0 , 3 , 5 , 6 , 7 , 8.*

PP-33

Studies on Heat Removal Unsteady-State SO_2 Converters (Abstract)

HUI WANG, WEN-DE XIAO and WEI-KANG YUAN*

UNILAB Research Center of Chemical Reaction Engineering, East China University of Science and Technology, Shanghai 200237, P.R.China

1.Introduction

Studies on unsteady-state SO_2 converters show that central heat removal structure achieves a high conversion through auto-thermal transfer. However, some problems arise in practical operation. So it is an important guidance in real production to make a thorough theoretical study of heat removal unsteady-state SO_2 converters, especially their stability and control plan.

2.The influence of parameters on unsteady state SO_2 converters

Here the influence of gas concentration, gas velocity, cycle duration and heat removal rate(β) on unsteady state catalytic processes is studied in detail.

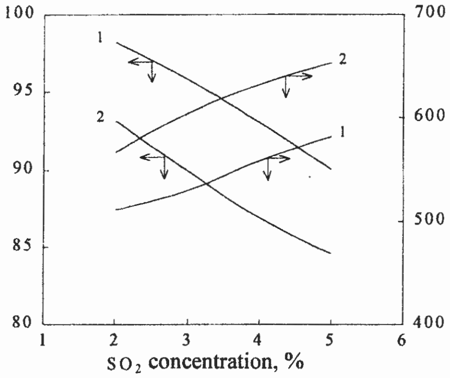


Fig 1. Effect of SO_2 concentration on the outlet conversion and temperature
u=0.3m/s, β =2.66%, cycle duration=20min
1—two-point heat removal; 2—adiabatic

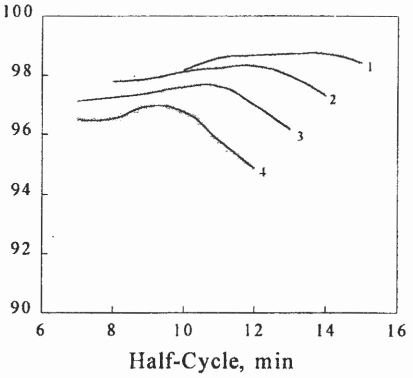


Fig 2. Effect of cycle duration on the outlet conversion
SO_2=3%, inlet temperature=60℃, distance=1.5m
gas velocity(m/s):1-0.26, 2-0.30, 3-0.33, 4-0.36

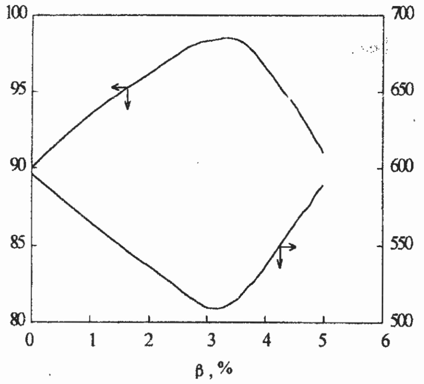


Fig 3 Effect of heat removal rate on the two-point unsteady-state SO_2 converter
SO_2=3%, distance=1.5m,
u=0.3m/s, cycle duration=20min

Fig 1 shows that under identical conditions, two-point heat removal structure, which removes excessive heat by way of central heat removal, has a comparatively better conversion. Studies show that: with constant gas concentration, wave velocity increases with gas velocity in a linear manner and the limited cycle duration is determined by wave velocity. Fig 2 shows that with different gas velocity, cycle duration can be optimized in terms of conversion. For heat

---

*Author to whom correspondence should be addressed.

Phone: 86-21-64253118. Fax: 86-21-64252814. E-mail: sane@npc.haplink.com.cn removal unsteady-state converters, there is an optimal cooling capacity with the highest conversion, as showed in Fig 3. The gas-room temperature in correspondence with optimal cooling capacity is 420 ~ 440 ℃.

3.Control strategy of two-point heat removal unsteady state SO_2 converters

The dynamic characteristics of converters is detected by step perturbation method and as a result, the first order response model for regulation channel is determined as $G_0(s)=\frac{K_0}{T_0 s+1}=\frac{2.363}{90.8s+1}$. From the model we know that the unsteady-state converter is a system with big time constant and consequently is capable of resisting high-frequency disturbance with satisfactory result.

After the step model is fixed, comparison is made among three controlling plans for a group of gas concentration in a factory: feedback, feedback plus feedforward and position control. The following quantitative conclusions are reached. ① Feedback control scheme: the maximum layer temperature is set between 500 ℃ and 560 ℃ and the gas-room temperature between 420 ℃ and 440 ℃. Temperature measured is a guidance to adjust the valve controlling cooling capacity and thus a feedback circuit is formed. The average conversion is 96.99%.② Feedback plus feedforward scheme: The disturbance variable of SO_2 concentration is detected and the transfer function of disturbance channel is decided as $G_f(s)=\frac{K_f}{T_f s+1}=\frac{81.8}{31.8s+1}$. The average conversion is 97.20%. ③ Position control scheme: Cooling valve is entirely open or closed according to the maximum catalyst temperature, which method is simpler and suitable for unsteady state converter, a system with big time constant. The average conversion is 97.09%.

4.Conclusions

Based on the mechanism model of heat removal unsteady-state SO_2 converter, the influence of parameters such as gas concentration, gas velocity, cycle duration and heat removal rate on unsteady-state converter is studied. It is found that the higher the gas concentration, the higher the overall temperature level in the layer. For high gas concentration (around 3%), two-point heat removal converter is recommended. With identical gas concentration, traveling wave velocity, according to which the maximum reversing cycle is chosen, is directly proportional to gas velocity. For two-point heat removal converter, cooling capacity and reversing cycle are two controllable variables to optimize the reaction. The optimal gas-room temperature is 420 ~ 440 ℃, the optimal heat removal rate is 3 ~ 4%. The cycle duration is inversely proportional to gas capacity. In view of two-point heat removal converter, the transfer function for converter regulation channel is determined. Three converter controlling plans dealing with tail gas from certain metallergical factory are compared, from which valve position control is chosen thanks to its easy operation and satisfactory control result.

PP-34

CO_2 reforming in a TAP reactor.

I. Model discrimination and parameter estimation.

V.C.H. Kroll and Y. Schuurman
Institut de Recherches sur la Catalyse, C.N.R.S.
2, Avenue A. Einstein, F-69626 Villeurbanne Cédex, France

A growing number of catalytic reactions are being studied in a TAP reactor. Most of these studies are limited to a qualitative analysis. However, a few number of publications have shown that meaningful kinetic parameters can be extracted from TAP transient responses and that a considerable insight in the reaction mechanism is obtained [1-4].

This paper discusses the modeling of the TAP data on the carbon dioxide reforming by methane over a supported nickel catalyst at 600 °C. The following mechanism has been proposed [5]:

$$CH_4 + 5^* \rightleftarrows C^* + 4H^* \qquad (1)$$

$$2H^* \rightleftarrows H_2 + 2^* \qquad (2)$$

$$CO_2 + {}^* \rightleftarrows CO + O^* \qquad (3)$$

$$C^* + O^* \longrightarrow CO + 2^* \qquad (4)$$

$$2H^* + O^* \rightleftarrows H_2O + 3^* \qquad (5)$$

This mechanism accounts for two routes for CO production, since two different CO responses were observed, when labeled $^{13}CO_2$ was used as a reactant.

The resulting non-linear partial differential equations were integrated numerically according to the method of lines and parameter estimation was accomplished by means of a Marquardt optimization routine. Figure 1 shows the experimental and model predicted TAP response curves for methane and hydrogen. The methane dissociative adsorption was found to be slightly reversible. The hydrogen formation is instantaneous, but dissociative readsorption takes place. Moreover, two distinct CO responses were obtained. These results are in good agreement with other transient and steady-state experiments [5].

A number of variations of the above scheme were taken into account such as step-wise dissociative methane adsorption, different active sites for carbon and oxygen adatoms, etc. The results are discussed in terms to which extend TAP experiments can aid to discriminate between rival models.

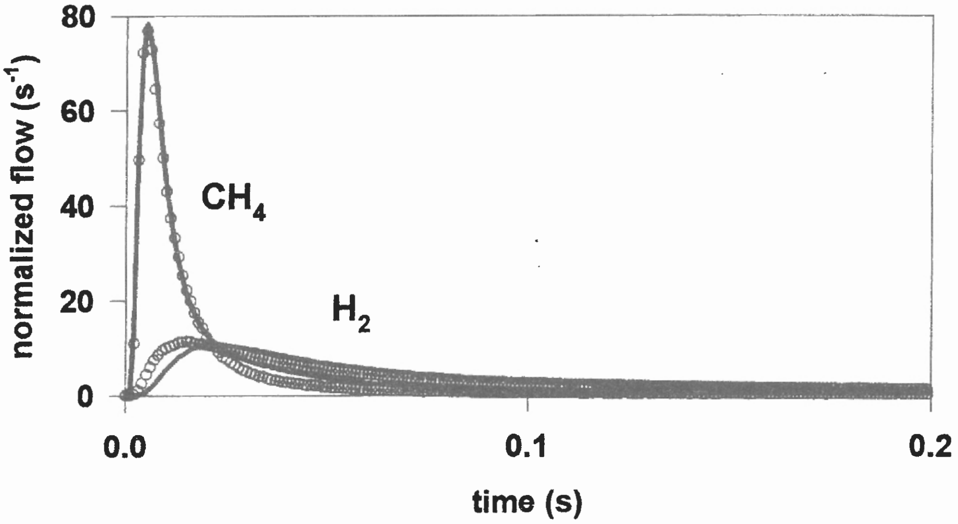


Figure 1. Experimental (open circles) and model predicted (solid lines) TAP transient responses on a pulse of methane over Ni/SiO_2 at 600°C.

References

1 G.D. Svoboda, J.T. Gleaves and P.L. Mills, Ind. Eng. Chem. Res. 31, (1992) 19.
2 G.Creten, D.S. Lafyatis and G.F. Froment, J. Catal., 154, (1995) 151.
3 Y. Schuurman and J.T. Gleaves, Catal. Today, 33 (1-3) (1997), 25.
4 J.H.B.J. Hoebink, J.P. Huinink and G.B. Marin, Appl. Catal. (1997) in press
5 V.C.H. Kroll, H.M. Swaan, S. Lacombe and C. Mirodatos, J. Catal., 164 (1997) 387.

PP-35

Thin-Zone TAP-Reactor Studies

S.O. Shekhtman, G.S. Yablonsky, J.T. Gleaves, S. Chen
Dpt. Of Chemical Engineering, Washington University, Campus Box 1198,
One Brookings Drive, St. Louis, MO, 63130, USA,
E-mail: SERGEI@GASCHE.WUSTL.EDU

The typical TAP-reactor, called a three-zone-reactor, has the catalytic zone sandwiched between two beds of inert particles. In the inert zones, the only diffusion process occurs. In the catalyst zone, the interplay between diffusion and chemical reaction takes place. The length of this zone is compared with the whole length of the reactor. Because of that, there are difficulties from both experimental and theoretical points of view. Firstly, it is difficult to maintain uniform surface coverages, temperature, etc. in the catalytic zone because of gas concentration gradient, which causes diffusion. Secondly, the analysis of three-zone TAP-models is sufficiently complicated.

In this work, a new thin-zone reactor model is proposed to modify the TAP-experiment and simplify the interpretation of its data using a new idea both experimental and theoretical. The idea of thin-zone reactor is to make the thickness of the catalytic zone very small compared with the length of reactor. A unique feature of the thin-zone model is that diffusion and chemical reaction terms can be mathematically separated and non uniformity of catalyst can be avoided.

It is shown that the dependencies for moments as functions of kinetic parameters are much simpler than dependencies in one-zone and three-zone reactor models. The thin-zone model is shown to be very useful for the investigating fast chemical reaction, since the extent of chemical reaction can be controlled by the thickness of the catalytic zone.

MODELING OF WAVE PROPAGATIONS OVER Pt(100) IN CO OXIDATION UNDER UNSTEADY-STATE CONDITIONS

N.I. Efremova and V.I. Savchenko

Boreskov Institute of Catalysis, pr. Akademika Lavrentieva, 5,
Novosibirsk 630090, Russia
E-mail: savch@catalysis.nsk.su

CO oxidation on densely packed Pt faces proceeds via a three-stage mechanism (I):

1. $O_2 + 2Z \Rightarrow 2ZO$; 2. $CO + Z \Leftrightarrow ZCO$; 3. $ZCO \Rightarrow CO_2 + 2Z$.

The scheme presumes the multiplicity of steady states, but no oscillations. To generate oscillations, the surface state should change under reaction medium action either due to phase transition (1x1) ⇔ (hex) in CO adsorption (Ertl [1]) or during the introduction of O_{ads} into the surface metal layer. The PEEM method (resolution ~ 1μ) permits one to observe reaction wave propagation during autooscillations on platinum monocrystals.

In this paper we compare the rate and nature of reaction wave boundary under unsteady-state conditions for the following cases: (1) "common" three-stage scheme and (2) the Ertl scheme, which accounts for phase transition (1x1) ⇔ (hex) in CO oxidation.

The simulation was performed with the Monte Carlo method. Reaction scheme II is as follows:

1. CO adsorption: CO + (hex) → CO-(hex); CO + (1x1) → CO-(1x1);
2. O_2 adsorption: O_2 + (1x1) → 2O - (1x1);
3. CO_{ads} desorption: CO-(hex) →(hex) + CO; CO-(1x1) + CO;
4. Reaction: O-(1x1) + CO-(1x1) → CO_2 + 2(1x1); O-(1x1) + CO-(hex) → (1x1) + (hex);
5. Surface rearrangement: CO-(hex) → CO-(1x1); (1x1) → (hex);
6. CO_{ads} diffusion: diffusion is given by a number of inner diffusion cycle (Nd) repetitions during a single Monte Carlo step, the number of diffusion cycles (Nd) being varied from 0 to 100. The probabilities of stages (1-5) are set close to the data of [3]. Scheme 1 allows for only one type of sites, Z ≡ (1x1) ≡ (hex), and, thus, does not have stage 5.

At the initial experimental conditions, a part of Pt(100) surface is covered by CO(1x1), and another part - by O(1x1), the boundary between the parts is a straight line parallel to axis X. When the reaction mixture is fed, O_{ads} or CO_{ads} waves start to propagate due to the excess of one of components in the reaction mixture.

When reaction mixture contains excess O_2, boundary O_{ads}/CO_{ads} shifts to the CO_{ads} layer. Regarding scheme I, the wave of reaction O_{ads} + CO_{ads} moves along the surface, and O_{ads} covers almost the whole surface, except for several isolated empty sites (1x1). For scheme II, the "oxygen" wave is of the definite width, since empty sites (1x1), formed in the reaction course, transit to (hex) with a probability of 0.01. After CO adsorption, they transit to CO(1x1). Thus, the whole surface is covered by CO_{ads} and the wave of "O_{ads}" (about 30-50 atomic raws) moves along. Moreover, wave width depends on the P_{CO}/P_{O_2} diffusion (Nd) and other parameters. Actually, the "oxygen wave" pattern correlates with the data obtained in [3]. Note that curves of reaction zone rate and diffusion rate (Nd = 10-100) versus oxygen concentration in the gas phase are very close for both schemes (I and II).

With CO "excess" in the reaction mixture, as the wave CO_{ads} moves in the course of its interaction with the CO_{ads} layer (either with the phase transition (scheme II) or without it (scheme I)), reaction zone exhibits a distinct boundary line. Dependences of moving rates, boundary and reaction zone widths are also very similar. If CO_{ads} adsorption is localized, i.e. Nd = 0, the reaction zone width is only 2-3 atomic raws, and the boundary outline becomes rather uneven. As CO_{ads} diffusion "starts" (Nd = 10-100), the reaction zone width increases significantly, whereas reaction boundary retains its straight-line shape (with insignificant fluctuations) in the course of moving. This permits us to obtain the distribution particle concentration and reaction rates by summing over the atom raws along reaction boundary. With the high rate of CO_{ads} diffusion (Nd = 100), the reaction zone measures up to 20 atomic raws in width, which agrees with the data of ref. [5].

Reference

1. R. Imbilh, M. P. Cox, and G. Ertl, J. Chem. Phys. 84, 3519 (1986).
2. G. Ertl, Catalysis Lett., 9, 219 (1991).
3. P. Moller, K. Wetzl, M. Eiswirth, G. Ertl, J. Chem Phys. 85, 5328 (1986).
4. N.I. Efremova, V.I. Savchenko, II Intern. Memorial G.K. Boreskov Conference, Novosibirsk,Russia,1997. Abstracts, PPI-3.
5. V. Gorodetskii, W. Drachsel, J.H. Block, 11th Intern. Congr. on Catalysis, Baltimore, USA, 1996. Abstracts, P_0 -138.

PP-37

Oscillations and surface waves in $H_2 + O_2$ reaction on Pd and Pt studies by FEM, FIM, HREELS

V.V.Gorodetskii[1], P.D.Cobden[2], B.E.Nieuwenhuys[2]

[1] *Boreskov Institute of Catalysis, Prospekt Lavrentieva 5, Novosibirsk 630090 Russia*

[2] *Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands*

Abstract

Kinetic oscillation phenomena in heterogeneous catalysis on metals have attracted considerable interest during the last decade. In this work the mechanism for the generation of movable waves in the course of oscillating O_2+H_2 reactions has been studied on Pt and Pd tips by Field Electron and Field Ion Microscopy. The nature of reaction intermediates has been studied by HREELS and TDS. A sequence of six reaction steps are described in the literature:

$$\begin{array}{lclcll}
H_{2(gas)} & + & 2^* & \longleftrightarrow & 2H_{(ads)} & (1)\\
O_{2(gas)} & + & 2^* & \rightarrow & 2O_{(ads)} & (2)\\
O_{(ads)} & + & H_{(ads)} & \rightarrow & OH_{(ads)} + {}^* & (3)\\
2OH_{(ads)} & & & \rightarrow & O_{(ads)} + H_2O_{(ads)} & (4)\\
H_{(ads)} & + & OH_{(ads)} & \rightarrow & H_2O_{(ads)} + 2^* & (5)\\
H_2O_{(ads)} & & & \rightarrow & H_2O_{(gas)} + {}^* & (6)
\end{array}$$

HREELS. The Pt(100) surface in the 1x1 phase is catalytically active due to its ability to dissociate H_2 and O_2 molecules. The reactivity of molecular peroxo O^{2-}_{2ads} with ν(OO) at 850-950 cm^{-1} and atomic O_{ads} with ν(PtO) at 490 cm^{-1} towards H_2 has been studied on Pt(100) and Pt(111) single crystal surfaces by HREELS and TDS. An atomic state of oxygen with extremely high activity has been found to be responsible for the reaction at low temperature of 100 K. At present, it is proposed that H_{ads} + O_{ads} reaction results in the formation of OH_{ads}, which is an important intermediate species for the H_2+O_2 reaction on platinum surfaces. HREELS spectra show two characteristic bands at 350 and 725 cm^{-1}, respectively. OH_{ads} is highly active due to the rapid attachment of a second hydrogen atom, H_{ads}, producing a water molecule H_2O_{ads}.

FIM. The Field Ion Microscope has been used to study in situ the H_2+O_2/Pt reaction at 300 K < T < 430 K and pressures of $P(O_2) = 4.10^{-4}$ torr, $P(H_2) = 2.10^{-4}$ to 6.10^{-4} torr. The H_2O

molecules produced act as imaging gas and display the distribution of the catalytically active surface centres with a resolution ~ 6 Å. The structure-sensitive H_2O formation has been studied under steady-state conditions, in the oscillatory regime and in the form of chemical waves. Islands of O_{ads} or H_{ads} can be formed in the adsorbed layer. The catalytic reaction then proceeds along the borderlines of these islands and chemical waves can develop. The oscillation cycles start on the Pt(100) plane with an O_{ads} layer that shows the formation of a highly reactive front yielding H_2O (H_2O^+/H_3O^+) product molecules. This wave spreads rapidly over the whole tip surface. The chemical waves are accompanied by a transformation of O_{ads} and H_{ads} layers in a number of reaction steps including the phase transition of nano(100) hex ↔ 1x1 plane (induced by hydrogen adsorption), which provides as the feedback process $H_{ads} \rightarrow O_{ads}$ during oscillations.

$$O_{ads} \rightarrow OH_{ads} \rightarrow H_2O_{ads} \rightarrow H_2O \uparrow + \text{empty site} + H_2 \rightarrow H_{ads}$$

FEM. Hydrogen dissociative adsorption on the surface of a Pd-tip at 300 K causes a monotonic work function increase to $\Delta\varphi = 0.2$ eV and oxygen adsorption to $\Delta\varphi = 0.4$ eV. The initial value of the isosteric heat of hydrogen adsorption is about 28 kcal/mole. The specifity of the individual crystallographic planes in reaction $H_2 + O_{ads}$ has been studied at temperatures $300\ K < T < 450\ K$ and $P(H_2) = 2.10^{-7}$ torr. The maximum initial rate of this reaction has been observed on the (110) planes; then the reaction zone boundary moves in the direction from (110) towards the (100) planes via the atomically rough (320), (210) and (310) planes. Isothermal, non-linear dynamic processes of H_2 oxidation under low partial pressure conditions ($P(O_2) = 1.10^{-5}$ torr, $P(H_2) = 1.10^{-5}$ torr) at $T = 450\text{-}500$ K on Pd have been investigated. Two spatially separated adlayers are formed on the palladium surface. The oxygen islands are formed on the (110), (320) and (210) planes, while H_{ads} or empty sites are formed on the (310), (100), (111) and (311) planes. Reaction on these neighbouring nanoplanes induces fast changes in surface concentration on the borderlines of O islands. In this case, the face-specific oxygen islands are associated with the O-induced subsurface oxygen layer. The oxygen islands size strongly depends on the H_2 partial pressure. This study approaches *catalysis on the atomic level* that is necessary for understanding the mechanism of processes on high-dispersion supported metal catalysts having metal microcrystallites of 100-300 Å in size as the active part of the catalyst.

Acknowledgement: This work is supported by RFBR Grant # 96-03-33211 and by Grant NWO.

SIMPLE MODELS OF CRITICAL PHENOMENA IN KINETIC REGION AND THEIR PARAMETRIC ANALYSIS

T.P. Puhskareva, V.I. Bykov

Institute of computing technologies, Krasnoyarsk, Russia

In given study the detailed parametric analysis of mathematical models of some simple of catalytic reactions [1, 2]:

1. autocatalytic three – step reactions with different buffer steps,

$$1)Z\leftrightarrow X,\qquad 2)X+2Z\rightarrow 3Z,\qquad 3)Z\rightarrow Y,$$
$$3')2Z\leftrightarrow Y,\quad 3'')Z+X\leftrightarrow Y,\qquad 3''')2Z\leftrightarrow 2Y$$

2. catalytic four – step reactions with different buffer steps[3, 4]:

$$1)2Z\leftrightarrow 2X,\qquad 2)Z\leftrightarrow Y,\qquad 3)X+Y\rightarrow 2Z,\qquad 4)X\leftrightarrow S\qquad (4')Z\leftrightarrow X)$$
$$1)Z\leftrightarrow X,\qquad 2)X\leftrightarrow Y,\qquad 3)2X+Y\rightarrow 3Z\qquad 4)Z\leftrightarrow S\qquad (4')X\leftrightarrow S)$$

3. $1)A+Z\leftrightarrow AZ,\qquad 2)AZ+2Z\rightarrow 3Z,\qquad 3)B+Z\leftrightarrow BZ$

is carried out.

Parametric analysis for concrete mathematical model includes the analysis of the number and the stability type of steady states (st.s.) , the construction of st.s. dependencies on the model parameters, study of the mutual disposition of multiplicity and neutrality curves on various parametric planes and the construction of phase portraits and time dependence.

Let us consider the reaction scheme

$$A+Z\leftrightarrow AZ,\qquad AZ+2Z\rightarrow 3Z,\qquad B+Z\leftrightarrow BZ \tag{1}$$

Where A, B are substances in the gas phase (the partial pressures p_A, p_B are considered as constants), AZ, BZ are substances adsorbed on the catalyst Z, the rate constants of the steps depend on the temperature T: $k_i = k_i^0\ \exp(-E_i/RT)$.

The mathematical model, corresponding to (1) is of the form ^

$$y' = k_3p_Bz - k_{-3}y = P(z, y),$$
$$z' = -k_1p_Az + k_{-1}(T)x + k_2(T)xz^2 - k_3p_Bz + k_{-3}y = Q(z, y), \tag{2}$$

Where k_i, p_A, p_B, T are parameters, $x=1-y-z$.

St.s. for the system (2) are the solutions of the equation

$P(z, y) = Q(z, y)=0$ or $G(Z, p_A, T) = 0$ (3)

As parameters , p_A, p_B appear in equation (3) linearly, it is not difficult to obtain the functions which are inverse to the unknown parametric dependencies :

The dependencies of st.s. on the various parameters are obtained.

The boundary of st.s. multiplicity region L_Δ(in the plane of parameters (p_A, T) is determined as a solution of the system

$G(z, p_A, T) = 0, \qquad \Delta(z, p_A, T) = 0,$ (5)

where Δ is determinant of Jacobi matrix of the right hand parts of the system (5). After substituting equation (4) into the second equation of system (5) we obtain

$$T=g(z)$$

So the st.s. multiplicity curve is written in the parametric form.

$PA=F(z, T), \qquad T=g(z).$

Similarly to above we can obtain the parametric form of the st.s. neutrality curve L_Δ, solving the system

$G(z, p_A, T) =0, \qquad \sigma(z, p_A, T) = 0$ (6)

Where σ is the trace of Jacobi matrix of the right hand parts of system (5).

Analysis of the mutual location of the curves L_Δ, L_σ on the parametric plane gives a picture of local st.s. bifurcations.

For the given model the bifurcation curves are obtained for the various planes of real dimensional parameters. The phase portraits are constructed, the influence of parameters on the amplitude and period of oscillations are analyzed.

The supposed method is realized on the set of more complex models of critical phenomena in kinetic region also [5].

References.

1. T.P. Pushkareva, V.I. Bykov. React. Kinet. Catal. Lett., v. 48, No. 1, pp. 127 – 133 (1992).
2. T.P. Pushkareva, V.I. Bykov. React. Kinet. Catal. Lett., v. 48, No. 1, pp. 265 – 271 (1992).
3. T.P. Pushkareva, V.I. Bykov. React. Kinet. Catal. Lett., v. 49, No. 1, pp. 45 – 51 (1993).
4. T.P. Pushkareva, V.I. Bykov. React. Kinet. Catal. Lett., v. 51, No. 2, pp. 285 – 291 (1993).
5. V.I. Bykov, T.P. Pushkareva, V.I. Savchenko. React. Kinet. Catal. Lett., v. 57, No. 1, pp. 141 – 146 (1996).

TRAVELING WAVES IN HETEROGENEOUS MEDIUM WITH CHEMICAL REACTIONS

Snytnikov V.N.

Boreskov Institute of Catalysis, Novosibirsk 630090, Russia

E-mail: snyt@catalysis.nsk.su

Traveling waves can be formed in heterogeneous media with chemical reactions. These waves are discontinuities in density and temperature on macroscopic scale. Fine structure of a such wave so called autosoliton is due to chemical conversions, effective thermal conductivity and the other characteristic properties of medium. An important example of a similar medium is a packing of solid grained catalyst with filtration of a gas mixture through it. The gaseous components take part in chemical reactions essentially on wave front.

Theory developed by Kolmogorov- Petrovsky - Piskunov deals with autosoliton solutions of the one-dimensional diffusion equation with nonlinear source function. This model is applicable for description a lot of physical processes such as combustion and other ones concerned with the waves traveling in nonlinear media. The velocity of a traveling wave is determined according to this theory by the bifurcation of the singular point. The square of velocity depends on derivative of source with respect to unknown function in the initial point. However there is another well- known Zeldovich- Frank-Kamenetsky relationship, according to which the square of wave velocity depends on source function as an integral over the whole exchange region. In the present paper it is shown that there is no discrepancy between both of these relationships for the example of the combustion waves in dissipative heterogeneous medium under chemical reactions proceeding.

In submitted work a correct method of construction of the autowave decisions is specified. The method is based on expansion of a temperature range up to 0K. In this method the approach Kolmogorov- Petrovsky - Piskunov is used. From a received limited spectrum of the autowave decisions are selected that, which satisfy to the third beginning of thermodynamics. The starting system of unsteady equations describes changes of the reactant concentration and the medium temperature on the assumption of the intense heat transfer between the gas and the solid phase under energy emission during irreversible reaction. For this model of gas filtration in dissipative heterogeneous medium with one irreversible chemical reaction the unique decision is found. It is found out dimensionless parameter, the critical meaning of which for chosen Zeldovich number determines a condition of existence of the autowave decision. Criterion of a range of reference temperatures is received, in which the chemical transformations in reactions do not influence a degree of transformation of substance for autowaves processes.

Reaction Dynamics and Unstability of CO oxidation over New Silica Glass Fibre Catalysts

I. Yuranov, V. Barelko
Institute of Chemical Physics RAS, Chernogolovka, Russia

L Kiwi-Minsker, Y. Jiao, A. Renken
Institute of Chemical Engineering, EPFL,CH-1015 Lausanne, Switzerland
phone: +41-21-693 31 81; fax: +41-21-693 31 90; e-mail: albert.renken@epfl.ch

The operation and performance of a catalytic combustion reactor depend on the type, texture, composition and surface properties of the catalyst used. Current development on exhaust and combustion catalysts is warranted, since the efficiency of the catalyst, manufacture and handling still need to be improved. Supported catalysts based on porous silica glass fibres (SGF) have shown properties /1,2/ that are promising in the present catalytic converter technology. For SGF applications the understanding of combustion reaction mechanisms over these new highly active catalysts is important. The detailed knowledge of the ignition and extinction limits, the bistability regions and oscillatory behaviour is also necessary for reactor safety and economic operations.

This study focuses on the catalytic ignition-extinction limits and oscillatory behaviour of the CO oxidation at atmospheric pressure as a base model of combustion reactions over supported Pd/SGF catalyst in relation to catalyst microstructure, specific surface area, porous distribution as well as surface concentration and dispersion of the active component.

Silica and alumoborosilicate glass fibres as woven fabrics are used as a starting material for the preparation of the Pd/SGF catalysts. The regulation of specific surface area (SSA) from 4 up to 250 m^2/g is achieved by the treatment of the SGF support in acidic media. Pd is deposited on the glass surfaces with concentration of 0.01-0.15 %wt. via impregnation and ion exchange from appropriate aqueous solutions. After drying at room temperature the catalysts were subsequently calcined in air at 400°C during 6 hours.

The CO oxidation is carried out in the fixed bed quartz reactor with an external recycling loop. The CO and CO_2 concentrations were continuously monitored by IR detectors/3/. The CO concentration is varied in the range of 0.1-2.5 %vol., the O_2 concentration is kept at 10 %vol. and argon is used as diluent during these experiments.

For all Pd/SGF catalysts three well defined activity regions were found: high reactivity regime with conversion close to 100% above the temperature of ignition (T_{ig}), a second low reactivity regime with conversion less than 10% below the extinction temperature (T_{ex}) and a third reactivity region in between T_{ig} and T_{ex} as an unstable regime (see Fig.1). The ignition - extinction limits depend on the CO concentration in the gas mixture, the gas flow rate and the catalyst used. For the same concentration of Pd 0.15% the T_{ig} decreased, when the SSA of the SGF catalyst was increased. Thus, the catalyst Pd

(0.15%)/SGF with a small SSA of $4m^2/g$ showed a $T_{ig} = 233°C$, but for the Pd (0.15%)/SGF with SSA of $140m^2/g$ a $T_{ig} = 145°C$ was found, all other reaction conditions being constant

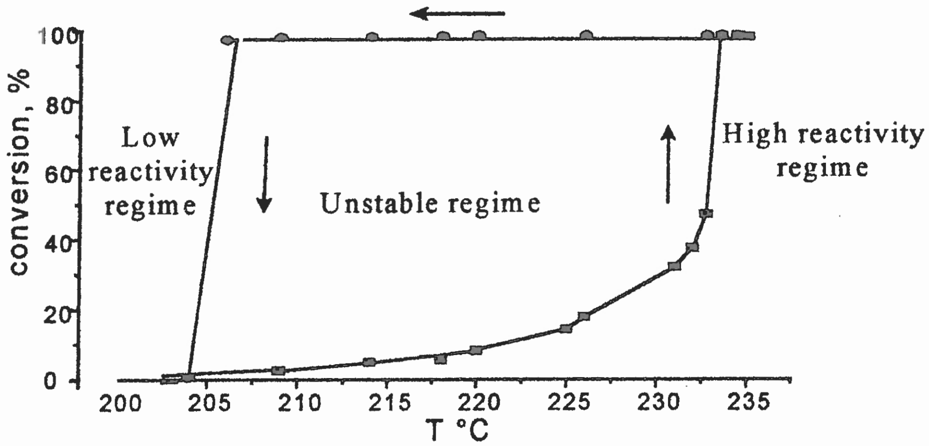


Fig. 1. Temperature hysteresis for CO oxidation over Pd (0.15%)/SGF ($4m^2/g$);
$C_{CO} = 2\%$; $C_{O2} = 10\%$; Flow = 200 Nml/min.

In the region of bistability (unstable regime) self-sustained oscillations were observed. The parameters of these oscillations (period and amplitude) as well as their regularity were shown to depend strongly on the reaction operating conditions and the catalyst properties. For the catalyst Pd(0.15%)/SGF ($4m^2/g$) self-sustained oscillations were detected with a period up to 6 hours of high regularity. The amplitude and the oscillation period were shown to increase with partial CO pressure at constant temperature and to decrease concomitantly with temperature under otherwise constant reaction conditions. With the increase in the catalyst SSA from $4m^2/g$ up to $250m^2/g$ in a catalyst containing 0.15% Pd the oscillations did loose regularity and disappeared. This may be due to the decrease in Pd amount per unit of catalyst surface, leading subsequently to changes in the Pd dispersion and its surface electronic state. The effect found can be used to control the limits (T_{ig} , T_{ex}) of the unstable regime and also to suppress any oscillatory reaction behaviour.

All catalysts were characterised via EM, XPS, BET and TPD methods and results will be reported in a full study.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the funding from the Swiss National Science Foundation under the contract N°7SUPJ048678 without which this work would not be initiated.

REFERENCES

1. Barelko V.V., Khal'zov P.I et.al. "Catalyst for Chemical Processes ", *Russian Federation Patent* N° 2069584, Bulleten Izobretenii (in Russian), N°33, 1996.
2. Barelko V.V., Khrushch A.P., Cherashev A.V., Yuranov I.A. "Catalysis on the eve of the XXI century", Novosibirsk, 1997, Abstracts, Part II, p.59.
3. Frank B., Doepper R., Emig G., Renken A. *Catalysis Today*, 38 (1997) 59-69.

Experimental Study of the Transient Phenomena Induced by Flow Changes in Countercurrent Trickle Beds

V. Stanek, B. Jakes, J. Ondracek and P. Svoboda

Institute of Chemical Process Fundamentals,
Academy of Sciences of the Czech Republic
165 02 Prague 6
Czech Republic
Fax +42-2-20920661
E-mail:STANEK@ICPF.CAS.CZ .

Abstract

An experimental study has been undertaken to investigate the phenomena taking place in trickle beds following a sudden change of the flow rate of phases. The transients driven by changes of the hydrodynamics will necessarily project into the effects on reaction rates and heat and mass interfacial transfer taking place in two-phase reactors.

The apparatus has been built to investigate reactors up to 0.3 m in diameter, although the currently used size is only 0.2 m. The flow arrangement is countercurrent when the liquid is brought on to the top of the layer of packing via a distributor ensuring reasonably uniform distribution. The gas is brought under the supporting grid from the space separated from the surroundings by a siphon.

The reactor is suspended on a tensometric balance providing weight measurement under the operating conditions. Along the height of the packed section there are six pressure ports allowing on-line measurements by means of piezoelectric pressure transducers.

Five centimeters above the supporting grid the reactor is equipped with a port for injecting helium into the streaming gas. Above the packed section there is a probe functioning as a katharometer detecting the concentration of helium in off gas.

The function of the whole set up is monitored and controlled by a Hewlett Packard data logger and computer. With all this equipment we are capable now of on-line monitoring:

- The instantaneous holdup of liquid in the reactor (computed from the measured instantaneous weight of the column and the overall pressure drop across the reactor),
- pressure drop profile along the depth of the packed section as well as the total pressure drop,
- eventual onset of the flooding condition through the formation of the gas-liquid mixture on top of the packed section (this information is provided by an auxiliary pressure transducer level with the top of the packed section),
- mean residence time of gas in the reactor and the distribution of the residence times around the mean (from the measurement of the response to helium injection).

The experimental data are obtained as a time series recorded in the computer to be processed off-line. The course of experiments is programmed in the computer using Hewlett Packard Visual Engineering Environment (VEE) Programming Language.

The aim of the work is to obtain maximum experimental evidence to form basis for physical interpretation and modeling of the transient phenomena under complex flow conditions in the counter-current trickle bed.

Experiments have been carried out to monitor the response of the trickle bed column to a sudden change of the flow rate of gas and liquid. Attempts have been made to interpret these results in terms of the first order kinetics. It has become apparent that first order kinetics is only an approximation to the reality that is more complex and probably superimposing two phenomena with different rates.

An interesting finding is that under certain regimes when the bed is exposed to a sudden change of gas velocity the experimentally observed pressure drops transient curve passes through a maximum. This shows as an overshoot on the response curve and the system reaches the new steady state, corresponding to the higher gas velocity, from the opposite direction.

Reversing Flow Catalytic Converter System for Dual Fuel Engines Meeting Strict Engine Emission Standards

M.D. Checkel[1], B. Liu[1], M.Zheng[2], G.A. Bunimovich[3] and V.O. Strots[3]
1. Dept of Mechanical Engineering, University of Alberta, Edmonton, Canada T6G 2G8
fax (403) 492-2200 phone (403) 492-2340 E-mail dave.checkel@ualberta.ca
2. Alternative Fuel Systems Inc, Calgary, Canada
fax (403) 237-7441 phone (403) 262-1833 E-mail afs@telus.com
3. Matros Technologies, St. Louis, USA, fax (314)995-6941, phone (314) 995-9850

Dual fuel engines are engines based on the compression ignition cycle but burning both natural gas and Diesel fuels to produce power. The natural gas is injected through the intake valve opening during the intake stroke, producing a lean, premixed gas mixture. A small "pilot" injection of Diesel fuel is injected near the time of peak compression to provide ignition. To control load, the quantity of natural gas is adjusted. For very low loads and idle operation, the diesel pilot is sufficient to operate the engine. With an engine computer controlling both natural gas and Diesel injection, the ratio of fuels can be adjusted for optimum performance at each operating point. Natural gas can be utilized at a high rate (over 80% diesel replacement) and with significantly higher efficiency than in spark ignition engines (due to the high Diesel compression ratio). Diesel engines produce troublesome emissions of soot particulates and oxides of nitrogen (NOx) when operated loads above idle. Dual fuel engines have much lower particulate and NOx emissions because of the advantages of premixed combustion. At idle, dual fuel engines operate essentially as a Diesel and share correspondingly low emissions. However in the low-load operating region, where the natural gas mixture is extremely lean, dual fuel engines can suffer partial burn problems leading to undesirable levels of carbon monoxide (CO) and unburnt hydrocarbon (THC) emissions. Available solutions to this problem include reverting to Diesel-only operation or using "skip-fire" where alternating cylinders are supplied with a richer mixture or no mixture to provide the right power without ultra-lean mixtures. However, to optimize natural gas utilization and emissions over the full operating range, it is desirable to develop an oxidizing catalytic converter capable of treating the exhaust of a dual fuel engine.

Developing a catalytic converter for dual fuel engines is a challenge. The hydrocarbon emissions are almost totally methane which is very unreactive and the exhaust temperature is quite low. Figure 1 shows the tailpipe emissions and engine-out exhaust temperature of a dual fuel engine with non-optimized combustion. Note that exhaust flow is roughly constant as torque is varied and the highest emission rates coincide with the lowest exhaust temperature. To attack this problem, highly active catalysts with high palladium/platinum ratio and high precious metal loading are required. However, promising initial results often degrade as the catalyst ages, (probably due to Diesel fuel sulphur contamination). Figure 2 shows how the THC reactivity of a typical catalyst degrades with time. A fresh catalyst achieves 50% THC conversion at 375°C and 80% conversion at 420°C monolith temperature. After about 20 hours of operation, performance stabilizes with 50% conversion at 475°C and 80% conversion at 580°C. The high temperatures required by an aging catalyst are not available in part load operation where pollutant production is significant. Even if the catalyst can be preheated by high load operation, it will cool and lose activity when exhaust temperature drops due to an engine load reduction. The monolith is heated by catalytic reactions but that heat is transferred downstream through the monolith by the "cool" exhaust flow.

A reversing flow catalyst (RFC) system has been developed for automotive engines. Periodically reversing the exhaust flow through a converter with the correct balance of switching period, heat capacity, and catalytic activity can maintain a hot zone in the centre of the monolith despite cool exhaust. Figure 3 illustrates the effect of the reverse flow system on catalyst temperature. The two central lines (squares) indicate operation at full torque. With no RFC, the catalyst monolith is close to the exhaust temperature (475°C). With RFC, the catalyst monolith stays about 20-30°C warmer. When torque is reduced, a more dramatic effect occurs. With no RFC, the catalyst cools off to the lower exhaust temperature, (about 410°C) despite higher amounts of methane and CO. With RFC, monolith temperature rises to over 575°C despite the exhaust temperature drop. Figure 4 illustrates the same process through a series of torque reductions from full load to 1/3 load. Catalyst temperature was raised from 475°C to over 650°C while exhaust temperature dropped from 475°C to 275°C. The RFC system was able to maintain catalytic converter effectiveness over 75% despite the low exhaust temperature and high methane loading.

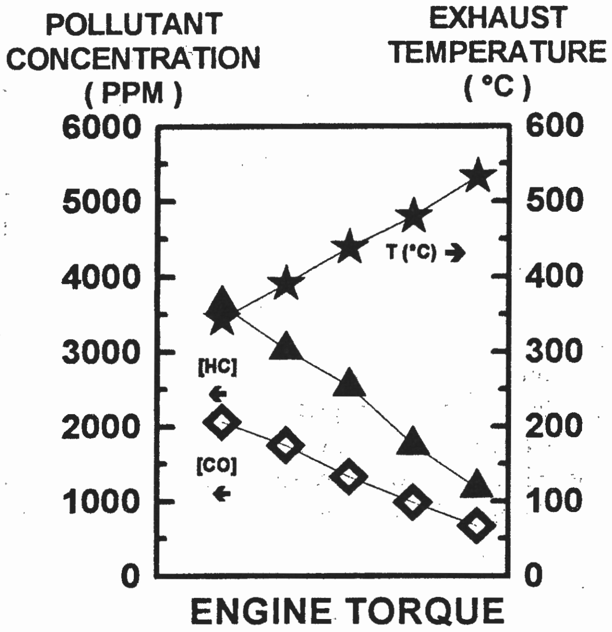


Fig. 1. Trends of exhaust temperature decrease combined with THC and CO increase at part load.

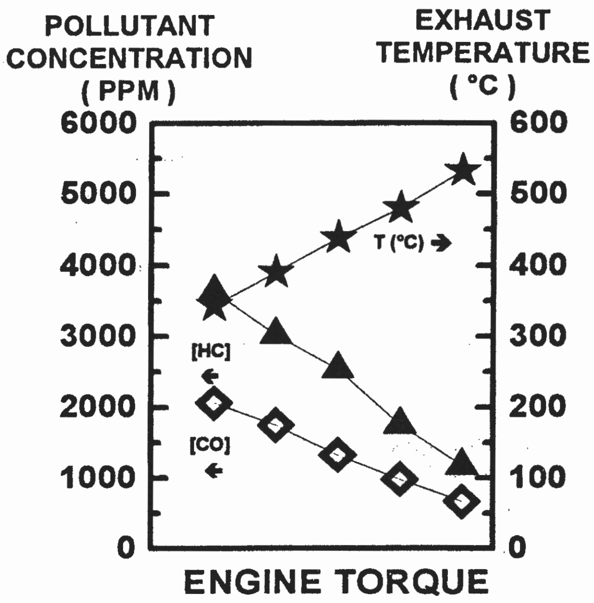


Fig. 2 Trend of degradation from fresh catalyst until stable performance after about 20 hours.

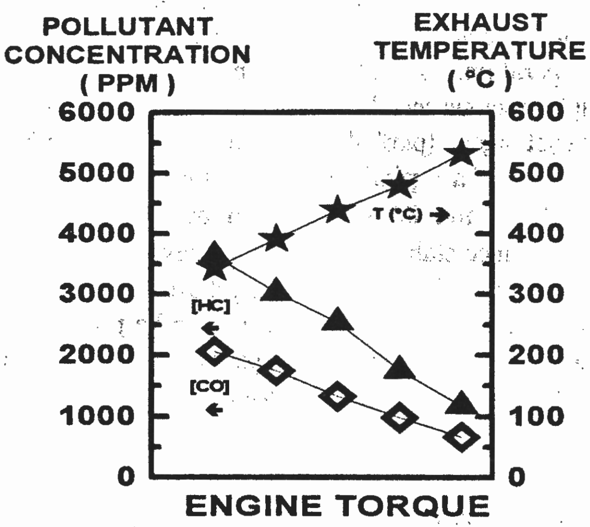


Fig. 3 Effect of Reversing Flow during transition from full torque to part load.
Squares = Full Torque, Circles = Part Load
Filled = Reversing Flow, Open = Steady Flow

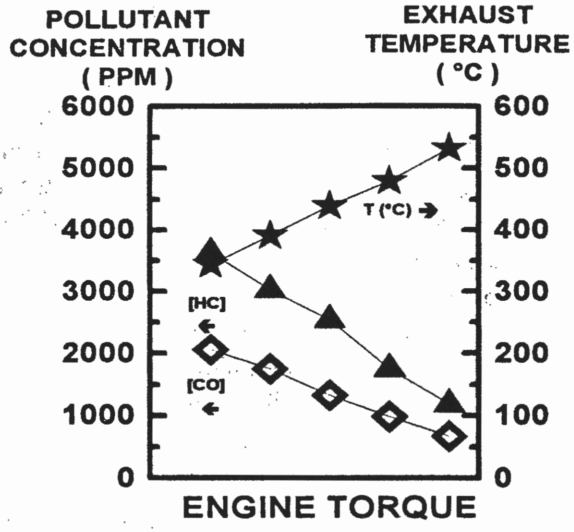


Fig. 4. Illustration of catalyst temperature control. 15 minute period of reduced exhaust temperature.

PP-43

NOVEL LOW TEMPERATURE CYCLIC PROCESS FOR PRODUCTION OF CONCENTRATED SULFURIC ACID FROM SO_2 - AIR MIXTURES

R.V. Vladea, R.R. Hudgins and P.L. Silveston

Department of Chemical Engineering
University of Waterloo
Waterloo, Ontario, Canada

Experiments have been undertaken on the oxidation of SO_2 in air or air diluted with inerts employing an activated carbon catalyst (Calgon Centaur Carbon), using a solvent in place of water as the liquid flush to strip acid from the carbon surface. Temperatures have ranged from 15°C to 40°C and SO_2 concentrations have ranged from 0.25 to 7 vol. %. Most experiments employed acetone as the solvent. Activated carbon was supported on a structured packing consisting of a coiled screen that was set vertically in the reactor so a single coil filled the reactor cross section. This support provided low pressure drop at high GHSV. Catalyst productivities up to 4.5 $g_{H_2SO_4}/g_{catalyst}.h$ have been achieved for low as well as for high SO_2 concentrations. These values are higher by 35-40times than the highest productivities shown by the commercial catalyst. Acid concentration can be adjusted from 100% H_2SO_4 to dilute acid through control of humidity in the SO_2 containing gas or by addition of water to the solvent.

Sulfuric acid has been recovered from its solution in the organic inert solvent by distillation. In order to avoid VOC generation while keeping the catalyst temperature under control, cyclic flushings with solvent is used. The flushing periods, solvent flow rates and flowing patterns are matched to the SO_2 concentration and superficial velocities of gaseous streams.

PP-44

Catalytic Partial Oxidation of Alkanes at Millisecond Contact Times

Lanny D. Schmidt
Department of Chemical Engineering and Materials Science
University of Minnesota
Minneapolis MN 55455

Recent results from this laboratory on the partial oxidation of alkanes to produce useful chemicals on monolith catalysts with millisecond contact times will be described. These include methane to syngas, higher alkanes to olefins, and higher alkanes to oxygenated hydrocarbons. Effects of flow rate, preheat, gas composition, and catalyst morphology on conversion and selectivities will be discussed. Recent modeling results will also be described which give considerable information about the role of homogeneous reactions in these processes.

A MODEL CALCULATION FOR CO OXIDATION UNDER NON STEADY STATE CONDITIONS

M. Kolb and Y. Boudeville

Institut de Recherches sur la Catalyse, 2 Avenue Albert Einstein, 69626
Villeurbanne Cedex, France.
and
Ecole Normale Superrieure de Lyon, 46 Allee d'Italie, 69364 Lyon Cedex, France.

Lattice model have been used successfully to understand and to model the basic steps of CO oxidation on Pt. These calculations suggest that a higher catalytic activity could possibly be achieved in the early, transient stages of the CO poisoned regime. Monte Carlo simulations were employed to probe this borderline region between active and CO-poisoned domains in an attempt to improve the overall yield by periodic changes of the reaction conditions. The calculations show that poisoning can indeed be prevented despite the temporary working in the poisoned state. The optimal overall rate is about as good as when working exactly at the limit of the active and the poisoned steady state, but is less sensitive to the exact values of the thermodynamic parameters.

PP-46

A NEW METHOD FOR SO_3 PRODUCTION

G.GROZEV, D.DIMITROV*
Institute of Chemical Engineering, BAS, Sofia 1113, Acad.G.Bontchev Str.,Bl.103,
E-MAIL: CHIMREAC@BGEARN.ACAD.BG, FAX: 359 (2) 70-75-23
* KCM S.A., Plovdiv 4009, Assenovgradsko shosse,
E-MAIL: 314@KCM.BG, FAX: 359 (32) 62-35-76, Bulgaria

In principal, the classical reactors with adiabatic fixed bed of catalyst can not operate effectively in non-ferrous metallurgy, because the gas flow and the sulphur dioxide concentrations are not constant. These variations generate less or surplus of a reaction heat in system. To receive a stable auto-thermal regime it is necessary to using a very costly system for regulation and control. Moreover, when the sulphur dioxide concentration is too low, the system can not operate. For the DC/DA scheme this limit is about 7 vol.% SO_2 and for single contacting - 4 vol.% SO_2. In this case it is need to use additionally energy to compensate the lack of heat or burning sulphur to increase the content of SO_2 in gas flow.

By means of the non-steady state method this problem can be eliminate. The theoretical foundations of this process are develop from several authors, but the best using in practice is achieve in KCM S.A. - Plovdiv (Bulgaria). The reactor is in operation with success since 1990.

The Institute of Chemical Engineering at Bulgarian Academy of Science and KCM S.A. - Plovdiv have designed and developed a new method for SO_2 oxidation. This process is entitle as ALTERNATIVE FLOW CONVERTER. For this method take out a patent in Bulgaria, USA, Belgium and Germany. SO_2 is oxidized to SO_3 by a two-stage catalyst oxidation of SO_2 in a contact apparatus (reactor), operating in non-stationary conditions, achieved by a periodic change of the direction of passing the gas flow trough the reactor and an intermediate absorption of SO_3.

This method gives possibility to realise DC/DA scheme for oxidation in very extended range of SO_2 content - from 1 to 10 vol.%. Also, it guarantees less than 0.5 vol.% at the stack. On the other hand, the investment and operation costs are lower in comparison by these at the classical reactors. The control and regulation of the process are very simplify.

KCM S.A. and ICE-BAS, in close collaboration with UNION MINIERE ENGINEERING (Belgium), can design and implement an <AF> CONVERTER and its associated flow sheet fitting with an existing acid plant or as a part of a new acid plant package.

CONTENT

PLENARY LECTURES

ORAL PRESENTATIONS

Section 1. Dynamic Processes on Catalyst Surface

Section 2. Dynamics of Chemical Reactors

Section 3. Forced Unsteady-State Operation

Section 4. Reactors with Flow Reversal

Section 5. TAP (Temporal Analysis of Products) Reactor Studies

Section 6. Dynamic Operation of Three Phase Reactors

Section 7. Nonlinear Phenopmena in Heterogeneous Catalytic Systems

Section 8. Dynamics of Automotive Converters

POSTER SESSION

PROGRAM

THE THIRD INTERNATIONAL CONFERENCE ON UNSTEADY-STATE PROCESSES IN CATALYSIS

30 June - 3 July, 1998 **St. Petersburg, Russia**

MONDAY, JUNE 29

15:00 - 21:00 Registration

20:00 - 23:00 Welcome Reception

TUESDAY, JUNE 30

8:00 - 18:00 Registration

9:00 - 9:30 Conference Opening. **Yu. Sh. Matros,** Matros Technologies, USA, **A. S. Noskov**, Boreskov Institute of Catalysis, Russia, **A. G. Corey**, Monsanto Enviro-Chem Systems, USA

9:30 - 10:30 *Dynamic Approaches to Heterogeneous Catalysis*, **B. S. Bal'zhinimaev**, Boreskov Institute of Catalysis, Russia.

10:30 - 11:00 ***Break***

11:00 - 12:00 *Industrial Applications of Unsteady-State* Processes. **G. A. Bunimovich, V. O. Strots, and Yu. Sh. Matros,** Matros Technologies, USA

12:00 - 13:30 ***Lunch***

	Dynamic Processes on Catalyst Surface	**Reactors with Flow Reversal**	**Forced Unsteady-State Operation**
	Chairs: **A. Varma**, University of Notre Dame, USA **G.S. Yablonskii,** Washington University, USA	**Chairs:** **G. F. Froment,** Universiteit Gent, Belgium **A.N. Zagoruiko**, Boreskov Institute of Catalysis, Russia.	**Chairs:** **J. J. Lerou,** DuPont, USA, **V. I. Bykov,** Krasnoyarsk State University, Russia
13:30 - 15:30	*The Dynamics of Surface Processes Under Non-Steady State Conditions,* **A. T. Bell,** University of California - Berkeley, USA **(Keynote lecture).** *Monte-Carlo Methods for Simulating Catalytic Reactions on Oxides. Example of the Oxidative Dehydrogenation of Propane over VMgO*	*Ammonia Off-Gas Purification by Reverse-Process,* **L. N. Bobrova, A. S. Noskov,** and **E. S. Borisova,** Boreskov Institute of Catalysis, Russia. *Catalysts for VOC Control under Unsteady-State Operation,* **V.A. Chumachenko, G.G. Isaeva, T.V. Mulina,** and	*Effects of Diffusion on Periodic Operation Performance of NO-CO Reaction,* **T. Aida, R. Kobayashi, D.Na-Ranong,** and **H. Niiyama,** Tokyo Institute of Technology, Japan. *Cyclic Operation of the Oxidative Dehydrogenation of Propane,* **D. C. Creaser,**

catalysts., **Y. Boudeville, M. Kolb, A. Pantazidis, C. Mirodatos,** Institut de Recherches sur la Catalyse, France, and **V. Elokhin,** Boreskov Institute of Catalysis, Russia.

Dynamic Behaviour of Mixed V-Sb Oxide Catalysts in Oxidative Dehydrogenation of Ethane, **V. Yu. Bychkov, Z. T. Fattakhova, M. Yu. Sinev, Yu. P. Tulenin,** Semenov Institute of Chemical Physics, Russia, and **V. P. Vislovskii,** Institute of Inorganic and Physical Chemistry, Azerbaijan

Unsteady State Studies of Oxidation and Hydrogenation Processes, **S. L. Kiperman, N. A. Gaidai, N. V. Nekrasov, M. A. Batavina,** and **Sh. E. Duisenbaev,** N. D. Zelinsky Institute of Organic Chemistry of RAS, Russia.

M.G.Makarenko, Katalizator Company, Russia.

Effect of the Intraparticle Mass Transport Limitations on the Temperature Profiles and Catalytic Performance of the Reverse - Flow Reactor for Partial Oxidation of Methane to Synthesis Gas, **K. Gosiewski,** Institute of Inorganic Chemistry, Poland, **U. Bartmann,** Ruhr-Universitaet Bochum, Germany, **M. MoszczyFlski,** Institute of Inorganic Chemistry, Poland, and **L. Mleczko,** Ruhr-Universitaet Bochum, Germany.

Investigation of Unsteady-Sate Methanol Synthesis by a Fixed-bed Reactor Operated in a Flow Reversal Mode, **Guo Yaoxing, Chen Xiaochun,** and **Li Chengyue,** Beijing University of Chemical Technology, P. R. China.

University of Waterloo, Canada, **B. Andersson,** Chalmers University of Technology, Sweden, **R.R. Hudgins,** and **P.L. Silveston,** University of Waterloo, Canada.

Reactor Performance Enhancement under Periodic Operation for the Ethanol Dehydration over Gamma-Alumina, a Reaction with a Stop-Effect, **S. Golay, R. Doepper,** and **Albert K. E. Renken,** EPLF, Switzerland.

Selective Hydrogenation of Ethyne in a Pressure Swing Reactor, **A. J. Kodde** and **A. Bliek,** University of Amsterdam, The Netherlands.

15:30 - 16:00 ***Break***

16:00 - 17:30 *Oxidative Dehydrogenation of Propane on V_2O_5/TiO_2 Catalysts under Transient Conditions,* **F. Genser** and **A. Pietrzyk,** Ecole Nationale Superieure de Chimie de Lille, France.

Unsteady- State Processes in Aerosol Catalyst, **M. Glikin, D. Kutakova,** and **E. Prin,** State Design and Research Institute for Chemical Engineering Khimtekhnologiya, Ukraine.

Role of Adsorption Heats and Entropies of Organic Compounds on Efficiency of Adsorption-Catalytic Method for Gas Purification, **Z. R. Ismagilov, S. A. Yashnik,** and **M. A. Kerzhentsev,** Boreskov Institute of Catalysis, Russia.

Regenerative Catalytic Oxidation in Environmental Protection: an Example of the Application, **J. Haber, T. Machej,** Institute of Catalysis and Surface Chemistry, Poland.

Dynamic Features of a Reverse-Flow Reactor, **J. Khinast** and **Dan Luss,** University of Houston, USA

The Reversed Flow Operation of a Cross-Flow Solid Oxide Fuel Cell Monolith, **S. G. Neophytides,** University of Patras, Greece.

SO_2 Oxidation Method. Mathematical Modeling Taking into Account Dynamic Properties of the Catalyst, **N. V. Vernikovskaya, A. N. Zagoruiko,** and **A. S. Noskov,** Boreskov Institute of Catalysis, Russia.

High Yields in the Catalytic Partial Oxidation of Natural Gas to Formaldehyde: Catalyst Development, Reactor Configuration and Operation Mode. **A. Parmaliana, F. Arena,** Università di Messina, **F. Frusteri,** and **A. Mezzapica,** Istituto CNR-TAE, Messina, Italy

Dynamics of CO Oxidation over EUROPT - 3: Suppression of Self-Oscillations by Periodic Operation, **F. J. R. van Neer** and **A. Bliek,** University of Amsterdam, The Netherlands.

WEDNESDAY, JULY 1

9:00 - 10:00 *Periodic Flow Reversal in Chemical (Reaction) Engineering*, **G. Eigenberger,** Universität Stuttgart, Germany

10:00 - 10:30 ***Break***

10:30 - 12:30

Dynamic Processes on Catalyst Surface

Chairs:
V. V. Lunin, Lomonosov Moscow State University, Russia, **A. T. Bell**, University of California - Berkeley, USA

Modeling Reduction of Oxide Catalysts with CO, **R. Doepper, H. Randall, F. Kollmer, A. K. E. Renken,** EPFL, Switzerland.

Formation and Dynamic Properties of Mobile Liquid Metal-Carbon Intermediates on the Low-Temperature Catalytic Graphitization of Amorphous Carbon By Fe, Co And Ni, **O. P. Krivoruchko** and **V. I. Zaikovskii,** Boreskov Institute of Catalysis, Russia.

Understanding the Dynamics of Heterogeneous Catalytic Reactions: Exact Computational Technology, **M. Z. Lazman,** Hyprotech, Canada.

The Mobile Structural Defects - Stimulants of the Processes in Highly Organized Catalytic Systems. **V. V. Lunin, N. N. Kuznetsova,** Lomonosov Moscow State University, **A. M. Kaplan**, and **N. I. Chekunaev**, Semenov Institute of Chemical Physics, Russia.

Dynamics of Automotive Converters

Chairs:
E. A. Mirosh, Alternative Fuel Systems, Canada, **Z. R. Ismagilov,** Boreskov Institute of Catalysis, Russia.

Fixed Bed Reactors with Cycling of the Feed, **J. H. B. J. Hoebink, A. J. K. Nievergeld**, and **G. B. Marin,** Eindhoven University of Technology, The Netherlands.

Using Transients in the Catalytic Treatment of Car Exhausts – Improving Light-off Performance and NO_x Reduction under Lean Conditions, **M. Skoglundh, P. Thormaehlen, E. Fridell, F. Hajbolouri, E. Jobson**, and **G. Smedler,** Chalmers University of Technology, Sweden.

Modeling Dynamic Phenomena in 3-Way Catalytic Converters, **G. C. Koltsakis, I. P. Kandylas**, and **A. M. Stamatelos,** Aristotle University Thessaloniki, Greece.

Reverse Flow Converter for Automotive Applications. **G. A. Bunimovich, V. O. Strots, Yu. Sh. Matros,** Matros Technologies, USA, and **E. A. Mirosh**, Alternative Fuel Systems, Canada.

Dynamics of Chemical Reactors

Chairs:
D. Luss, University of Houston, USA
N. N. Chumakova, Boreskov Institute of Catalysis, Russia.

Using Neural Networks to Model Fast Dynamic Systems, **J. L. Fontaine** and **A. Germain,** Université de Liege, Belgium.

The Dynamic Instability and Stabilization of Packed-bed Reactors, **M. Menzinger, V. Z. Yakhnin,** University of Toronto, Canada.

The Effects of Temperature and Concentration Fluctuations on Catalyst Particle Conversion in the Methanol and Ammonia Syntheses, **O. A. Asbjornsen,** SKARPODD Co, and **M. Hillestad,** Statoil Research Center, Norway.

Application of the Markovian Inrensites Approach to Reactors with Complex Chemical Reactions. **B.Gutsche** and **K. Hartmann,** Technical University of Berlin, Germany

12:30 - 14:00 ***Lunch***

	Dynamic Processes on Catalyst Surface	**Reactors with Flow Reversal**
	Chairs: **A. K. E. Renken,** EPLF, Switzerland. **B. S. Bal'zhinimaev**, Boreskov Institute of Catalysis, Novosibirsk, Russia.	**Chairs:** **A. G. Corey**, Monsanto Enviro-Chem, USA **A. S. Noskov**, Boreskov Institute of Catalysis, Russia
14:00 - 15:30	*Measurement and Modeling of the Transient Adsorption, Desorption and Diffusion Processes in Zeolites,* **T. A. Nijhuis, L. J. P. van den Broede, J. M. van de Graaf, M. Makkee, A. D. van Langeveld, F. Kapteijn,** and **J. A. Moulijn,** Delft University of Technology, The Netherlands. *On the Oxygen Promoting Effect in the Reaction of NO Reduction with CH_4 on Co/ZSM-5,* **L. Pinaeva, A. Suknev, E. Sadovskaya, V. Goncharov, V.A. Sadykov, B. Balzhinimaev,** Boreskov Institute of Catalysis, Russia, **Y. Schuurman, T. Décamp,** and **C. Mirodatos,** Institut de Recherches sur la Catalyse, France. *Investigation of the Catalytic Decomposition of NO and N_2O with Transient Techniques,* **K. Rahkamaa** and **T. Salmi,** Abo Akademi University, Finland.	*Application of a Reversed Flow Reactor for the NO Reduction with NH_3 using Transient Kinetic Models,* **W. S. Kijlstra, P. Koopmans, R. Bastiaens,** and **Alfred Bliek,** University of Amsterdam, The Netherlands. *Recent Advancements in Regenerative Catalytic Oxidizer Technology,* **C. R. Roach, Q. V. Jackson,** Monsanto Enviro-Chem Systems, **G. A. Bunimovich, V. O. Strots,** and **Yu. Sh. Matros,** Matros Technologies, USA. *Reduction-Oxidation-Cycling in a Reverse Flow Reactor: Given Constraints,* **H. G. Seiler** and **G. Emig,** Universität Erlangen-Nürnberg, Germany. *Modelling of a Rotating Monolith Forced Unsteady State Reactor for Propane Dehydrogenation,* **E. H. Stitt, S. D. Jackson, D. G. Shipley** and **F. King,** ICI Katalco, UK.
15:30 - 16:00	***Break***	
16:00 - 18:00	*Incubation, Acceleration, Retardation, Reanimation and Deactivation: The Dynamic Kinetic Regimes of Conversion of Methanol and Hydrocarbons on Zeolite H-ZSM-5,* **H. Schulz** and **M. Wei,** Universitaet Karlsruhe, Germany. *Mechanisms of CO_2 Reforming and Partial Oxidation of Methane Investigated with Pulsed Reaction Technique,* **T. Suzuki, N. Ikenaga, N. Matsui, and Kiyoharu Nakagawa,** Kansai University, Japan.	*Parametric Sensitivity in Fixed-bed Catalytic Reactors with Reverse-Flow Operation,* **H. Wu,** Ausimont R&D Center, Italy, **R. Rota,** Politecnico di Milano, Italy, **M. Morbidelli,** ETH Zentrum, Switzerland, and **A. Varma,** University of Notre Dame, USA. *Practical Studies of the Commercial Flow-Reversed SO_2 Converter,* **Wen-De Xiao, Hui Wang, Wei-Kang Yuan,** East China University of Science and Technology, P. R. China.

Deep Oxidation of Methane on Alumina-Manganse Catalyst IC-12-40, **P. G. Tsirulnikov, V. S. Salnikov, V. A. Drosdov,** Omsk Branch of the Boreskov Institute of Catalysis, Russia, **N. A. Chumakova, V. K. Ermolaev,** and **I. V. Malakhova,** Boreskov Institute of Catalysis, Russia.

The Temperature Behaviour of the Oxygen Species on Silver Surface, **E. A. Ivanov, A. I. Boronin, S. V. Koscheev,** and **G.M. Zhidomirov,** Boreskov Institute of Catalysis, Novosibirsk, Russia.

Conference Dinner

Application of Nonstationarity of Catalyst Surface for Development of New Catalytic Technologies, **A. N. Zagoruiko** and **A. S. Noskov,** Boreskov Institute of Catalysis, Russia.

THURSDAY, JULY 2

Nonlinear Phenomena in Heterogeneous Catalytic Systems

Chairs:
N. I. Jaeger, Universität Bremen, Germany.
M. M. Slinko, Institute of Chemical Physics, Russia

9:00 - 10:40

Chemical Waves on Catalytic Surfaces, **R. Imbihl**, Universität Hannover, Germany **(Keynote lecture)**.

The Surface Specificity of the Oscillating Co-Oxidation on Small Pd and Pt Single Crystal Planes Investigated by FEM, **V. V. Gorodetskii,** Boreskov Institute of Catalysis, Russia, **P. D. Gobden**, and **B. E. Nieuwenhuys,** Leiden University, The Netherlands.

Unsteady Behavior of CO Oxidation over Supported Pt Catalysts and Pt Single Crystals: Self-sustained Rate Oscillations in the Torr Pressure Range, **G. Bonilla, T. D. Pletcher, G. Haas,** and **J. A. Lauterbach,** Purdue University, USA

TAP (Temporal Analysis of Products) Reactor Studies.

Chairs:
J. T. Gleaves, Washington University, USA
Y. Schuurman, Institut de Recherches sur la Catalyse, France.

The Third Kinetic Strategy , **J. T. Gleaves, G. S. Yablonsky,** Washington University, USA, and **Y. Schuurman,** Institut de Recherches sur la Catalyse, France **(Keynote lecture)**.

The Role of Brönsted Acid Sites in the DeNOx Reaction - A Mechanistic Study Applying the Temporal Analysis of Products Reactor and FTIR, **T. Gerlach** and **M. Baerns,** Institute for Applied Catalysis Berlin- Adlershof, Germany.

The Conversion of Methanol to Olefins: a Transient Kinetic Study, **O. Dewaele, V. L. Geers, G. F. Froment,** and **G. B. Marin,** Universiteit Gent, Belgium.

Dynamic Operation of Three Phase Reactors

Chairs:
P. L. Silveston, University of Waterloo, Canada, **J. Hanika,** Institute of Chemical Technology, Czech Republic

Overview of the Periodic Operation of Three Phase Reactors, **P. L. Silveston,** University of Waterloo, Canada, and **J. Hanika,** Institute of Chemical Technology, Czech Republic **(Keynote lecture)**.

Safe Operation and Control of Trickle Bed Reactor, **J. Hanika,** Institute of Chemical Technology, Czech Republic.

Thermal Effects in the Periodic Operation of a Trickle Bed Reactor, **J. Ochoa, L. G. Gabarain, J. O. Cechini,** and **P. M. Haure,** INTEMA, Argentina.

10:40 - 11:00 ***Break***

11:00 - 13:00

Chaos, Synchronization And Phase Death Phenomena in Globally Coupled Kinetic Oscillators, **M. M. Slinko,** Institute of Chemical Physics, Russia, **E. S. Kurkina,** Moscow State University, Russia, **M. A. Liauw,** Universitat Erlangen-Nurnberg, Germany, and **N. I. Jaeger,** Universität Bremen, Germany.

The Mechanism of Kinetic Oscillations in the Catalytic N_2O Decomposition over Cu-ZSM-5, **T. Ochs** and **T. Turek**, Universitaet Karlsruhe, Germany.

Spontaneous Isothermal Oscillations In N_2O Decomposition, **P. Ciambelli,** University of Salerno, Italy, **A. Di Benedetto,** University of Napoli, Italy, **R. Pirone, G. Russo,** CNR Napoli, Italy.

Spatiotemporal Patterns in a Homogeneous Fixed-bed Reactor Model, **M. Sheintuch** and **O. Nekhamkina,** Technion, Israel.

Selective and Non-Selective Oxygen Species Determining the Product Selectivity in the Oxidative Conversion of Propane over Vanadium Mixed Oxide Catalysts, **H. W. Zanthoff, S. A. Buchholz,** Ruhr-Universitaet Bochum, Germany, **A. Pantazidis,** Total, France, and **C. Mirodatos,** Institute de Recherches sur la Catalyse - CNRS, France.

CO_2 Reforming in a TAP reactor. Role of the Metal on the Reaction Mechanism: Experiments and Modeling, **Y. Schuurman,** and **C. Mirodatos,** Institut de Recherches sur la Catalyse, France.

Propane Ammoxidation on an Al-Sb-V-W-Oxide Catalyst. A Mechanistic Study Using the TAP-2 Reactor System, **A. Hinz** and **A. Andersson,** Lund University, Sweden.

Kinetic Studies of Propylene Oxidation over VPO Catalyst Using the TAP-2 Reactor System, **T. Brownscombe,** Shell Chemical Co., Houston, USA, **S. Chen** and **J. T. Gleaves,** Washington University, St. Louis, USA.

Induced Pulsing Flow in Trickle Bed Reactors, **H. W. Piepers, J. G. Boelhouwer,** and **A. A. H. Drinkenburg,** Eindhoven University of Technology, The Netherlands.

Enhancing Performance of Three-Phase Packed-Bed Catalytic Reactors by Pulsing-Flow Regime, **R. Wu, M. J. McCready,** and **Arvind Varma,** University of Notre Dame, USA.

Mass Transfer in Taylor-Flow Monoliths: Enhancement of the Mass Transfer Rate as a Result of the Periodic Character, **T. A. Nijhuis, R. K. Edvinsson, P. J. M. Lebens, F. Kapteijn,** and **J. A. Moulijn,** Delft University of Technology, The Netherlands.

13:00 - 14:30 ***Lunch***

14:30 - 16:30 Poster Session

16:30 - 17:00 ***Closing*****, Yu. Sh. Matros,** Matros Technologies, USA

Poster session

PP-1 *Mechanistic Aspects of Kinetic Models for Simulation of Unsteady-State Behaviour of SCR Reaction,* **L. N. Bobrova, E. A. Paukshtis,** and **L. G. Pinaeva.**

PP-2 *Modeling of Methanol Synthesis Reactor under Flow Reversal (I),* **Chen Xiaochun , Rao Guoying, Li Chengyue,** Beijing University of Chemical Technology, P.R. China.

PP-3 *Oxygen Partial Pressure Effects on Transient and Steady State Oxidative Dehydrogenation of Propane,* **D. C. Creaser,** University of Waterloo, Canada, **B. Andersson,** Chalmers University of Technology, Sweden, **R. R. Hudgins**, and **P. L. Silveston,** University of Waterloo, Canada.

PP-4 *Unsteady State Effects in Process of Mechano-Chemical Activation of catalysts,* **P. E. Davydov**, **O. A. Dehtjar**, **N. N. Kuznetsova**, and **V. V. Lunin**, Moscow Lomonosov State University, Russia.

PP-5 *Studies of Kinetics of CFC Formation at Catalyst Deactivation,* **G. G. Kuvshinov, Yu. I. Mogilnykh**, and **D. G. Kuvshinov,** Boreskov Institute of Catalysis, Russia.

PP-6 *Adsorptional-Catalytic Conversion of Dimethylformamide,* **R. I. Kuzmina, V. P. Sevostianov, T. G. Panina, N. N. Mel'nichenko,** Saratov State University, Russia.

PP-7 *Study of Thermocatalytic Decomposition of Polyethylene and Polyvinyl Alcohol under Unsteady State of a Fe-Containing Catalyst,* **N. I. Maksimova and O. P. Krivoruchko,** Boreskov Institute of Catalysis, Russia.

PP-8 *Transient Response Study of the Oxidation Formaldehyde to Formic Acid on V-Ti-O Catalyst: FTIR and Pulses Investigations,* **G. Ya. Popova, T. V. Andrushkevich, Yu. A. Chesalov**, and **E. S. Styanov,** Boreskov Institute of Catalysis, Russia.

PP-9 *The Dynamic Behanior of Hydrocarbon DeNO$_x$ Catalysts in the Presence of Sulfuric Compounds,* **V. A. Sazonov**, **Z. R. Ismagilov**, and **S. R. Khairulin,** Boreskov Institute of Catalysis, Russia.

PP-10 *Mechanism of Nucleation and Growth of Surface Adsorption Structures in the Ethylene Reaction with Oxygen on Silver,* **A. N. Salanov, V. N. Bibin**, and **O. V. Yapryntseva,** Boreskov Institute of Catalysis, Russia.

PP-11 *Intellectual Software System for Treatment of Non-Stationary Kinetic Experimental Data,* **A. N. Tomilov, A. N. Zagoruiko**, and **P. L. Kuznetsov,** Boreskov Institute of Catalysis, Russia.

PP-12 *Algorithm And Software For Complex Catalytic Reactions Mechanisms Reduction,* **A. M. Vaiman,** Institute of Petrochemistry and Catalysis, Russia, **S. I. Spivak,** and **G. K. Galina,** Bashkir State University, Russia.

PP-13 *About New Fundamental Reasons of the Formation of Non-Stationary Conditions in the Industrial Reactors*, **N. K. Valitov,** Bashkirian State University , Russia.

PP-14 *Unsteady-State Phenomena in the Course of Ethylene Glycol Oxidation into Glyoxal on Silver Catalyst,* **O. V. Vodyankina, G. A. Izatulina, L. N. Kurina,** Tomsk State University, Russia.

PP-15 *Dynamics of Activity of Oxide Catalysts in the Process of Nitrogen Oxides Decomposition,* **Xu Yunlong, A. S. Savenkov**, and **M. A. Sibirtseva,** Kharkiv State Polytechnic University, Ukraine.

PP-16 *Catalytic Reactor With Controlled Structure Of Activity,* **V. V. Andreev,** Chuvash State University, Russia.

PP-17 *Simulation Of Ethylene Oxychlorination Process In Catalytic Fluidized Bed,* **A. V. Balaev, M. M. Zalimova, Ju. K. Dmitriev, Ya. M. Abdrashidov,** Institute of Petrochemistry and Catalysis AS RB, AO "Kaustic", Russia.

PP-18 *The Dynamics of Intermediate Processes in Running Reactor with Fixed Bed of Catalyst,* **G. T. Balakaeva**, and **U. K. Zhapbasbaev,** Kazakh State University, Kazakhstan.

PP-19 *Estimation of Quasi-Steady State of the Catalyst in a Fluidized Bed Reactor,* **V. P. Gaevoi** and **S. I. Reshetnikov,** Boreskov Institute of Catalysis, Russia.

PP-20 *Method for Investigation of Dynamic Processes on Catalyst Surface,* **V. V. Kafarov,** Universidad Industrial de Santander, Colombia, and **V. N. Pisarenko,** Russian University of Chemical Technology D. I. Mendeleyev, Russia.

PP-21 *Mathematical Method for Analysis of Dynamics Processes in Catalyst Pellets and Chemical Reactors,* **V. V. Kafarov,** Universidad Industrial de Santander, Colombia, **V. N. Pisarenko,** Russian University of Chemical Technology D. I. Mendeleyev, Russia, and **B. Mayorga,** Universidad Industrial de Santander, Colombia.

PP-22 *Influence of Unsteady-State Catalyst Surface on Process Conversion and Selectivity in Reactor with Ascenting Catalyst Flow,* **V. A. Kernerman, K. A. Mishenina,** and **M. G. Slinko,** State Research Center "Karpov NIPCI", Russia.

PP-23 *Kinetics of Rapid Heterogeneous Reactions on the Small Catalyst Particles on a Support: A Monte Carlo Modelling,* **A. V. Myshlyavtsev,** Tuvinian Interdisciplinary Institute, Russia, **M. D. Myshlyavtseva,** Tuvinian State University, Russia.

PP-24 *Catalytic Reaction Dynamics in the Presence of Capillary Condensation,* **N. M. Ostrovskii** and **N.M. Bukhavtsova,** Omsk Branch of the Boreskov Institute of Catalysis, Russia.

PP-25 *Mathematical Simulation of Ethane Oxidation in Cnemical Reactor,* **I. S. Verzhbitska, P. G. Itskova,** and **A. T. Lukyanov,** Kazakh State University, Kazakhstan.

PP-26 *Mathematical Modeling of Unsteady-State Operation Taking into Account Adsorption and Chemisorption Processes on the Catalyst Pellet,* **N. V. Vernikovskaya, A. N. Zagoruiko, N. A. Chumakova,** and **A. S. Noskov,** Boreskov Institute of Catalysis, Russia.

PP-27 *The Efficiency of Claus Catalyst in Technology of Sulfide Metallurgical Off-Gases Utilization,* **V. N. Galantsev, A. I. Oruzheinikov, O. I. Platonov, A. V. Severilov, S. P. Yatsenko,** Mining-Metallurgical Research Center, Russia.

PP-28 *The Increase of Activity and Selectivity During the Oxidative Coupling of Methane under Non-Steady State Operation,* **E. S. Kurkina,** Moscow State University, Russia, **M. M. Slinko,** Institute of Chemical Physics, Russia, **D.Wolf** and **M.Baerns,** Institut fьr Angewandte Chemie Berlin-Adlershof, Germany.

PP-29 *Modeling of Periodic Production of Filamentous Carbon in a Fluidized Catalyst Bed Reactor*, **G. G. Kuvshinov, Yu. I. Mogilnykh,** and **D. G. Kuvshinov**, Boreskov Institute of Catalysis, Russia.

PP-30 *Comparison of Flow-Reversal and Inner-Recirculation Nonadiabatic Reactors,* **M. Ben-Tullilah** and **M. Sheintuch,** Technion, Israel.

PP-31 *The Unsteady State Catalytic Apparatus "KART",* **Yu. V. Ostrovski, G. M. Zabortsev,** and **A. A. Shpak,** Novosibirsk Design and Research Institute VNIPIET, Russia.

PP-32 *Analysis of a Partial Oxidation Reaction in a Flow Reversal Reactor,* **R. M. Quinta Ferreira, C. S. Santos,** and **A. C. Almeida-Costa,** University of Coimbra, Portugal.

PP-33 *Studies on Heat Removal Unsteady-State SO_2 Converters,* **Hui Wang, Wen-De Xiao**, and **Wei-Kang Yuan**, East China University of Science and Technology, P. R. China.

PP-34 *CO_2 Reforming in a TAP reactor. Model Discrimination and Parameter Estimation,* **V. C. H. Kroll** and **Y. Schuurman,** Institut de Recherches sur la Catalyse, France.

PP-35 *Thin-Zone TAP-Reactor Studies,* **S. O. Shekhtman, G. S. Yablonsky, J. T. Gleaves,** and **S. Chen,** Washington University, USA.

PP-36 *Modeling of Wave Propagations over Pt(100) in CO Oxida-tion under Unsteady-State Conditions,* **N. I. Efremova**, and **V.I. Savchenko,** Boreskov Institute of Catalysis Russia.

PP-37 *Oscillations and Surface Waves in H_2 + O_2 Reaction on Pd and Pt Studied by FEM, FIM, HREELS,* **V. V. Gorodetskii,** Boreskov Institute of Catalysis, Russia, **P. D. Gobden**, and **B. E. Nieuwenhuys,** Leiden University, The Netherlands.

PP-38 *Simple Models of Critical Phenomena in Kinetic Region and Their Parametric Analysis,* **T. P. Pushkareva** and **V. I. Bykov**, Krasnoyarsk State University, Russia.

PP-39 *Travelling Waves in Heterogenous Medium with Chemical Reactions,* **V. N. Snytnikov,** Boreskov Institute of Catalysis, Russia.

PP-40 *Reaction Dynamics and Unstability of CO Oxidation over New Silica Glass Fibre Catalysts,* **I. Yuranov, V. Barelko,** Institute of Chemical Physics, Russia, **L. Kiwi-Minsker, Y. Jiao**, and **A. K.E. Renken,** EPLF, Lausanne, Switzerland.

PP-41 *Experimental Study of Transient Phenomena Induced by Flow Changes in Counter-Current Trickle Beds,* **V. Stanek, B. Jakes, J. Ondracek** and **P. Svoboda,** Institue of Chemical Process Fundamentals, Czech Republic.

PP-42 *Reversing Flow Catalytic Converter System for Dual Fuel Engines Meeting Strict Engine Emission Standards,* **M. D. Checkel, B. Liu,** University of Alberta, Canada, **G. A. Bunimovich, V. O. Strots**, Matros Technologies, USA, and **M. Zhang,** Alternative Fuel Systems, Canada.

PP-43 *Novel Low Temperature Cyclic Process for Production of Concentrated Sufuric Acid from SO_2 - Air Mixtures,* **R. V. Vladea, R. R. Hudgins and P. L. Silveston,** Department of Chemical Engineering, University of Waterloo, Canada.

PP-44 *Catalytic Partial Oxidation of Alkanes at Millisecond Contact Time,* **Lanny D. Schmidt**, University of Minnesota, Minneapolis MN 55455.

PP-45 *A Model Calculation for CO Oxidation under Non Steady State Conditions,* **M. Kolb**, Institut de Recherches sur la Catalyse, France, and **Y. Boudeville**, Ecole Normale Superrieure de Lyon, France.

PP-46 A New Method for SO_3 Production, **G. Grozev**, Institute of Chemical Engineering, BAS, Bulgaria, **D. Dimitrov**, KCM S.A., Bulgaria.

FRIDAY, JULY 3

Symposium and dinner in honor of Professor Yurii Sh. Matros' 60th birthday

matros
seminar

SYMPOSIUM

in Honor of Professor Yurii Sh. Matros' 60th Birthday Presented in conjunction with the 3rd International Conference on Unsteady State Processes in Catalysis (USPC-3)

July 3, 1998, 15:00
The House of Scientists,
St. Petersburg, Russia

ANNOUNCEMENT

Born in Odessa, Ukraine in 1937, Yurii Matros graduated from Odessa Polytechnical Institute in 1959. He received Ph.D. in engineering in 1964 while working at the Novosibirsk Chemical Plant. The same year Dr. Matros started his 30 years long academic career at the Boreskov Institute of Catalysis in Novosibirsk. There he became a Full Doctor of Sciences (1974), Professor, and a head of department of unsteady state catalytic processes. In 1994, after short engagements at the University of Waterloo (Canada) and Washington University (St. Louis, USA), Yurii Matros settled in St. Louis, Missouri and started up his own R&D and engineering company, Matros Technologies.

Professor Yurii Sh. Matros is rightly considered a founder of one of the promising directions in chemical engineering science, forced unsteady state operation of heterogeneous catalytic reactors. His research, presented in hundreds of publications and several fundamental monographs, resulted in the development of a new paradigm in catalytic reactor engineering: reactor with periodical flow reversals (also known as Matros reactor). Notably, Dr. Matros' theoretical findings resulted in extensive commercial applications throughout the world.

The symposium, organized and chaired by Prof. Alexander S. Noskov (Boreskov Institute of Catalysis, Novosibirsk, Russia), will include 10 min. flash talks given by:

Alex Bell, University of California – Berkeley, USA
John Kilkenny, Monsanto Enviro-Chem Systems, Inc., USA
Gilbert Froment, University of Gent, Belgium
Jan Lerou, Du Pont, USA
Dan Luss, University of Houston, USA
Albert Renken, Institute of Chemical Engineering, EPFL-LGRC, Switzerland
Peter Silveston, University of Waterloo, Canada
Arvind Varma, University of Notre Dame, USA
Grigorii Yablonskii, Washington University, USA

Joint talk:
Victor Chumachenko, Katalizator Company, Russia
Gregorii Bunimovich, Matros Technologies, USA
Il'ya Zolotarskii, *Boreskov Institute of Catalysis, Russia

An anniversary dinner will take place at the restaurant 'Podvorie' or at one of the other St. Petersburg's finer establishments. The dinner should be paid for at the USPC-3 registration desk, in cash. Estimated price for dinner is $ 60 (organizers reserve the right to adjust the price).

LIST OF PARTICIPANTS

Takashi Aida
Research Associate
Dept. of Chem. Eng.
Tokyo Institute of Technology
2-12-1 O-okayama
Meguro-ku Tokyo 152
Japan
Tel.: 81-3-5734-2140
Fax: 81-3-5734-2883
taida@chemeng.titech.ac.jp

Boris V. Alekseev
Chuvash State University
Moskovskii Prospekt 15
Cheboksary 428015
Russia
phone: +7 7835 423432, 492539
fax: +7 7835 428090
e-mail: main@chgu.chuvashia.su

Arne Andersson
Dept. of Chemical Engineering II
Lund University, Chemical Center
P.O. Box 124
S-221 00 Lund
Sweden
Tel. +46-46-2228280
Fax : +46-46-149156

Vsevolod V. Andreev
Chuvash State University
Moskovskii Prospekt 15
Cheboksary 428015
Russia
e-mail: main@chgu.chuvashia.su

Manfred Baerns
Institute for Applied Catalysis Berlin- Adlershof
Rudower Chaussee 5
Berlin D-12484
Germany
49 (0) 30 6392 4444
49 (0) 30 6392 4454
baerns@aca.fta-berlin.de

Alexander V. Balaev
Institute of Petrochemistry and Catalysis AS RB
Oktyabrya Prospekt 141
Ufa 450075
Bashkortostan
phone: +7 3472 312236, 422033
fax: +7 3472 312750
e-mail: root@ink.ufanfi.ru

Gulnar K. Balakaeva
Kazakh State University
Almaty
Kazakhstan
phone: +7 3272 672015
e-mail: Pavel.Tepikin@cbank.kz

Bair S. Bal'zhinimaev
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.:+7-383-2-34-47-70
fax: +7-3832-34-30-56
E-mail: iccct@catalysis.nsk.su
balzh@catalysis.nsk.su

Anatolii G. Bazanov
RSC "Applied Chemistry"
pr. Dobrolubova 14,
St. Petersburg, 197198
Russia
Tel.: +7-812-325 66 45
Fax: +7-812-325 66 46

Alex T. Bell
Dept. of Chemical Engineering
University of California – Berkeley
Berkeley CA 94720-1462
USA
bell@cchem.berkeley.edu

Alfred Bliek
Dept of Chem. Eng.,
University of Amsterdam
Nieuwe Achlergracht, 166,
Amsterdam, 1018 WV
The Netherlands
Fax: 31-20-525 5604
bliek@chemeng.chem.uva.nl

Ludmila N. Bobrova
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.:7 (383)-2-34-12-78
fax: 3832 343056
e-mail: root@catalysis.nsk.su

Jacobus Gerrit Boelhouwer
Eindhoven University of Technology
Department of Chemical Engineering
PO Box 513, 5600 MB Eindhoven
The Netherlands
Fax: 31-(0) 40-2446104
tgtcjb2@chem.tue.nl

Anthony Peter Bolton
General Manager
Zeolyst International
D-6 Dukes Court
Woking GU21 5BH,
UK
Tel.: 44-1483 749730
Fax: 44-1483 730312
44-1483 749713

Yves Boudeville
Institut de Recherches sur la Catalyse
CNRS2, avenue Albert Einstein
F-69626 VILLEURBANNE Cedex
France
Tel.: +33 (0)4 72 44 53 06/33 (0)4.72.44.53.50
(Secretary)
Fax : +33 (0)4 72 44 53 90 (Secretary)
E-mail :probel@catalyse.univ-lyon1.fr

Grigori A. Bounimovitch
Matros Technologies, Inc
2080 Concourse Dr.
St. Louis, Missouri 63146
USA
tel.: 314 995 9850
fax: 314 995 6941
E-mail: stronk@ix.netcom.com

Valerii I. Bykov
Institute of Computing Modelling
Krasnoyarsk 660036
Russia
phone: +7 391-2-49-47-24
fax: +7 391-2-43-98-30
e-mail: bykov@cckr.krasnoyarck.su

Li Chengyue
Beijing University of Chemical Technology
College of Chemical Engineering
Beijing 100029
P.R.China 64284781
licy@gate930.buct.edu.cn
nlee@iname.com

Natalia A. Chumakova
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.:+7-3832 34 12 78
fax: +7-3832 343056
E-mail

Victor A. Chumachenko
Katalizator Company
ul. Tikhaya 1
Novosibirsk 630052
Russia
fax:7-383-2-33-22-52
tel.: 7-383-2-32-94-45
e-mail: vic@katcom.nsk.ru

David A. Claridge
Publishing Editor
Elesevier Science Ltd
Landgford Lane
Kidlington
Oxford, OX5 1GB
UK
Tel.: 44 (1865) 843 545
Fax: 44 (1865) 843977
E-mail: d.claridge@elsevier.co.uk

Anthony G. Corey
Monsanto Enviro-Chem Systems, Inc
14522 South Outer 40 Road
Chesterfield, MO 63017
USA
Tel.: 1 (314) 275 5700
Fax: 1 (314) 275 5701
E-mail: enviroch@monsanto.com

Derek C. Creaser
Research Assistant
Chemical Technology Division
Lufea University of Technology
Lulea S - 971 87
Sweden
Tel.:46-920-72155
Fax: 46-920-9599
Derek.creaser@km.luth.se

Olivier Dewaele
University of Ghent
Belgium
Fax: 32 9 264 49 99
Olivier.Dewaele@rug.ac.be

Ivan Apostolov Dgurdgev
«NEOCHIM» SA, Institute for Low
Tonnage Chemical Products
Dimitrovgrad 6400
Bulgaria
fax: 359391 27576

Laurent van Dierendonck
Ryeks University of Groningen
Montjoie Str 6
Munster ge Leen 6151 JD
The Netherlands
Fax: 0031 (0) 46 464 110484 (private)
Tel.: 0031 (0) 46 464 110840

Elenko Georgiev Dimitrov
«NEOCHIM» SA
Institute for Low
Tonnage Chemical Products
Dimitrovgrad 6400
Bulgaria
fax: 359391 27576

Dimitre Spassov Dimitrov
Basic & Detailed Eng.Dept.
KCM-S.A.
Plovdiv 4009, Assenovgradsko shosse,
Bulgaria
Fax: +359 32 62-35-76

Ravindra Dixit
The Dow Chemical Company
2301 N. Brazosport Blvd., B-4011
Freeport, TX 77541-3257
USA
Tel.: 1-409-238-5165
Fax: 1-409-238-0266.
E-mail:ravidixit@dow.com

Ralf Doepper
Institute of Chemical Engineering
EPFL – LGRC
Lausanne CH-1025
Switzerland
Fax: 41-21-693-3190

Dr.-Ing. Gerhart Eigenberger
Stuttgart UniversityBoblinger Straße 72
70199 Stuttgart
Stuttgart
Germany
Tel.: (0711) 641-2230
Fax: (0711) 641-2242
eigenberger@icvt.uni-stuttgart.de

Vladimir I. Elokhin
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
fax: +7-383-2- 34-30-56
E-mail: root@catalysis.nsk.su

Cemal Ercan
Technology Development Center
ABB LUMMUS GLOBAL, INC.
1515 Broad Street
Bloomfield, New Jersey, 07003-3096
USA
tel.: 973-893 2193
Fax: 973-893-2745
E-mail: cemal.ercan@uslum.mail.abb.com

Rosa M. Quinta Ferreira
Departamento de Engenharia Quimica
Faculdade de Ciencias e Tecnologia
Universidade de Coimbra
Largo Marques de Pombal
3000 Coimbra
Portugal
Tel.: +351-(0)39-828392
Fax: +351-(0)39-841138
E-mail: eqlrqf@eq.uc.pt

Jean-Luc Fontaine
Laboratoire de Chimie Industrielle
Universite de Liege
C10R, Institut de Chimie B 6
Sart Tilman
Liege B-4000
Belgium
Tel.: 32-43-66-35-86
Fax: 32-43-66-35-45
jl.fontaine@ulg.ac.be

Gilbert Froment
University of Gent, Belgium
Ruitersdreef 4
B-9831 Deurle
Belgium
tel.:32-9-282-4434
Fax: (+32) 9 264 49 99/281 2722
E-mail:gilbert.froment@skynet.be

Marek Edmund Galantowicz
Zaklady Azotowe «Kedzierzyn»
Spolka Akcyjna
Centr. Lab. Bad.
47-220 Kedzierzyn-
skr.pocztowa 163
Poland
phone: +4877812476, +4877819243
fax: +4877812076

Galiya K. Galina
Bashkir State University
Ufa
Russia
phone: +7 3472 236774
fax: +7 3472 236680
e-mail: root@vayman.ufanet.ru

Markus Galle
University of Dortmund
Emil-Figge-Str. 66
D-44221 Dortmund
Germany
Phone: 0049 231 755 5332
FAX: 0049 231 755 2698
e-mail: galle@chemietechnik.uni-dortmund.de

Dr. Douglas Galloway
UOP
50 E. Algonquin Rd.
Des Plaines, IL 60017,
USA
Fax: 1 (847) 391-3582
DBGallow@UOP.COM

Abdul Rahman Garayhi
Technische Universitat Hamburg – Harburg
Arbeitsbereich Chemische Reaktionstechnik
Eissendorfer Strasse 38
D-21071 Hamburg
Germany
tel:+4940-77-18-24-91
fax:+4940-77-18-21-45
e-mail: a.garayhi@tu-harburg.de

Florence Genser
Universitй de Technologie de Compiиgne
Ecole Doctorale
B.P. 529, 60 205 COMPIEGNE CEDEX
France
Tel.: 33-3-20 335437
Fax: 33-3-20335499
E-mail: merrien@ec.lille.fr

Till Gerlach
Institute for Applied Catalysis Berlin- Adlershof
Rudower Chaussee 5
Berlin D-12484
Germany
Tel: +49/30/63924414
Fax: +49/30/63924454
e-mail: gerlach@aca-berlin.de

John Gleaves
Washington University
USA

Serge Golay
Institute of Chemical Engineering
EPFL – LGRC
Lausanne CH-1025
Switzerland
Fax: 41-21-693-3190

Andrei Ya. Gorbachevskii
Lomonosov Moscow State University
Vorobievy Gory
Moscow 119899
Russia
tel.:+7- 095-939-32-07
fax: +7-095-932-88-46
gorba@radio.chem.msu.su

Vladimir V. Gorodetskii
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: 7-383-2-39-73-15
fax: 3832 343056
e-mail: gorodesk@catalysis.nsk.su

Krzysztof Gosiewski
Ass. Professor
Institute of Inorganic Chemistry
ul. Sowinskiego 11
Gliwice 44-101
Poland
Tel.: 4832-313051, ext. 254
Fax: 4832-31-75-23
gosiew@kuria.gliwice.pl

Georgi Grozdanov Grozev
ICE - BAS, Sofia
Bulgaria
Fax: +359 (2) 70 32 73
E-mail: CHIMREAC@BGEARN.ACAD.BG

Irek M. Gubaidullin
Institute of Petrochemistry and Catalysis AS RB
Oktyabrya Prospekt 141
Ufa 450075
Bashkortostan
phone: +7 3472 505500 (869)
fax: +7 3472 312750

Jerzy Haber
Professor, Director of the Institute
Institute of Catalysis and Surface Chemistry,
Polish Academy of Sciences
ul. Niezapominajek
Krakow PL – 30239
Poland
Tel.:48 12 – 4252814
Fax: 48 12-425 1923
E-mail: nchaber@cyf-kr.edu.pl

Zlatka Kostadinova Hadjiivanova
«NEOCHIM» SA, Institute for Low
Tonnage Chemical Products
Dimitrovgrad 6400
Bulgaria
fax: 359391 27576

Joseph Haggin
Industrial Catalysis News (ICN)
P.O. Box 845
Arlington Heights, Illinois 60006-0845
USA
Tel.: 1-847-255-3849
Fax:1-847-577-4526
E-mail: joechem@home.interaccess.com

Jiri Hanika
Czech Republic
E-mail: jiri.hanika@vscht.cz

Andreas Hinz
Dept. of Chemical Engineering II
Lund University, Chemical Center
P.O. Box 124
S-221 00 Lund
Sweden
Tel. +46-46-2228280
Fax #: +46-46-149156

Jozef H. B. J. Hoebink
Senior Lecturer
Lab voor Chemische Technologie
Eindhoven University of Technology
P.O.Box 513
5600 MB Eindhoven
The Netherlands
Tel.:31-40-2472850
Fax: 31-40-2446653
tgtcjh2@chem.tue.nl

Ronald Imbihl
Institut fuer Physikalische Chemie
und Elektrochemie
Universitaet Hannover
Callinstr. 3-3a
D-30167 Hannover
Germany
Tel. 0511-762-2349
Fax. 0511-762-4009
ronald.imbihl@mbox.pci.uni-hannover.de

Galina G. Isaeva
Katalizator Company
ul. Tikhaya 1
Novosibirsk 630052
Russia
fax:7-383-2-33-22-52
tel.: 7-383-2-32-92-49
e-mail: vic@katcom.nsk.ru

Takeshi Ishikawa
Mitsubishi Chemical Corporation
5-2, Marunouchi 2-Chome,
Chiyoda-ku, Tokyo 100-0005
Japan
tel.: 81-3-3283-6191
Fax: 81-3-3283-5809
E-mail: 3206014@cc.m-kagaku.co.jp

Zinfer R. Ismagilov
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: +7-383-2-34-12-19, 34-26-70
fax: +7-383-2-34-30-56
E-mail: zri@catalysis.nsk.su

Polina G. Itskova
Kazakh State University
Almaty
Kazakhstan
phone: +7- 327-2- 67-48-71
e-mail: itskov@laskoz.almaty.kz,
itskov@laskoz.almaty.kz,
itskov@laskoz.almaty.kz

Eugenii A. Ivanov
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.:+7-383-2-39-73-08
fax: +7-3832 343056
E-mail:root@catalysis.nsk.su

Quenton Victor Jackson
Monsanto Enviro-Chem Systems, Inc
14522 South Outer 40 Road
Chesterfield, MO 63017
USA
Tel.: 1 (314) 275 5700
Fax: 1 (314) 275 5701
E-mail: enviroch@monsanto.com

Nils I. Jaeger
Germany
Institute of Physical Chemistry of Bremen
University
Universitat Bremen FB-2, PF 330440, D-28334
Germany
Tel: (0421) 218 2500
Fax: (0421) 218 4918
E-mail: ise@alf.zfn.uni-bremen.de

Vyacheslav V. Kafarov
Universidad Industrial de Santander,
AA678, Bucaramanga
Colombia
Tel.: 57 76344746
Fax: 57 76344746

Vladimir A. Kernerman
State Research Center «Karpov NIPCI»
Borontsovo Pole 10
Moscow 103064
Russia
tel.: +7-095-917-78-70
fax: +7-095-975-24-50

Sergei I. Kharkevich
Moscow Office SY-LAB
Krymskii Val 4-28
Moscow 117049
Russia
Tel. +7-095-236-77-51, 238-27-35
Fax: +7-095-238-29-35
E-mail:oleg@oldmi.msk.ru

Sergey P. Kil'dyashev
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: +7-383-2-34-46-85
fax: +7-383-2-34-30-56
E-mail: spk@catalysis.nsk.su

John Early Kilkenny
Monsanto Enviro-Chem
1387 Thornwick (home)
St. Louis, Missouri 63011
USA
Fax: (314) 275-5701
PATRICIA.A.WALTERS@monsanto.com

Samuil L. Kiperman
N.D.Zelinsky Institute of Organic Chemistry
Leninskii Prospekt 47
117913 Moscow B-334
Russia
E-mail: kip@carc.ioc.ac.ru

Lioubov Kiwi-Minsker
Institute of Chemical Engineering
EPFL – LGRC
Lausanne CH-1025
Switzerland
tel.: 41-21-693-3182
Fax: 41-21-693-3190
41-21-693-6161
E-mail: kiwi@igcsun3.epfl.ch

Adriaan J. Kodde
Dept of Chem. Eng.
University of Amsterdam
Nieuwe Achlergracht, 166
Amsterdam
1018 WV
The Netherlands
Tel.: 31-20-525 7019
Fax: 31-20-525 5604
akodde@chemeng.chem.uva.nl

Vasilii V. Kolesnik
Institute of Gas Ukraine NAS
Kiev
Ukraine
phone: +7-044-4-46-21-81
e-mail: kolesnik@gas.freenet.kiev.ua

Nikolay Ivanov Konarev
Plovdiv 4009
Assenovgradsko shosse,
KCM-S.A.
Basic & Detailed Eng. Dept.
Bulgaria
Fax: +359 32 62-35-76

Igor' V. Kozhevnikov
Chuvash State University
Moskovskii Prospekt 15
Cheboksary 428015
Russia
phone: +7-783-5-42-34-32, 21-45-74
fax: +7-783-5-42-80-90
e-mail: main@chgu.chuvashia.su

Oleg P. Krivoruchko
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: +7-383-2-34-12-22
fax: +7-383-2-34-30-56
E-mail:opkriv@catalysis.nsk.su

Larisa N. Kurina
Tomsk State University
pr. Lenina 36
Tomsk 634050
Russia
phone: +7-382-2-42-39-44
fax: +7-382-2-41-55-79

Elena S. Kurkina
Lomonosov Moscow State University
Vorobievy Gory
Moscow 119899
Russia
tel. : +7-095-939-18-89
fax: +7-095-939-25-96
E-mail: kurkina@cs.msu.su

Raisa I. Kuzmina
Saratov State University
ul. Astrakhanskaya 83/1
410026 Saratov
Russia

Natalya N. Kuznetsova
Lomonosov Moscow State University
Vorobievy Gory
Moscow 119899
Russia
tel.: +7-095-939-33-22
fax: +7-095-939-00-67

Alexander A. Lamberov
Kazan State Technological University
Kazan
Russia
тел.: +7-843-2-36-58-92
факс: +7-843-2-36-58-92
e-mail: kataliz@cnit.ksu.rus.ru

Jochen Lauterbach
Germany
School of Chemical Engineering
Purdue University
West Lafayette, IN 47907-1283
USA
phone: (765) 494-4076
fax: (765) 494-0805
jochen@ecn.purdue.edu
http://che.www.ecn.purdue.edu/CHE/people/fac.staff/jochen/

Jan J. Lerou
DuPont Nylon Intermediates R&D
Sabine River Laboratory
Orange, TX 77360-1089
Wilmington, Delaware
USA
tel.: 409-886-6244/409 886 9423
Fax: 409-886-6196

Marcel Liauw
Lehrstuhl fur Technische Chemie
Universitat Erlangen-Nurnberg
Egerlandstr. 3
Erlangen D-91058
Germany
Phone: 0049-9131-857423
Fax: 0049-9131-857421
E-mail: liauw@rzmail.uni-erlangen.de

Vladimir A. Likholobov
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.:+7-383-2-34-24-53
fax: +7-3832 34-30-56
E-mail:LIKHVL@catalysis.nsk.su

Aleksei T. Lukyanov
Kazakh State University
Almaty
Kazakhstan
phone: +7-327-2-67-48-71, 63-39-59
fax: +7-327-2 -69-61-96

Valerii V. Lunin
Lomonosov Moscow State University
Vorobievy Gory
Moscow 119899
Russia
tel.:+7-095-939-47-75
fax:+7-095-939-00-67
e-mail: knn@cge.chem.msu.su

Dan Luss
Dept. of Chemical Engineering
University of Houston
Houston TX 77204-4792
USA
Tel.: 713-743-4305
Fax: 713-743-4323
dluss@uh.edu

Tadeusz Machej
Institute of Catalysis and Surface Chemistry,
Polish Academy of Sciences
ul. Niezapominajek
Krakow PL – 30239
Poland
Tel.:48 12 – 4252814
Fax: 48 12-425 1923
E-mail: ncmachej@cyt-kr.edu.pl

Mikhail G. Makarenko
Katalizator Company
ul. Tikhaya 1
Novosibirsk 630052
Russia
tel.:+7-383-2-32-92-49
fax:+7-383-2-33-22-55
e-mail: vic@katcom.nsk.ru

Nadezhda I. Maksimova
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: +7-383-2-34-37-62
fax: +7-383-2-34-30-56
e-mail: maksin@catalysis.nsk.su

Guy B. Marin
University of GENT
Laboratorium voor Petrochemische Technick
Gent B – 9000
Belgium
Tel.: 32-9-264 4517
Fax: 32-9-264 4999
guy.marin@rug.ac.be

Yurii Sh. Matros
Matros Technologies
2080 Concourse Dr.
St. Louis, Missouri 63146
USA
Tel.: 1 314 995 69 21
Fax: 1 314 995 6941
E-mail: you@aol.com

Michael Menzinger
Department of Chemistry
University of Toronto
Toronto Ontario M5S 3H6
Canada
Tel.: 416-978 6158
Fax: (416)-978 6158
menzinger@chemistry.utoronto.ca

Vladimir Mikhailov
RSC "Applied Chemistry"
pr. Dobrolubova 14,
St. Petersburg, 197198
Russia
Tel.: +7-812-238 98 02
Fax: +7-812-325 66 47
E-mail: giph@rscac.spb.su
rscac@mail.w+.net

Claude Mirodatos
Institut de Recherches sur la Catalyse
CNRS2, avenue Albert Einstein
F-69626 VILLEURBANNE Cedex
France
Tel.: +33 (0)4 72 44 53 06/33 (0)4.72.44.53.50
(Secretary)
Fax : +33 (0)4 72 44 53 90 (Secretary)
E-mail : probel@catalyse.univ-lyon1.fr (Secretary)

Edward A. Mirosh
Alternative Fuel Systems Inc.
#420, 1207 - 11th Avenue S.W.
Calgary, Alberta,
Canada T3C 0M5
tel.: (403) 262-1833
Fax: (403) 237-7441

Massimo Morbidelli
Chemical Engineering Department/LTC
ETH
ETH Zentrum, Cab C40,
Universitatstrasse 6,
Zurich CH-8092
Switzerland
phone: 004116323034
fax: 004116321082
e-mail: morbidelli@tech.chem.ethz.ch

Alexander B. Myshlyavtsev
Tuvinian Interdisciplinary Institute
ul. Internatsional'naya 117 a
Kyzyl 667007
Russia
phone: +7-394-22 -35835, 33828
e-mail: root@tko.tuva.su

Katsu Nakabayashi
Hitachi Zosen Europe Ltd.
Sixth Floor
38 Finsbury Square
London EC2A 1PX
Tel.:(0171)628 3891
Fax: (0171)638 1309

Drs. Frank J. R. van Neer
Dept. of Chemical Engineering
University of Amsterdam
Nieuwe Achtergracht 166
Amsterdam 1018 WV
The Netherlands
Tel.: 31-20-525 696304 ?
Fax: 31-20-525 5604
neer@chemeng.chem.uva.nl

Stylanios G. Neophytides
Institute of Chemical Engineering and
High Temperature Chemical Processes
University of Patras
P.O.Box 1414
Patras GR-26500
Greece
Tel.: 30-61-997-269
Fax: 30-61-965-223
E-mail: neoph@iceht.forth.gr

Olga Nekhamkina
Dep. of Chem. Eng. Technion
Technion City, Haifa
Haifa 32000
Israel
phone: 97248292829
fax: 97248230476
e-mail:olgan@cestar.technion.ac.il

Ben E. Nieuwenhuys
Leiden Institute of Chemistry,
Gorlaeus Laboratories
Leiden University
Einsteinweg 55 / P.O. Box 9502 2300RA,
Leiden
The Netherlands
Phone: +31 71 5274251
Fax: +31 71 5274537
nieuwe_B@chem.leidenuniv.nl
b.nieuwe@chem.leidenuniv.nl

Dr. ir. Xander Nijhuis
Delft University of Technology
Chemical Process Technology Department
Section Industrial Catalysis
Julianalaan 136, 2628 BL Delft,
The Netherlands
Tel. + 31 15 2786458
Fax: +31 15 2784452
E-mail: t.a.nijhuis@stm.tudelft.nl

Aleksandr S. Noskov
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: +7-383-2-34-18-78
fax: +7-383-2 -34-30-56
E-mail: noskov@catalysis.nsk.su,
alex@reverse.nsk.su

Vladimir N. Orlik
Institute of Gas
Ukraine NAS
Kiev
Ukraine
tel.: 38 044 446-03-24
fax: 38 044 446-88-30
E-mail: orlyk@gas.freenet.kiev.ua

Farid Ousmanov
Engier-Bunte-Institute
University Karlsruhe
Kaiserstr.12, 76128 Karlsruhe
Germany
Tel.: +49 721 608 4238/2961
Fax: +49 721 693019

Alexander I. Oruzheinikov
Omsk Branch of the Boreskov
Institute of Catalysis
ul. Neftezavodskaya 54
Omsk 644040
Russia

Nikolai M. Ostrovskii
Omsk Branch of the Boreskov
Institute of Catalysis
ul. Neftezavodskaya 54
Omsk 644040
Russia
phone: +7-381-2-66-44-74
fax: +7-381-2-64-61-56
e-mail: ostr@incat.omsk.net.ru

Yurii V. Ostrovskii
Novosibirsk Design and Research
Institute VNIPIET
ul. B.Khmel'nitskogo 2
Novosibirsk 630075
Russia
phone: +7-383-2-76-96-35
e-mail: ost@pri.sib.ru

Anatolii N. Parfenov
SIF «OXIDE»
Ugrehskaja str., 2
Moscow 109432
Russia
phone: +7-095-279-8258
fax: +7-095-742-88-51

Victor N. Parfenov
SIF «OXIDE»
Ugrehskaja str., 2
Moscow 109432
Russia
phone: +7-095-279-8258
fax: +7-095-742-88-51
Russia

Adolfo Parmaliana
University of Messina,
Dept. of Industrial Chemistry, Via
Salita Sperone 31,
98166-Sant'Agata di Messina, Messina
Italy
E-mail: parmaliana@itae.me.cnr.it

Vadim P. Patskov
Coal Energy Tecknical Center of Ukraine
NAS and Ministry of Energetic of Ukraine
Kiev
Ukraine
phone:38 044 4166915, 4527121
fax: 38 044 4162510
e-mail: root@dutec.kiev.ua

Huub W. Piepers
Eindhoven University of Technology
Department of Chemical Engineering
PO Box 513, 5600 MB Eindhoven
The Netherlands
Fax: 31-(0) 40-2446104
tgtcjb2@chem.tue.nl

Stanislaw Pietrzyk
Ecole Nationale Supérieure de Chimie de Lille
Laboratoire de Génie Chimique et d'Automatique
B.P. 108,
59 652 VILLENEUVE D'ASCQ CEDEX
France
Tel.: 33-3-20335443
Fax: 33-3-20335499

Larisa G. Pinaeva
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: +7-383-2-34-36-79
fax: +7-383-2-34-30-56
E-mail: root@catalysis.nsk.su

Raffaele Pirone
Istituto di Ricerche sulla Combustione (CNR)
Italy
tel.: 39 (81) 7682220/7682233
Fax: 39 (81) 5936936/2391800
E-mail: pirone@irc.irc.na.cnr.it

Irina V. Pivovarova
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: +7-383-2-34-18-78
fax: +7-383-2 -34-30-56
E-mail: noskov@catalysis.nsk.su,
alex@reverse.nsk.su

Svetlana A. Pokrovskaya
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.:+7-383-2-34-12-78
fax: +7-3832 343056
E-mail:root@catalysis.nsk.su

Elena M. Prin
State Design and Research Institute for
Chemical Engineering «Khimtekhnologiya»
Prospekt Dzerzhinskogo 1
Severodonetsk 349940
Lugansk Region
Ukraine
E-mail: prin@ixt.sed.lg.ua

Tatyana P. Pushkareva
Krasnoyarsk State Technical University
ul. Kirenskogo 26
Krasnoyarsk 660074
Russia
phone: +7-391-2-49-57-80

Yurii I. Pyatnitskii
Institute of Physical Chemistry
Ukraine NAS
Prospekt Nauki 31
Kiev 252039
Ukraine
phone: 380-44-2656645,
fax: 380-44-2656216
e-mail: yupyat@ipcp.kiev.ua

Katariina Rahkamaa
Ebo Akademi University
Laboratory of Industrial Chemistry
Piispankatu 8, 20500 Turku
Finland
tel.: 358-2-215 4559
Fax: 358-2-215 4479
E-mail: Jan.J.Lerou@usa.dupont.com

Victor Redekop
Alternative Fuel Systems Inc.
#420, 1207 - 11th Avenue S.W.
Calgary, Alberta
Canada
T3C 0M5
tel.: (403) 262-1833
Fax: (403) 237-7441

Albert Renken
Institute of Chemical Engineering
EPFL – LGRC
Lausanne CH-1025
Switzerland
Fax: 41-21-693-3190

Albert Renouprez
Institut de Recherches sur la Catalyse
CNRS2, avenue Albert Einstein
F-69626 VILLEURBANNE Cedex
France
Tel.: +33 (0)4 72 44 53 06/33 (0)4.72.44.53.50 (Secretary)
Fax : +33 (0)4 72 44 53 90 (Secretary)
E-mail : probel@catalyse.univ-lyon1.fr

Sergei I. Reshetnikov
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: +7-383-2-35-76-72
fax: +7-383-2-34-30-56
e-mail: resh@catalysis.nsk.su

Tatiana V. Reshetnyak
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: 7-383-2-39-73-05
fax: 3832 343766
e-mail: root@catalysis.nsk.su

Christopher R. Roach
Monsanto Enviro-Chem Systems, Inc
14522 South Outer 40 Road
Chesterfield, MO 63017
USA
Tel.: 1 (314) 275 5700
Fax: 1 (314) 275 5701
E-mail: enviroch@monsanto.com

Raziya G. Romanova
Kazan State Technological University
Kazan
Russia
тел.: +7-843-2-36-58-92
факс: +7-843-2-36-58-92
e-mail: kataliz@cnit.ksu.rus.ru

Gennaro Russo
Istituto di Ricerche sulla Combustione (CNR)
Italy

Giovanna Ruoppolo
University of Naples
Italy

Dmitrii A. Salimonenko
Ufa State Aviation Technical University
ul. Mingazhieva 19/a
Ufa 450000
Russia
phone: +7-347-2 23-52-44, 22-24-69
fax: +7-347-2 23-66-80
e-mail: root@vayman.ufanet.ru

Tapio Salmi
Ebo Akademi University
Laboratory of Industrial Chemistry
Piispankatu 8, 20500 Turku,
Finland
tel.: 358-2-215 4559
Fax: 358-2-215 4479

Valerii I. Savchenko
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.:+7-383-2-34-42-55
fax: +7-383-2-34-30-56
e-mail: savch@catalysis.nsk.su

Anatolii S. Savenkov
Kharkiv State Polytechnic University
ul. Frunze 21
Kharkiv 310002
Ukraine
tel.: 380-572-400256
E-mail: root@polyt.kharkov.ua

Peter Carl Sehestedt Schoubye
Haldor Topsoe A/S
Nymollevej 55
DK-2800 Lungbu
Denmark
tel.: 45-45-27-20-00
Fax: 45-45-27-29-99

Hans Schulz
Engier-Bunte-Institute
University Karlsruhe
Kaiserstr.12, 76128 Karlsruhe
Germany
Tel.: +49 721 608 4238/2961
Fax: +49 721 693019

Yves Schuurman
Institut de Recherches sur la Catalyse
CNRS2, avenue Albert Einstein
F-69626 VILLEURBANNE Cedex
France
Tel.: +33 (0)4 72 44 53 06/33 (0)4.72.44.53.50
(Secretary)
Fax : +33 (0)4 72 44 53 90 (Secretary)
E-mail : probel@catalyse.univ-lyon1.fr (Secretary)

Harald G. Seiler
Research Assistent
Lehrstuhl für Techn. Chemie I
UNIVERSITÄT ERLANGEN-NURNBERG
Egerlandstr. 3
Erlangen D-91058
Germany
Tel.: 49-9131-85-74-20
Fax: 49-9131-85-74-21
seiler@rzmail.uni-erlangen.de

Peter L. Silveston
Dept. of Chemical Engineering
University of Waterloo
Waterloo Ontario N2L 3G1
Canada
Tel.:519-885-1211
Fax: 519-746-4979
E-mail: silvesto@cape.uwaterloo.ca

Mikhail Yu. Sinev
Institute of Chemical Physics RAS
ul. Kosygina 4
Moscow 117334
Russia
phone: +7-095-9397547
fax: +7-095-9382156
e-mail: kinet@glas.apc.com
sinev@center.chph.ras.ru

Jean-Carlo Sioli
Ammonia Casale S.A.
Switzerland
tel.: 091 9674182
fax: 091 9674447
E-mail: l.santoro@casale.ch

Magnus Skoglundh
Competence Centre for Catalysis
Chalmers University of Technology
Goeteborg 412 96
Sweden
Tel.: 46-31-772 29 58
Fax: 46-31-772 29 67
skoglund@tk.chalmers.se

Valerii N. Snytnikov
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: +7-383-2-34-44-91
fax: +7-383-2-34-30-56
e-mail: root@catalysis.nsk.su

Liliane Spector
University of Montreal
Canada
Fax: (416)-978 6158

Semen I. Spivak
Bashkir State University
Ufa
Russia
phone: +7-347-2-23-61-62
fax: +7-347-2-23-66-80

Alexei A. Spiridonov
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: +7-383-2-39-73-09
fax: +7-3832 34-30-56
e-mail: pub@catalysis.nsk.su

Marina M. Slin'ko
Karpov Institute of Physical Chemistry RAS
ul. Kosygina 4,
Moscow 117334
Russia
phone: +7-095-939-75-55
e-mail: marina@slinko.msk.ru

Tatiana G. Starostina
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: +7-383-2-34-12-78
fax: +7-383-2-34-18-78
e-mail: tatyana@reverse.nsk.su

Ludmila Ya. Startseva
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: +7-383-2-34-12-97
fax: +7-383-2-34-30-56
e-mail: star@catalysis.nsk.su

Edmund Hugh Stitt
ICI Katalco,
PO Box 1,Billingham,
Cleveland
UK
tel.: 44 1642 522704
Fax: 44 1642 522606
E-mail: hugh_stitt@ici.com

Vadim O. Strots
Matros Technologies, Inc
2080 Concourse De
St. Louis, Missouri 63146
USA
tel.: 314 995 9850
fax: 314 995 6941
E-mail: stronk@ix.netcom.com

Aleksei P. Suknev
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: +7-383-2-34-36-79
fax: +7-383-2-34-30-56
e-mail: root@catalysis.nsk.su

Toshimitsu Suzuki
Dept. of Chemical Engineering,
Kansai University, Osaka, Japan
3-3-35 Yamate
Suita Osaka 564
Japan
Tel.: 81-63-680865
Fax: 81-63-888869
E-mail: tsuzuki@ipcku.kansai-u.ac.jp

Max Thorhauge
Haldor Topsoe A/S
Nymollevej 55
DK-2800 Lungbu
Denmark
tel.: 45-45-27-20-00
Fax: 45-45-27-29-99

Lars Peter Thormaehlen
Competence Center for Catalysis
Chalmers University of Technology
S-412 96 Goeteborg
Sweden
Tel.: 46-(0)31-722 30 06
Fax: 46-(0)31-722 29 67
E-mail: peter@cre.chalmers.se

Kai Tolonen
Ebo Akademi University
Laboratory of Industrial Chemistry
Piispankatu 8, 20500 Turku,
Finland
tel.: 358-2-215 4559
Fax: 358-2-215 4479
E-mail: krahkama@abo.fi

Viktor N. Tomilov
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: +7-383-2-34-44-91
fax: +7-383-2-34-30-56
e-mail: root@catalysis.nsk.su

Thomas Heinz Turek
Institute for Chemical Process Engineering
University of Karlsruhe
Kaiserstrasse 12
76128 Karlsruhe
Germany
Tel. +49 721 608 4267
Fax. +49 721 608 6118
e-mail:thomas.turek@ciw.uni-karlsruhe.de

Wen-De Xiao
UNILAB Research Center of Chemical
Reaction Engineering
East China University of Science and Technology
Shanghai 200237
P.R. China
E-mail: sane@npc.haplink.com.cn

Alexander M. Vaiman
Institute of Petrochemistry and Catalysis AS RB
Ufa
Russia
phone: +7-347-2-31-35-21, 32-99-16
fax: +7-347-2-23-66-80
e-mail: root@vayman.ufanet.ru.

Kurt M. VandenBussche
Research and Development Specialist
UOP - Engineering Science Skill Centre
25 East Algonquin Road, P. O. Box 5017
Des Plaines IL 60102
USA
Tel.: 847-375-7073
Fax: 847-391-3753
847-391 3491
E-mail: KVANDENB@UOP.COM

Arvind Varma
Dept. of Chemical Engineering
University of Notre Dame
Notre Dame, IN 46556
USA
Tel: 219-631-6491
Fax: 219-631-8366
E-mail: avarma@darwin.cc.nd.edu

Nadezhda V. Vernikovskaya
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: +7-383-2-34-12-78
fax: +7-383-2-34-30-56
e-mail: root@catalysis.nsk.su

Irina S. Verzhbitska
Kazakh State University
Almaty
Kazakhstan
phone: +7-327-2-67-48-71
e-mail: irina@high-school.almaty.kz

Dorit Wolf
Institute of Applied Chemistry
Berlin-Adlershof
Rudower Chaussee 5
Berlin D-12484
Germany
Fax: 49 (0) 30 6392 4454
dwolf@aca.fta-berlin.de

Gregory Yablonskii
Washington University
USA
E-mail: gy@wuche2.wustl.edu

Andrey N. Zagoruiko
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: +7-383-2-34-44-91
fax: +7-383-2-34-30-56
E-mail: zagor@catalysis.nsk.su

Tatiana V. Zamulina
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: +7-383-2-34-12-97
fax: +7-383-2-34-30-56
e-mail: zam@catalysis.nsk.su

Horst Zanthoff
Ruhr-Universitad Bochum
Lehrstuhl fur Technische Chemie
D-44780 Bochum
Germany
tel.: (49) 234-700-4518
Fax: (49) 234-7094-115
E-mail: horst@techem.ruhr-uni-bochum.de

Olga P. Zhukova
Institute of Coal SB RAS
ul. Rukavishnikova 21
Kemerovo 650610
Russia

Il'ya A. Zolotarskii
Boreskov Institute of Catalysis SB RAS
Prospekt Akademika Lavrentieva, 5
Novosibirsk, 630090
Russia
tel.: +7-383-2-34-44-91
fax: +7-383-2-34-30-56
E-mail: zol@catalysis.nsk.su

Natalyia G. Zubritskaya
RSC "Applied Chemistry"
pr. Dobrolubova 14,
St. Petersburg, 197198
Russia
Tel.: +7-812-238 90 22

THE THIRD INTERNATIONAL CONFERENCE ON UNSTEADY-STATE PROCESSES IN CATALYSIS

Editor: Professor Yu. Sh. Matros
Professor Alexander S. Noskov

The most of abstracts are printed as presented in camera-ready texts and all responsibilities we address to the authors. Some abstracts underwent a correction of misprints and rather mild editing procedure.

Compilers: Tatiana V. Zamulina
Elena L Mikhailenko

Computer processing of text: Yulia V. Klimova

Cover design: Nina F. Poteryaeva

Подписано в печать 10.06.98 Формат 60x84/8
Печ. л. 33.25 Заказ 82 Тираж 300

Отпечатано на полиграфическом участке издательского отдела
Института катализа СО РАН
630090, Новосибирск, пр. Академика Лаврентьева,5