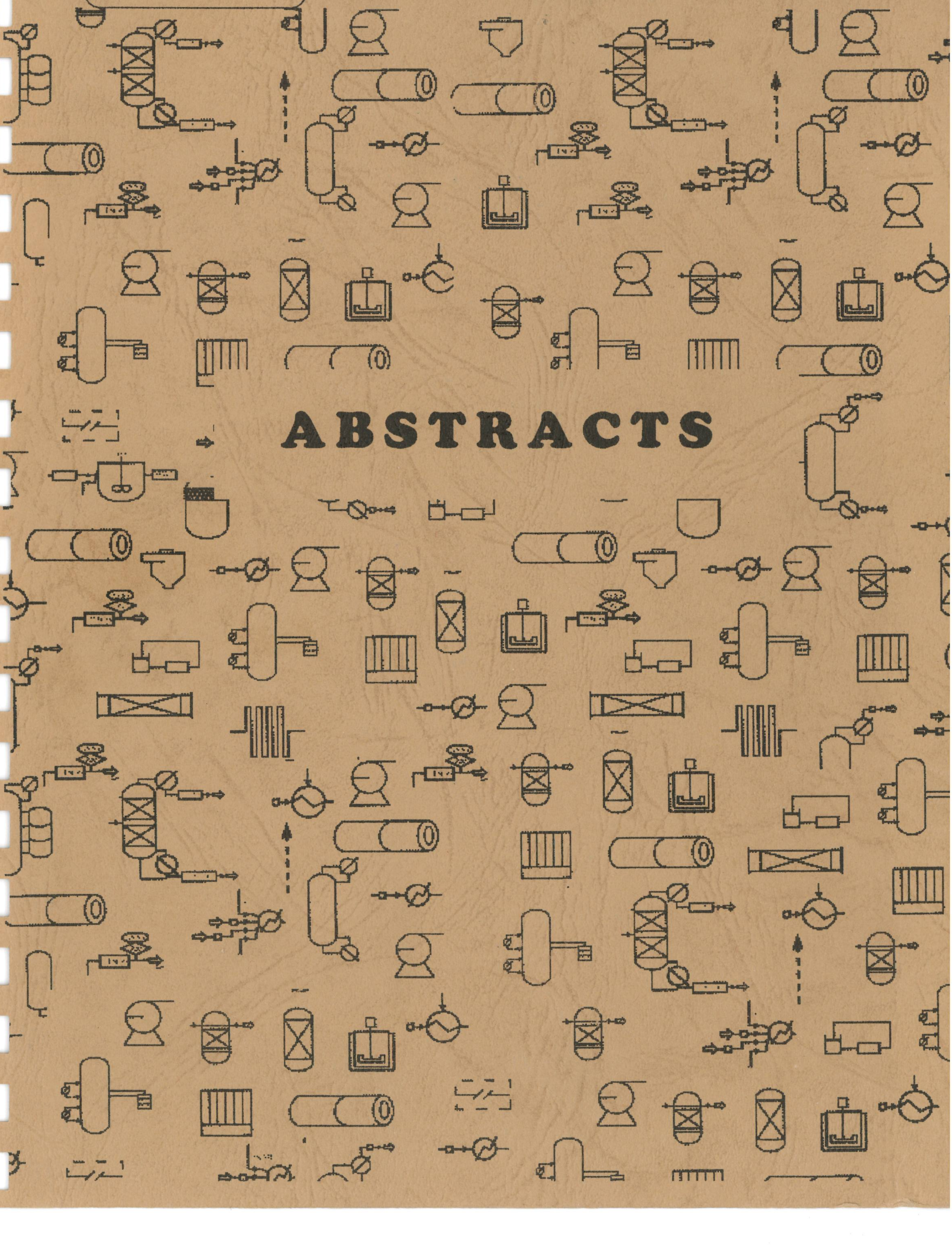
XIV International Conference on Chemical Reactors
CHEMREACTOR-14
Tomsk, Russia, June 23-26, 1998



# ABSTRACTS

Boreskov Institute of Catalysis of the Siberian Branch
of Russian Academy of Sciences

State Research Centre of Russia «Karpov NIPCI»

Tomsk Polytechnic University

East Oil Company

Scientific Council on Catalysis and its Industrial Application of RAS and Ministry of Russian Federation on Sciences and Technologies

Siberian Association of Chemical Engineering

# XIV International Conference on Chemical Reactors

# CHEMREACTOR-14

Tomsk, Russia
June 23-26, 1998

## ABSTRACTS

Novosibirsk, 1998

## INTERNATIONAL SCIENTIFIC ADVISORY COMMITTEE

| | |
|---|---|
| M.G. Slinko, Co-Chairman | State Research Centre "Karpov NIPCI", Moscow, Russia |
| V.N. Parmon, Co-Chairman | Boreskov Institute of Catalysis, Novosibirsk, Russia |
| V.I. Bykov | Krasnoyarsk Computer Center, Krasnoyarsk, Russia |
| M.P. Dudukovic | Washington University, St. Louis, USA |
| L.I. Filimonov | East Oil Company, Tomsk, Russia |
| G. F. Froment | University of Gent, Gent, Belgium |
| P. Forzatti | Technical University of Milan, Milan, Italy |
| H.P.K. Hofmann | University of Erlangen, Erlangen, Germany |
| V.P. Mangazeev | East Oil Company, Tomsk, Russia |
| V.N. Novoseltsev | Ministry on Sciences and Technologies, Moscow, Russia |
| A.V. Putilov | State Research Centre "Karpov NIPCI", Moscow, Russia |
| A. Renken | Swiss Federal Institute of Technology, Lausanne, Switzerland |
| A.A. Samarskii | Moscow State University, Moscow, Russia |
| G. Sioli | Casale Chemicals S.A., Lugano, Switzerland |
| G.F. Tereshchenko | Ministry on Sciences and Technologies, Moscow, Russia |
| K.R. Westerterp | University of Twente, Twente, The Netherlands |

## ORGANIZING COMMITTEE

| | |
|---|---|
| A.S. Noskov, Chairman | Boreskov Institute of Catalysis, Novosibirsk, Russia |
| P.N. Reshetov | East Oil Company, Tomsk, Russia |
| A.N. Mezentsev | East Oil Company, Tomsk, Russia |
| A.V. Kravtsov | Tomsk Polytechnical University, Tomsk, Russia |
| S.A. Pokrovskaya | Boreskov Institute of Catalysis, Novosibirsk, Russia |
| V.A. Chumachenko | Katalyzator Company, Novosibirsk, Russia |
| N.V. Usheva | Tomsk Polytechnical University, Tomsk, Russia |
| T.V. Zamulina, Secretary | Boreskov Institute of Catalysis, Novosibirsk, Russia |

# The General sponsor of the Conference – East Oil Company, Tomsk, Russia

EOC is the main distributor of oil in Siberia. It's activities – prospecting, production, processing and sales of oil and petrochemicals. Since 1998 East Oil Company is incorporated in the world largest oil holding UKSI.

Ministry of Russian Federation on Sciences and Technologies and Boreskov Institute of Catalysis of the Siberian Branch of Russian Academy of Sciences also provide financial assistance to the Conference.

The Organizers express their gratitude to **East Oil Company, Ministry of Russian Federation on Sciences and Technologies and Boreskov Institute of Catalysis** for their generosity.

# PLENARY LECTURES

# PHYSICAL METHODS FOR HANDLING THE PROBLEMS OF CHEMICAL TECHNOLOGY

V.N. Parmon

*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

The aim of this presentation is to discuss new applications of modern physico-chemical methods for the designing and optimization of catalytic technologies. The main attention is paid to the development of modern methods of tomography, first of all, NMR-tomography, allowing to investigate transport phenomena and various physico-chemical processes on the "microlevel" (that is, inside the porous materials of arbitrary shape), as well as on macrolevel, including the reactors with disordered catalyst grains loading. The results of NMR-tomographic investigation of the processes of porous grains drying and their saturation by moisture from the gas phase by method of are presented.

The novel methods of speed gas chromatography and other modern methods of the chemical analysis of gas phase composition, together with some physical methods, for *in situ* diagnostic of the catalysts surface state and composition, including those at high reagent pressures, are discussed.

## PL-3

# UNSTEADY STATE REACTION ENGINEERING

Ralf Doepper and Albert Renken

*Swiss Federal Institute of Technology CH-1015 Lausanne, Switzerland*

Experimental and theoretical studies have proved that forced periodic operation of heterogeneous catalytic reactors can be a versatile tool to improve reactor performance [1]. For complex reaction systems the product distribution can be altered leading to higher selectivities and yields of the desired product. The special interest for periodic operation results from the fact that it can be possible to get improvements compared to optimal steady state in the admissible range for the used control variables. The catalyst unsteady state can be controlled in two ways:

- By forced concentration oscillations [2, 3, 4] or flow reversal [5, 6, 7, 8] in fixed beds,
- By spatial regulation when input conditions of the reactor do not change with time but the catalyst moves in a field of variable reactant concentrations and/or temperatures e.g. in a fluidized bed [9, 10,11]
- By periodic change of the gas/liquid flow ratio in trickle bed reactors [12, 13]

In general the dynamic behavior of individual reaction steps in the reactor can be used by unsteady state approach to obtain selectivity and performance which cannot be attained in steady state operations. This will be shown for different examples recently published in the open literature.

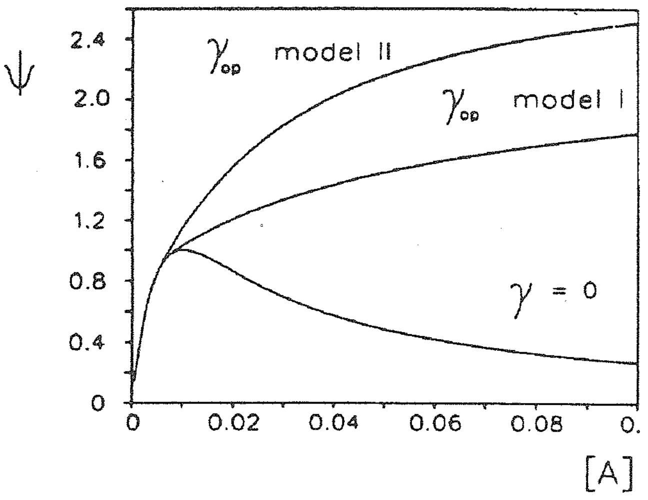


Fig. 1: Predicted enhancement factors for the catalytic dehydration of ethanol [15]

The overall performance of chemical reactors can be considerably increased by periodic or unsteady state operation for reactions with educt inhibition. This was demonstrated experimentally and theoretically for the production of ethylacetate by heterogeneous catalytic addition of acidic acid to ethylene [14] and the dehydration of alcohols [15]. In both cases the mean reaction rates under forced concentration oscillations are higher than the maximum steady state values. The achievable rates under dynamic conditions are strongly influenced by the sorption kinetics of the inhibiting species. Increasing sorption rates will increase the effect of periodic operation. At the same time the optimal frequency under periodic operation becomes higher. For instantaneous sorption rates leading to instantaneous adsorption equilibrium, highest reactor performances are found under relaxed steady state conditions (Fig.1).

Isolating catalytic steps can be used to get higher productivity or better selectivity. In various heterogeneous catalyzed oxidations, such as the oxidation of butane to maleic anhydride or the oxidation of o-xylene, the catalyst is first oxidized and the oxidation of the organic compound subsequently takes place on the catalyst surface. An excess of oxygen in the gas phase has often a negative effect on the product selectivity. Therefore, oxygen loading of the catalyst and hydrocarbon oxidation are separated in time or the catalyst is circulated between this two stages.

An example is given by Dubuis et al. [16] for the oxidative coupling of toluene. Periodic experiments which alternated reacting and regenerating time intervals are carried out at 537 °C over 8 g of Pb/Li/MgO. The toluene flow is set to $3 \cdot 10^{-4}$ mol/s during the reacting intervals and the oxygen flow is set to $2.4 \cdot 10^{-4}$ mol/s during the regenerating intervals. The mean flows of toluene and oxygen all over a period and the total flow, kept constant using $N_2$ as an inert, correspond to the flows of a steady-state experiment. The comparison of the periodic results is done with the corresponding steady-state experiment.
Benzene and 1,2-diphenylethane yields during a periodic experiment are plotted as a function of time in Fig. 2. It is interesting to remark that benzaldehyde is no longer detectable, corresponding to a benzaldehyde selectivity below 0.01. After three periods, the cycles are time invariant.

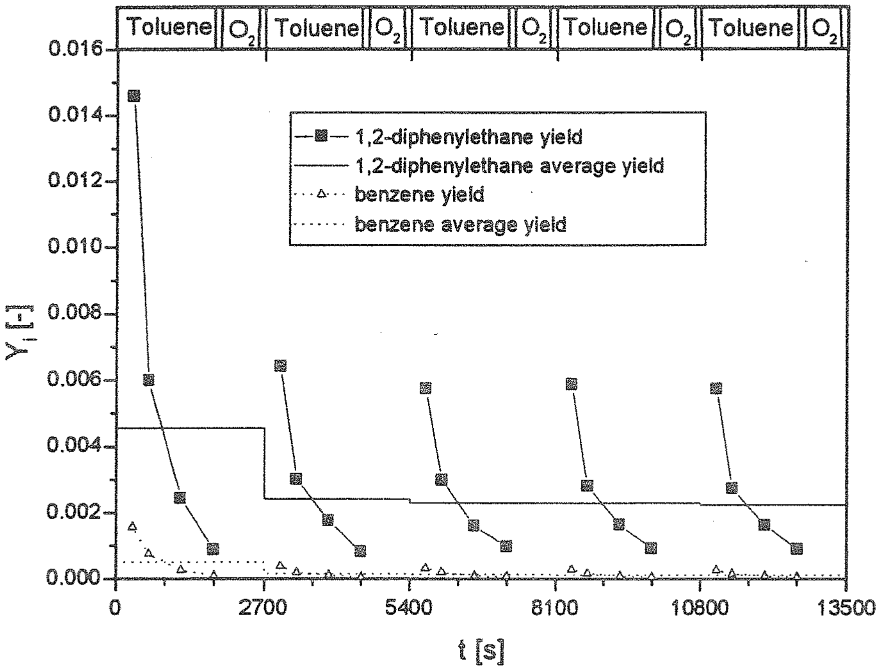


Fig.2: Yields as a function of time under periodic conditions.
Period = 2700 s,
T = 527 °C,
Split ratio = 3:1,
$m_{cat}$ = 0.008 kg.

Under periodic conditions, the 1,2-diphenylethane selectivity compared to steady-state conditions is increased from 0.6 to 0.9 by suppressing gas phase oxygen (Fig. 3). The interaction between the catalyst and the toluene methyl group produces benzyl intermediates which react selectively to form 1,2-diphenylethane and benzene.

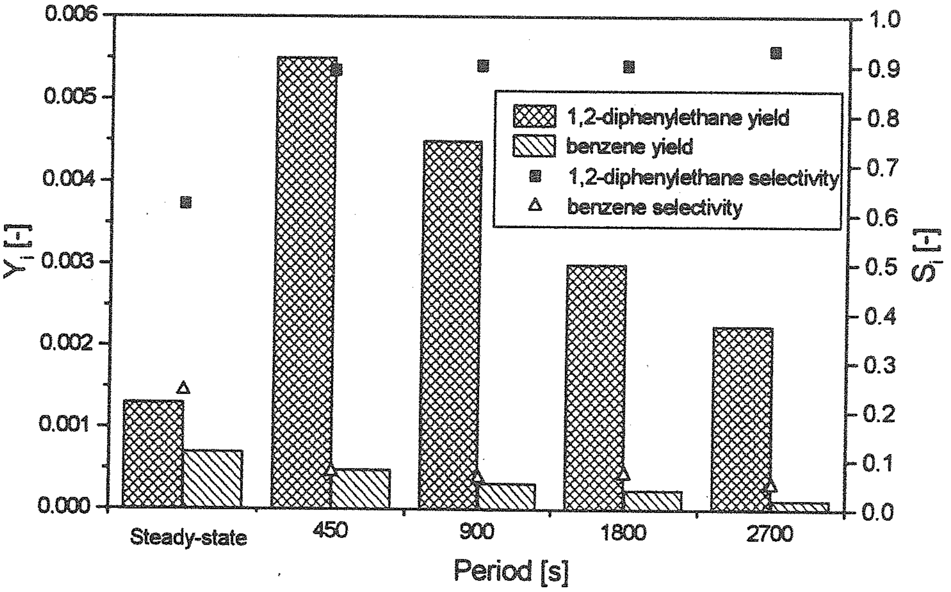


Fig.3: Comparison of periodic and steady-state yields and selectivities.T = 527 °C, Split ratio 3:1, $m_{cat}$ = 0.008 kg.

The yield of 1,2-diphenylethane is also higher under periodic conditions compared to the steady-state experiment. It increases with shorter periods, due to a shorter reacting interval which leads to less deactivation of the catalyst. The catalyst is therefore globally more active at short periods.

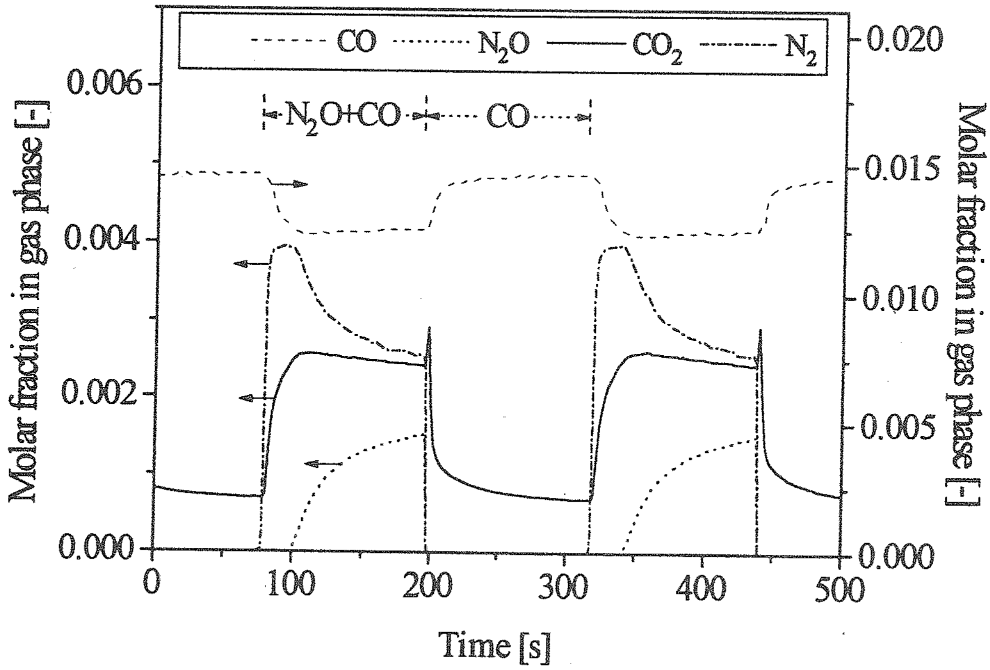


Fig.4: Reduction of $N_2O$ by CO under periodic inlet conditions at cycle-invariance.
Conditions: T = 310°C, period = 240 s

A 2nd example for the successful isolation of catalytic steps concerns the reduction of $N_2O$ by CO over silica-supported iron oxide. Randall et. al. [17] showed that the activity of the reduced catalyst is considerably higher as compared to steady state, where the catalyst is partially oxidized. On this basis, it was attempted to keep the catalyst in the reduced state by periodically reducing it with CO. The dynamic responses of reactants and products at cycle invariance for a period of 240 s are given in Fig. 4. During the half-cycle under CO, $CO_2$ is still produced, due to the reduction of the catalyst. During the period under $N_2O$ and CO, $N_2O$ is totally converted during approximately 25 s; then $N_2O$ molar fraction increases due to oxidation of the catalyst. In Fig. 4, the time-average conversions of CO and $N_2O$ as well as the yields of $CO_2$ and $N_2$ over several periods at cycle-invariance are compared to the values obtained at steady-state and at quasi steady-state (QSS). It appears that concentration cycling with short periods of about 30 - 60 s leads to an increase in $N_2O$ conversion and $N_2$ yields of approximately 30%, which presumably arises from a higher time-average degree of reduction of the catalyst as compared to the steady-state situation.

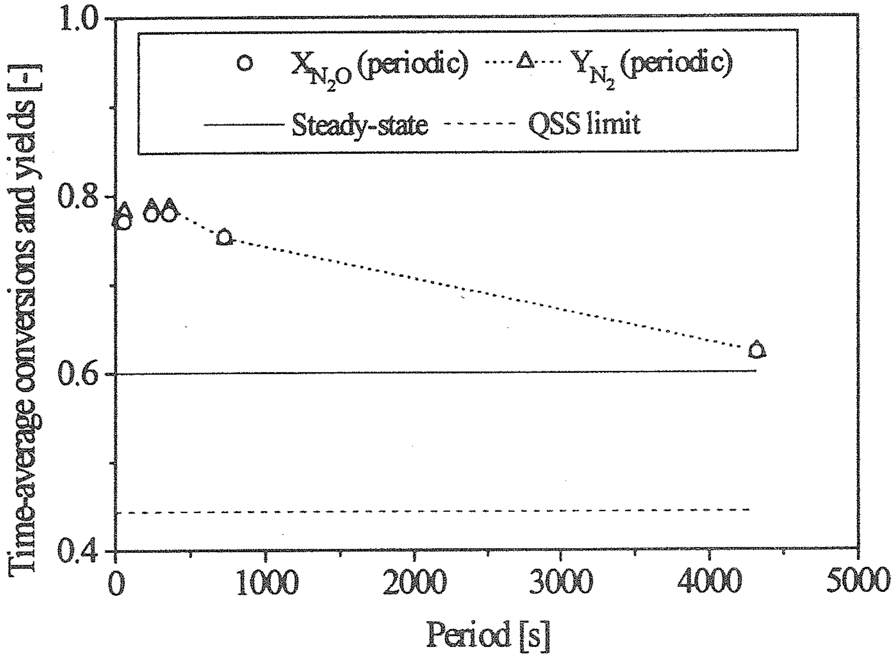


Fig.5: Time-average yields and conversions in function of period. Comparison between periodic operation and steady-state.

The reaction behavior under transient conditions can be understood on the basis of the kinetic model given in Equation (1) - (8).

$$N_2O + () \longrightarrow N_2 + (O) \quad (1) \qquad CO(O) \longrightarrow CO_2 + () \quad (2)$$

$$N_2O + (O) \longrightarrow N_2 + O(O) \quad (3) \qquad N_2O + () \longrightarrow N_2 + O() \quad (4)$$

$$CO + O(O) \longrightarrow CO_2 + (O) \quad (5) \qquad O() \longrightarrow (O) \quad (6)$$

$$CO + (O) \longrightarrow CO(O) \quad (7) \qquad CO + O() \longrightarrow CO_2 + () \quad (8)$$

The initially high activity of the reduced catalyst can be explained by a fast redox reaction on reduced sites, ( ), by which a highly reactive surface oxygen species adsorbed on reduced sites is formed (O( )) (Equations (4) and (8)), which would be the precursor to the formation of lattice oxygen (Equation (6)) — in this way, it is suggested that the oxidation of the catalyst (Equation (1)) really takes place via a two step mechanism (Equations (4) and (6)).

Such a precursor is known to exist in oxidation catalysis on solid oxides. For instance, Sokolovskii [18, 19] has proposed a generalized scheme of the catalytic oxidation, by which in a first step, gas phase oxygen forms highly reactive surface oxygen species which can be transformed into less reactive oxygen of the catalyst lattice. Adsorption of oxygen on a partially reduced surface may occur if there is only a partial charge transfer between the reduced surface cation to adsorbed oxygen or if the oxygen species occupies a site different from a surface lattice site [20].

The reactions in Equations (4)-(8), combined to reactions in Equations (3)-(2), are consistent with the gas phase responses to $N_2O$+CO concentration steps over initially reduced and oxidised catalysts. As a matter of fact, if reactions in Equations (4) and (8) are fast compared to the other reactions, the activity of the catalyst would be higher at the beginning of the transient over the initially reduced catalyst with respect to the initially oxidised catalyst, as is observed experimentally. Over the initially reduced catalyst, $N_2$ and $CO_2$ responses would both go through a maximum at the beginning of the transient, and subsequently decrease towards steady-state, due to deactivation by emergence of adsorbed oxygen into the lattice (Equation (6)).

In summary, the use of non-stationary or dynamic operation of chemical reactors can lead to considerable increases of the reactor performance and a substantial gain in selectivity. This could be shown for both homogeneous and heterogeneous reaction systems described in the literature. But besides the reversed flow operation, industrial implementations of dynamic operation are still very scarce. This fact is principally due to the lack of basic understanding of the effects occurring under non-stationary operation. Therefore further research is needed to broaden our basic knowledge and to create reliable models describing the complex behavior of non-stationary reactor processes.

Financial support by the Swiss National Foundation is gratefully acknowledged.

## References

1 P.L.Silveston, R.R.Hudgins, A.Renken, Catalysis Today, 25 (1995) 91
2 A.Renken, Int.ChemEng., 24 (1984) 202
3 H.Amariglio, P.Pareja, A.Amariglio, Catalysis Today, 25 (1995) 113
4 E.Gulari, X.Zhou, C.Sze, Catalysis Today, 25 (1995) 145
5 Y.S.Matros, Catalytic processes under unsteady state conditions, Studies in Surface Science and Catalysis 43 (1989) B.Delmon, J.T.Yates (eds)
6 U.Nieken, Abluftreinigung in katalytischen Festbettreaktoren bei periodischer Strömungsumkehr, VDI-Fortschrittsber. 328, 1993
7 B.van de Beld, R.A.Bormann, O.R.Derkx, B.A.A.van Woezik, K.R.Westerterp, Ind.Eng.Chem.Res. 33 (1994) 2946
8 G.A.Bunimovich, N.V.Vernikovskaya, V.O.Strots, B.S.Balzhinimaev, Y.S.Matros, Chem.Eng.Sci. 50 (1995) 565
9 R.M.Contractor, A.W.Sleight, Catalysis Today, 3 (1988) 175
10 S.I.Reshetnikov, B.S.Balzhinimaev, V.P.Gaevoi, A.A.Ivanov, Chem.Eng.Journal 60 (1995) 131
11 A.A.Ivanov, A.A. Yabrov, L.M. Karnatovskaya, N.A. Petukova, Chaikovskii, React. Kinet. Catal. Lett. 61(1997) 75
12 J. K. Lee, S. Ferrero, R.R. Hudgins, P.L. Silveston, Can. J. Chem. Eng. 74 (1996) 706
13 L. Gabarain, J. Cechini, P. Haure, in "Dynamics of surfaces and reaction kinetics in heterogeneous catalyis", G.F. Froment, K.C. Waugh (Ed). 1997, 459
14 M.A. Truffer, A. Renken, AIChE Journal 32 (1986) 1612

15 J. Thullie, A. Renken, Chem. Eng. Sci. 46 (1991) 1083
16 S. Dubuis, M. Lorenzi, R. Doepper, A. Renken, in "Dynamics of surfaces and reaction kinetics in heterogeneous catalyis", G.F. Froment, K.C. Waugh (Ed). 1997, 469
17 H. Randall, R. Doepper, A. Renken, ECCE 1
18 V.D. Sokolovski, React. Kinet. Lett. 35 (1987) 337
19 V.D. Sokolovski, Catal. Rev. Sci. Eng. 32 (1990) 1
20 H.H. Kung, in Studies in Surface Science and Catalysis, B.Delmon, J.T.Yates (eds), Vol. 45 (1989) 110

**PL-4**

# PROSPECTS FOR DEVELOPING HETEROGENEOUS CATALYTIC PROCESSES

Slin'ko M.G.

State Research Center "Karpov NIPCI", Moscow, Russia

Noskov A.S.

Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

Key problems of industrial catalysis were solved in the 20th century related to production of fertilizers, pertrochemistry, oil-processing, polymerization, atomic energy production, jet technique, medicine and environment protection.

During this period catalysis, born as empirical art, becomes a science. In 30s mathematical modeling started to develop basing on the fundamental knowledge of physical and chemical laws and well balanced computational and natural experiments. During the same years kinetics of heterogeneous catalytic reactions was founded, and methods were designed to study catalysts activity. Mass, heat and pulse transfer were studied regarding their influence on the rate of chemical conversions in multi-phase systems.

The second half of the 20th century gave us a fundamental theory for designing chemical reactors using the laws of chemistry, physics, physical chemistry, and non-linear dynamics. Software was created to calculate reactors, and many reactors were designed working on various multi-phase media with a large unit capacity. Unsteady state oil cracking was launched, and zeolite catalysts were discovered. In the last quarter of the century we witness intensively developing physical methods for studying the surface of catalysts. Nowadays catalyst processes are modeled and studied starting from molecular level especially, when the composition of catalyst surface is in unsteady state towards the gas phase composition.

In the 21st century both fundamental and application of heterogeneous catalysis are expected to be more and more dependent on non-linear dynamics of chemical reactions, processes and reactors on all levels starting from the molecular one. With this regard quantum chemistry methods shall rapidly insert into catalysis fundamentals. They will help to go from the knowledge on matter structure to scientific ideas about the properties of catalyst surface reactivity and to catalyst design in whole. Research methodology shall still base on the balanced contribution of natural and computational experiments on all levels of catalytic process performance including the aero(hydro)dynamics of catalytic reactors. Of special significance shall be studies related to heterogeneous reaction kinetics and kinetic modeling basing on data about process performance peculiarities on molecular level. These studies shall as always help optimization of process operation conditions and catalytic reactor design.

In the 21st century we shall find catalysts for the direct synthesis of valuable products via thermodynamically permitted reactions. Among the latter are methanol synthesis

from methane, benzene conversion to phenol, and many others. Photocatalysis will attract special attention as a way to produce inexpensive energy. Biocatalysis will become of particular importance. Catalysis role on production of materials with desired properties will significantly increase. Theory and practice of heterogeneous, homogeneous and enzyme catalysis will merge more and more. Intensively developing computation capacities will allow us to model hydrocarbons combustion considering numerous reactions and turbulent diffusion in order to perform environmentally harmless combustion and to purify various type exhaust gases including automotive emissions.
We expect catalytic technologies to develop by directions changing the conditions of conventional processes such as:

- transfer to catalytic processes performance at millisecond contact times, in some cases allowing to avoid thermodynamic limitations imposed. This method will demand advanced technologies for preparing honeycomb catalysts to be used for non-traditional purposes (beside exhaust gas purification);
- catalytic process performance under critical and over-critical conditions to develop new routes of chemical conversion; such processes allow one to intensify mass transfer and to use in production chemicals that are not demanded in conventional processes;
- processes and multi-functional reactors that help to overcome the equilibrium limitations by means of combined conversion and separation, or using unsteady state catalyst surface;
- energy tense catalytic processes used to decrease equipment weight and production costs.

For launching competitive chemical industry in the CIS countries in the nearest future, most likely catalysts and catalytic technologies will be developed towards:

A) New generation catalysts and technologies to be used in energy production and chemical industry:

- catalysts and technology to produce nitric acid;
- catalysts of high activity and selectivity for partial oxidation, oxidative dehydrogenation, oxidative ammonolysis, oxidative chlorination;
- catalysts based on metallocenes to polymerize olefins;
- environmentally harmless technologies for fine organic synthesis allowing lower production costs;
- catalysts and technologies to synthesize halogen containing organic compounds;
- production of domestic cracking catalysts to process various composition oil to provide strategic safety of Russia.

B) Design and implementation of highly efficient new generation technologies for deep oil processing and to convert natural and condensed gas:

- creation of pilot-industrial production of catalysts to produce alkylate gasoline using solid super acid catalysts;
- design of technologies using methane and other light natural gas components to produce motor fueles;
- development of technologies to process hydrocarbons C3-C4 to valuable chemical products it motor fuel directly at the places of oil development;

- pilot production of liquid fuels based on high density hydrocarbons of high energy tension.

C) Design and implementation of efficient chemical and catalytic technologies and related processes to produce sorbents and catalysts to neutralize industrial wastes:

- design and implementation of technologies to produce synthetic carbon sorbents with desired and easily controlled properties from new raw materials;
- design and implementation of high capacity technologies to process wastes under super critical conditions;
- design and production of prototypes of energy producing plants for autonomous environmentally harmless energy production using non-traditional and/or renewable energy carriers.

The 21st century will essentially increase catalysis role for improvement of life standards and for better national security.

# PL-5

# EXPLOSIONS IN FLOWING GASES

K. R. Westerterp, J. W. Bolk

*Chemical Reaction Engineering Laboratories, Department of Chemical Engineering, Twente University of Technology, P.O. Box 217, 7500 AE Enschede, The Netherlands*

In the University of Twente in the High Pressure Laboratory we have investigated explosions in flowing gases. To this end a large installation has been built in which in a tube a flowing mixture of air, ethylene and nitrogen is ignited with a hot wire. Tube diameters of 2, 5 and 10 cm., temperatures up to 300°C, gas velocities up to 25 m/s and pressures up to 30 bar have been used.

It has been found, that in a diagram of the electric energy supplied to the wire and the oxygen concentration in the gas stream - for a constant pressure, gas temperature, tube diameter and gas flow rate - three regions can be distinguished - of no reaction, of explosion and of local reaction but no explosion, respectively. The trifurcation point in the diagram, where the three regions meet, has been defined as the explosion point. So in this point we find the minimum energy supply and minimum oxygen concentration in the gas necessary for a deflagration.

It can be concluded that the partial oxidation of ethylene to ethylene oxide must be possible even at stoichiometric compositions (33% oxygen), provided care is taken to keep the gas flowing.

All experimentally determined explosion points can be correlated in a single equation with the operating pressure, temperature, flow rates and tube diameters. This correlation is founded on combustion and reactor theory. It appears there is nothing mysterious about explosions. It is just a matter of Heat Production Rates (HPR) and Heat Withdrawal Rates (HWR) for the reactions around the wire: as HPR no more equals HWR, an explosion occurs.

It has been found that the higher the flow rate the more difficult to provoke an explosion. All experiments were confirmed with CFD calculations, which predict the experimentally determined explosion points within 10%. Also obstacles and dead zones have been tested.

# ORAL PRESENTATIONS

# SECTION A

## PHYSICO-CHEMICAL AND MATHEMATICAL FUNDAMENTALS OF PROCESSES ON CATALYSTS SURFACE

**OP-A-1**

# HYDROGENATION OF ACETYLENE-ETHYLENE MIXTURES. NEW PROSPECT BY MONTE CARLO STUDIES

**Dario Duca** and **Tamás Vidóczy**

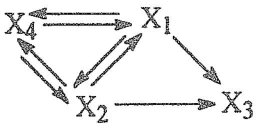
Istituto di Chimica e Tecnologia dei Prodotti Naturali del CNR,
via U. La Malfa 153, 90146 Palermo, Italy
(dduca@cuc.unipa.it)
and
Central Research Institute for Chemistry of the Hungarian Academy of Sciences,
H-1525 Budapest Pf. 17, Hungary
(tvid@cric.chemres.hu)

Selective hydrogenation of alkynes in the presence of alkenes is an important industrial target and a challenging research in catalysis[1]. Acetylene hydrogenation in ethylene rich feedstocks on Pd catalysts is also a good reaction model for studying[2] the kinetics and the mechanism of this relevant catalytic process. However, the usual approach to the mechanistic aspects of this reaction does not seem amenable to suggest any new idea in order to increase the activity-selectivity performance of these catalysts, thus new lines of approach are needed. Actually, the title reaction on the metal catalysts is generally described by the following Scheme:

$$C_2H_2 \rightarrow C_2H_4 \rightarrow C_2H_6$$

Scheme 1

The macroscopic reaction model of Scheme 1 is supported by microscopic evidences although, definitive insight into the microscopic involvement of the surface process was not provided up to now. Thermodynamic effects, metal dispersion, presence of different catalytic sites and/or formation of surface species (hydride and/or carbonaceous ones) were hypothesized as determining the surface reactivity of the metal. However, the thermodynamic effects claimed earlier are not anymore convincing, and, at least in our experiences, the metal dispersion does not influence the mechanism[2,3] and the presence of hydride species in the catalyst if any is negligible and not playing any role[2-4]. On the contrary, in our opinion, the mutual interaction of the surface carbonaceous species (reaction, ageing and/or poisoning), could influence the reactivity of the metal surface. In this respect, two different surface reaction models have been proposed. These two surface models, although disagreeing each other, are both considering the hypothesis that different catalytic sites are involved for the different reacting surface species. Their basic idea has recently been formalized[2,3] by a mathematical algorithm, surface site evolution model (SSEM). This model, based on an ordinary differential equation system (ODEs), is able to reproduce the macroscopic evidences of the acetylene hydrogenation in ethylene rich feedstocks but it is not able to suggest any possible alternative meaning and/or origin for the different catalytic sites. These sites, indicated as $X_1$, $X_2$, $X_3$ and $X_4$, are related according to the Scheme:



Scheme 2

where $X_1$ are the original metallic sites, or formed from these ones very rapidly by coating of carbonaceous species before the reaction system stabilizes and before the other sites are produced (sites $X_1$ are accessible to all the species involved in the reaction). $X_2$ are surface sites originated from $X_1$ (they can be occupied only by acetylene and hydrogen). $X_3$ and $X_4$, are originated from $X_1$ and $X_2$, and are irreversibly poisoned sites and sites accessible only to hydrogen atoms respectively.

For having new insight in the mechanism of the unsaturated hydrocarbon hydrogenation we have developed a Monte Carlo model to mimic the ethylene hydrogenation on Pt catalysts[5]. Our Monte Carlo algorithm, although working on very simple events (i.e. adsorption, desorption and diffusion of the molecules involved in the reaction), was able to reproduce all the experimental aspects and gave a detailed microscopic picture of the reaction. In addition, this model allowed us to point out the importance of the steric hindrance of the molecules involved in the catalytic process. Owing to this finding, we have tried to find a new possible interpretation of the meaning and of the origin of the different catalytic sites on a metal surface during the acetylene-ethylene hydrogenation based on the influence of the different steric hindrances of the reacting molecules.

The simulation had to account for the following experimental results:

1) The rate of adsorption of acetylene and ethylene on a metal surface is almost the same when it occurs separately, while the latter becomes much slower when acetylene and ethylene are adsorbed together.
2) The rate of hydrogenation of ethylene is almost the same of that of acetylene when the first one is hydrogenated separately. Conversely, ethylene is practically not hydrogenated also in presence of traces of acetylene.
3) The reaction rate of acetylene in acetylene-ethylene mixtures using metal catalysts increases with the ageing of the catalysts to reach a constant value.
4) The above result is not related to the gradual reduction of the surface sites.

5) As the reaction rate in the acetylene hydrogenation (point 3) increases, increasing formation of $C_4$ species are observed in the G.C. analysis.

6) The formation of the $C_4$ species is accompanied by an increased selectivity to ethylene.

7) The relative amount of the $C_4$ species does not agree with the thermodynamic stability of the species, and, on the contrary, seems to be conditioned by the steric hindrances of the molecules on the surface.

8) The reactivity of the catalyst to the ethylene hydrogenation after the hydrogenation of acetylene is larger than that of the same fresh catalyst.

9) When Pd catalysts react with gas mixtures containing different percentage of hydrogen and ethylene, there is a progressive poisoning of the surface of the catalysts. The poisoning rates increase with decreasing $H_2/C_2H_4$ ratio.

10) Small amount of acetylene added to $H_2/C_2H_4$ mixtures decreases the rate of poisoning of the catalyst.

11) Metal catalysts deactivated by the ethylene hydrogenation can not be reactivated by addition of acetylene.

In the Monte Carlo simulation we have used a (100) metal surface and only simple events. Besides the hydrogenation of acetylene and ethylene, the adsorption, desorption and diffusion of the different molecules involved in the reaction are taken into consideration. Since we wanted to have only qualitative information on the idea, for the reactions and for the simple events of acetylene and ethylene we have used the same probabilities obtained earlier by Monte Carlo studies[5] for ethylene in the ethylene hydrogenation. However, considering points 1 and 2 and considering that the simple events are independent of each other, this one should not be a critical approximation. Therefore, in this Monte Carlo study, we have used the experimental pressure of the different species and we have changed only the steric hindrance of the molecules on the surface. By these simulations, points 1-3 and 8-11 have been reproduced and evidence for the justification of points 4-7 has been found. One of the possible constellations around the different surface species, corresponding to a successful Monte Carlo mimicking, are reported in Scheme 3:

| | | | | |
|---|---|---|---|---|
| $X_1\,X_1\,X_1\,X_1$ | $X_1\,X_2\,X_2\,X_1$ | $X_1\,X_4\,X_4\,X_1$ | $X_1\,X_4\,X_4\,X_1$ | $X_2\,X_2\,X_2\,X_2$ |
| $X_1\,S_H\,S_H\,X_1$ | $X_4\,S_1\;\;S_1\,X_4$ | $X_4\,S_2\;\;S_2\,X_4$ | $X_4\;S_3\;\;S_3\,X_4$ | $X_2\,X_3\,X_3\,X_2$ |
| $X_1\,X_1\,X_1\,X_1$ | $X_1\,X_2\,X_2\,X_1$ | $X_1\,X_4\,X_4\,X_1$ | $X_1\,X_4\,X_4\,X_1$ | $X_2\,X_2\,X_2\,X_2$ |

Scheme 3

# OP-A-1

where $X_n$ are the same surface sites of the SSEM model, $S_H$ are surface sites occupied by hydrogen atoms and $S_1$, $S_2$ and $S_3$ surface sites occupied by carbon atoms of acetylene, ethylene, and ethane, respectively. Scheme 3 shows that the steric hindrances of the surface molecules can drive the catalyst reactivity. The constellations therein reported explain that the surface **poisoning** and/or reacting molecules can **increase** the reaction rate of one or more species involved in the reaction, since hindered species can selectively increase the presence of sites on the catalyst surface that can be used only by some of the reacting molecules. Therefore, this Monte Carlo simulation shows for the first time the possible activating effect of the poisoning on a catalyst surface, gives new insight and integrate earlier views in the field of catalyst activation.

1 J. Houzvcka, R. Pestman and V. Ponec, Cat. Lett., 1995, **30**, 289.
2 D. Duca, F. Frusteri, A. Parmaliana and G. Deganello, Appl. Catal., A:, 1996, **146**, 269.
3 D. Duca, F. Arena, A. Parmaliana and G. Deganello, Appl. Catal., A:, in press.
4 D. Duca, L.F. Liotta and G. Deganello, J. Catal., 1995, **153**, 69.
5 D. Duca, L. Botár, and T. Vidóczy, J. Catal., 1996, **162**, 260.
D. Duca, P. Baranyai and T. Vidóczy, J. Comput. Chem., in press.

OP-A-2

# DETONATION AUTOWAVES IN BOILING AS A TECHNOLOGICAL TOOL FOR FORMATION OF CATALYTICALLY ACTIVE PHASE ON SURFACES OF METAL SUPPORTS

V.V. BARELKO, P.I. KHALZOV, E.A. FEDORIN

*IChPh RAS in Chernogolovka, Russia*

Detonation-like-mechanisms as applied to heterogeneous vapor generation were introduced in physics of boiling processes in [1] where dynamics of self-sustaining wave regimes of functioning of heat generating elements attended by boiling due to surface boiling of "cold" liquid media (liquids not heated to the boiling point) were studied. It is the concept of detonation-like boiling, proposed in a field that seems to be very far from catalysis, which underlies the present investigation and has enabled us to formulate a new approach to solving an important problem of catalyst preparation, namely, formation of catalytically active phases on metal surfaces. Not going to details of the detonation-like-boiling mechanism (see [1] for detailed information), we emphasize characteristic peculiarities of this phenomenon that will be needed for understanding the results of this study.

In accordance with the concepts discussed in [1], transition from a free-convection-controlled heat transfer from the heat generating element surface placed in a cold liquid to a mode controlled by surface boiling has the following specific features:

— the temperature field in the liquid media near surface of the heat generating element (HGE) loses its stability, and heat transfer becomes highly nonsteady locally; this phenomenon in associated with formation in the boundary layer of a periodically repeated pattern of alternating phase states: (I) single-phase heating of the liquid surface layer to temperatures exceeding the boiling points and (II) subseguent decay this metastable state with explosion-like vapor generation;

— the decay of the overheated liquid film is in its physical nature similar to detonation, it differs from classical detonation only in a very low energy content in the "fuel" (the relative vapor content in the overheated liquid layer is much less than unity) and in a small "fuel" mass (very thin layer);

— as any other detonation-like explosion, the decay of overheated liquid surface layer generates shock waves and cavitation voids in the vicinity of the HGE surface. The generated perturbations are responsible for rapid destruction of HGE casings and for intense scaling (deposites formation).

# OP-A-2

From the above-discussed concepts it follows that in conditions of detonation-like boiling the narrow zone arising near the HGE surface is a domain within which the liquid is intence treated by shock-wave and cavitation impacts, i.e. is a kind of an acoustic reactor. Hence, detonation-like boiling (DB) may serve as an efficient means for chemical degradation of liquids sensitive to mechanical (acoustic) impacts. In particular, one can hope that use of liquids capable of evolving free metals and their oxides (or other catalytically active phases) when decomposed in cavitation fields in devices with detonation-like boiling will provide a new approach to preparation of catalytic systems on metal supports. In this work we explored and described the opportunities offered by this approach by way of example of the reaction of ammonia oxidation on wires plated by platinum and palladium using the DB technique.

At the first stage of our work we studied the dynamics of active-zone formation on the wire surface under the conditions of a DB-process, the effect of wire heat loading on the level of the achieved catalytic activity of prepared elements, and the fit of the range within which deposition of the active component onto the wire surface is stable to the range within which the DB regime can be realized.

Formation of the platinum phase on the surface is of the threshold nature. At undercritical thermal loads of wires do not gain sufficient catalytic activity and is incapable of providing the conditions needed for ammonia oxidation to proceed in a self- sustained thermal regime. Above this threshold, the platinum deposition process (i.e. surface decomposition of Pt salt) is abruptly accelerated, and after holding the element in the solution not more then 10 s it acquires activity commensurate with the activity of pure platinum (this applies to all the three catalytic characteristics: the ignition temperature, dynamics of self-maintained transition to the steady state, and ammonia oxidation rate). The above-indicated limiting thermal load is a lower boundary of the DB range, and transition through it is attended by generation of intense acoustic perturbations; before this boundary, the surface boiling process is inoperative. Replacement of the support material changes catalytic characteristics of the elements only little. However, a macroscopic relief and its topological properties of the deposited layers are sensitive to changes in the degree and type of surface oxidation of the support. On the surface of acid- and heat- resistant stainless steel (coated with a thin, dense, and indestructible film of oxides) the catalytic phase is formed in the of ridge- shaped fragments firmly tied to the support. When a support coated with a porous macroscopic oxide layer (oxidized surface of a nickel wire) is used, the platinum catalytic phase is deposited on rarely spaced sites, as a result, an "island" microscopic relief is formed that consists of separately positioned crystallite grains weakly tied with the oxidized support surface. Finally, if the platinum phase precipitates on an unoxidizable surface of related metal (platinum- palladium-rhodium alloy) decomposition of the solution on the surface of such a support produces a continuous metal layer, which, is a "platinum scaling" in its visual properties and in physical essence of the process of its preparation. This type of a catalytic element features a high strength of the precipitated-phase adhesion to the support surface and also significant resistance of the active layer to catalytic corrosion.

Summing up these studies, we emphasize some kinetic discrepancies between the parameters of ammonia oxidation on elements coated with platinum and palladium by the DB technique. Platinum coating of a steel wire can provide an activity nearly equal to that of monolith platinum (as on a platinum wire, the process in a stable regime homogeneously throughout the element length). As distinct from monolith palladium, the ammonium oxidation reaction on a steel wire coated with palladium under the same conditions and of the same density (the layer precipitated metal phase is about 0,1 mcm thick, as recalculated to the continuous film) proceeds in an essentially nonsteady regime with profound manifestation of time- and coordinate-dependent domain instability.

The phenomenon of detonation-like boiling of cold media on solid surfaces discovered previously is shown it is efficient, high-productivity, and easily controllable means for producing catalytic coatings of metal surfaces. The dynamics of platinum and palladium deposition onto various metal surfaces is studied as a function of the parameters governing detonation-like boiling and data on the kinetics of ammonia oxidation reaction on the catalytic surfaces produced are reported. Detonation -like boiling as a fine method for producing complex catalytic systems of present composition and density is very promising for both academical studies and practical applications. The first investigation data are published in [2,3].

We are grateful to RFBR for support of this investigation.

REFERENCES

1. S.A. Zhukov, V.V. Barelko, I.J. Heat Mass Transfer, 1992, v.35, No4, p.759
2. V.V. Barelko, P.I. Khalzov,E.A. Fedorin, Khimicheskaya fizika (russ), 1996, v.15, No3, p.122
3. V.V. Barelko,P.I. Khalzov,E.A. Fedorin, Dokladi RAN (russ), 1997, v.354, No1 ,p.1

## OP-A-3

# A NOVEL ANNULAR REACTOR FOR HIGH-TEMPERATURE KINETIC STUDIES

Alessandra Beretta and Pio Forzatti

Dipartimento di Chimica Industriale e Ingegneria Chimica, POLITECNICO di Milano, Piazza L. da Vinci 32, 20133 Milano - ITALY
e-mail: pio.forzatti@polimi.it
fax: +39-(0)2-70638173

## Introduction

Standard fixed-bed micro-reactors are traditionally used in catalysis for the study of reaction kinetics and for screening purposes. Major draw-backs of this configuration, though, are represented by the pressure and temperature gradients which arise within the catalytic bed when dealing with high flow rates and highly exo- or endothermic reactions. Besides, high values of space velocity can be guaranteed by reducing the amount of catalyst, but its dilution can cause by-pass of the reactant stream. Such non-uniformities make critical the reproducibility as well as the analysis (reactor modeling, derivation of kinetics) of the catalytic data. In practice, space velocities in the range 10,000-100,000 L(NTP)/kg catalyst/h and reaction temperatures below 400-600°C are the usual operating fields for lab-scale fixed-bed reactors.

In this work, the development of a structured catalytic reactor with annular configuration is reported. The reactor is schematically represented in Figure 1.

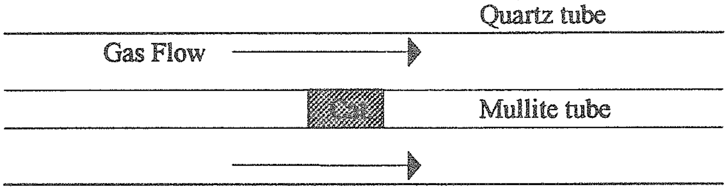


**Figure 1** - Reactor section

Small amounts of catalyst (few milligrams) are loaded in the reactor in the form of a thin (50-100 μm) and short (0.5-5 cm) layer deposited onto a tubular ceramic support (O.D. = 4.75 mm), placed internally to quartz tube (I.D. = 7÷9 mm); the catalytic bed is longitudinally contacted by the gas stream which flows in laminar regime across the resulting annular duct. Pressure drop is practically absent, which allows realization of very high space velocities. In principle, this allows to test catalytic materials and perform kinetic studies in the range of high temperatures (that is closer to the operating field for industrial application, as in the case of catalytic combustion) without reaching complete conversions. The present design was originally reported by McCarthy (1995) and Papadias et al. (1997).

The aim of the present paper is to demonstrate on both an experimental and a theoretical basis the performance of an annular reactor. The approach of investigation was of fundamental character; the chemical engineering analysis involved the extent of mass transfer, the performance under chemically controlled regime and the thermal behavior. The catalytic oxidation of CO was chosen as simple probe reaction, due to its suitable characteristics (a unique reaction product, the existence of known catalysts for this reaction).

### Analysis of interphase mass transfer

In analogy with the behavior of monolith-structured reactors (Uberoi and Pereira, 1995), also the present annular reactor may be subject to mass transfer control in the presence of very high reaction rate at the catalytic wall. This was observed by running CO combustion tests over a very active $Pt/Al_2O_3$ catalyst. As shown in Figure 2 reports, CO conversion increased with increasing temperature up to nearly 500°C; at high temperatures mass transfer became the rate-determining step and conversion kept almost constant.

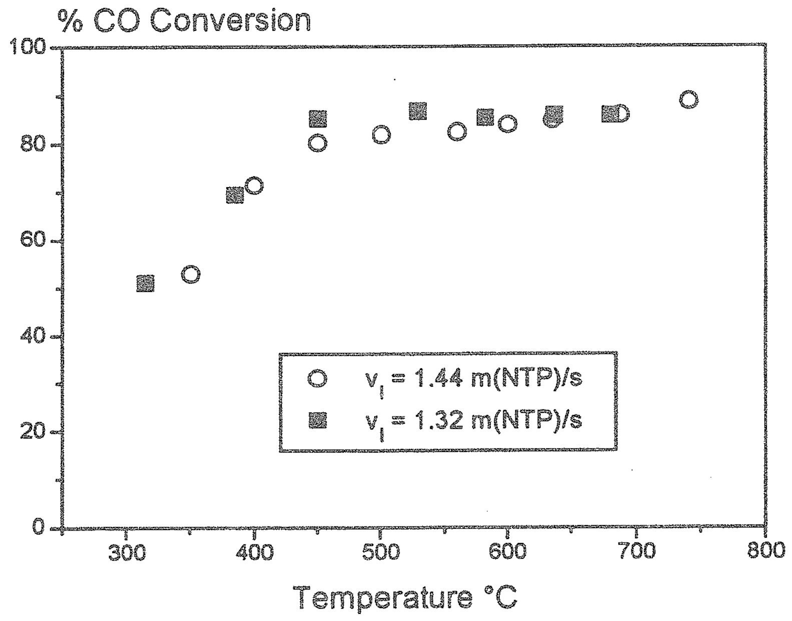


**Figure 2** - CO combustion experiments at different linear velocity over a 1.5 cm long $Pt/Al_2O_3$ catalytic layer.

A systematic analysis of mass transfer was performed by studying the effects of linear velocity and catalyst-layer length. The results were modeled and the following correlation for the local Sherwood number was developed:

$$Sh = 2.845 + 37.64 \exp(-21.57 z^*) (1000 z^*)^{-0.35} \text{ with } z^* = \text{dimensionless axial coordinate}$$

The asymptotic value of Sherwood number was found very close to the typical value of honeycomb monoliths (Tronconi and Forzatti, 1992), but much more pronounced entrance effects were estimated in the present annular reactor. Thus, even if the presence of mass transfer resistances appear a potential limitation to the application of this reactor for high-temperature measurements over very active catalysts, it turned out that such resistances become indeed much weaker when using sufficiently high gas linear velocities (>1.5 m(NTP)/s).

### High-temperature kinetics

The reactor behavior was very different when a less active Ba-Mn-hexa-aluminate catalyst was tested. As illustrated by the results in Figure 3, in that case reaction rate was always the rate controlling step and CO conversion was an increasing function of temperature over the whole wide T-range investigated. The advantages of the present annular reactor could thus be fully appreciated.

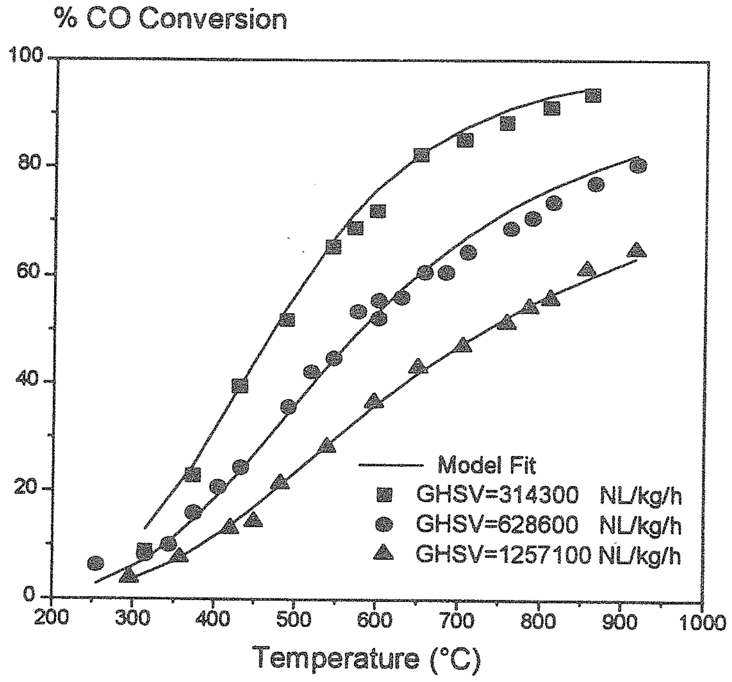


**Figure 3** - CO combustion tests over a 5 cm long layer of $BaMnAl_{11}O_{19}$

The realization of space velocities as high as $10^6$ L(NTP)/kg cat/h allowed to extend towards very high temperatures the range of intermediate conversion values, that is the range which is relevant for kinetic measurements. CO conversion was, in fact, still below 70% at temperature close to 900°C. As a comparison, the same reaction was tested over the same catalyst inside a microreactor at standard flow rates (GHSV = 50,000 L(NTP)/kg cat/h); in the packed bed, CO conversion was complete at 350-400°C.

Finally, it is worthwhile noticing that the experiments herein presented were obtained under almost isothermal conditions; a very desirable feature of the present configuration is in fact represented by the geometrical distribution of the catalyst, which allows an efficient heat dissipation via radiation from the catalyst surface towards the oven inlet wall.

## Conclusions

The present annular-structured catalytic reactor was found to be a very useful tool for exploring ranges of space velocity and reaction temperature which are far beyond the standards for lab-scale fixed bed reactors.

These features make the present design especially attractive for the study of reactions and/or to measure the activity of catalytic materials which are industrially applied in the field of high space velocity and high temperature, like in the case of methane or bio-gas catalytic combustion; in comparison with standard fixed-bed reactors, the use of the annular configuration allows to carry out the lab-scale investigation under operating conditions which are much closer to those of industrial use with consequent great advantages for scale-up and process design. Also, the present novel reactor seems suitable to study those reaction which suffer from strong selectivity problems and need micro÷milli seconds contact times (like in the case of catalytic selective oxidation of alkanes), and/or those reactions which are associated with great thermal phenomena (like in the case of deep oxidations or dehydrogenations).

This work was financially supported by CNR-Roma

## References

McCarty J. G., *Catal. Today*, 26, 283 (1995).

Papadias D., Johansson E. M., Edsberg L., Bjornbom P., Preprints, Div. Petrol. Chem., ACS Symposium, San Francisco, April (1997).

Tronconi E, Forzatti P., *AIChE J.*, 38, 201 (1992).

Uberoi M., Pereira C. J. , Ind. Eng. Chem Res. 35, 113 (1995).

## OP-A-4

# STUDY OF OSCILLATORY AND AUTOWAVE PHENOMENA IN CARBON MONOXIDE OXIDATION REACTION OVER Pt(100) BY MEANS OF THE STATISTICAL LATTICE MODELLING

*E.I. Latkin*[a], *V.I. Elokhin*[b]

[a] Novosibirsk State University RIMIBE, Novosibirsk, Russia

[b] Boreskov Institute of Catalysis, Novosibirsk, Russia

The current knowledge of the $CO+O_2$ reaction mechanism over Pt(100) makes possible to state rather justified theoretical models giving insight to the features of spatio-temporal dynamics of reaction on the platinum surface. It was shown that under certain conditions (partial pressures of reactants and temperature) the adsorbate coverages and the reaction rate undergoes self-oscillations attended by the autowave propagation of $CO_{ads}$ and $O_{ads}$ islands on the surface. The observed phenomena are associated with the reversible adsorbate-induced surface phase transition *hex* ↔ 1×1. The platinum state in 1×1 phase is catalytically active due to the ease of oxygen molecules dissociation: $S^{1\times1}(O_2) \approx 0.3 \div 0.4 >> S^{hex}(O_2) \approx 10^{-3}$ [1]. As STM-data evidence that upon attaining some critical coverages $\approx 0.05 \div 0.1$ ML, the *hex* → 1×1 surface phase transition proceeds with formation of $CO_{ads}/1\times1$ islands [1]. When the $CO_{ads}$ coverage falls below a critical value, than the reverse surface phase transition (1×1) → *hex* is initiated. It has been shown recently by molecular beam studies that the (1×1)-*CO* island growth rate, and therefore, the (1×1) phase, is governed by a strongly non-linear power law $\dot{\Theta}_{1\times1} \sim (\Theta_{CO}^{hex})^n$, where $\Theta_{1\times1}$ is a part of the surface transformed into (1×1) phase, $\Theta_{CO}^{hex}$ is the *CO* coverage on the *hex* phase, and $n \approx 4$ [2].

The statistical lattice model based on the Monte Carlo technique for describing of the self-oscillatory and autowave phenomena in the *CO* oxidation reaction over Pt(100) is studied in this contribution. The model incorporates the modern view on the stages of reaction mechanism $(CO+O_2)$/Pt(100), primarily the experimental data concerning the local change of catalytic properties under the reversible surface structure transformation *hex* ↔ 1×1 of Pt(100) surface induced by *CO* adsorption.

The catalyst surface is modelled by means of the lattice (N×N square cells, in our simulations N was varied from 60 to 1000) with periodic boundary conditions. Each cell corresponds to the active centre (*) of the platinum surface and can exist in one of five states: $*_{hex}$, $CO_{ads}^{hex}$, $*_{1\times1}$, $CO_{ads}^{1\times1}$ and $O_{ads}^{1\times1}$. The main processes governing the dynamics of the model are:

1) $CO + * \rightarrow CO_{ads}$;
2) $CO_{ads}^{hex} \rightarrow CO + *_{hex}$;
3) $(hex) \rightarrow (1\times1)$: $4CO_{ads} \rightarrow 4CO_{ads}^{1\times1}$;
4) $(1\times1) \rightarrow (hex)$: $*_{1\times1} \rightarrow *_{hex}$;
5) $O_2 + 2*_{1\times1} \rightarrow 2O_{ads}^{1\times1}$;
6) $O_{ads}^{1\times1} + CO_{ads} \rightarrow CO_2 + *_{1\times1} + *$;
7) $CO_{ads} + * \rightarrow * + CO_{ads}$.

So-called Monte Carlo step (MCS) consisting from N×N elementary action was used as a time unit, i.e. on average every MCS calls each cell at least once (except for diffusion and reaction processes, see below). In our model by elementary action it is meant a trial to change a state of the randomly chosen centre in such a manner as it was with the substances named in above mentioned processes 1) - 5). The probability of some particular process $w_i$ is determined by a ratio between the rate coefficients for stages 1) - 5): $w_i = k_i/(k_1 + k_2 + k_3 + k_4 + k_5)$, therewith the rate coefficients for the adsorption processes are multiplied by the relevant partial pressures (the rate coefficients of the elementary processes 1) - 5) were partly taken from the available literature, e.g., [3]). When appropriate process is chosen according to the adjusted $w_i$ ratio then an attempt of its realization is undertaken. Depending on the state of the randomly chosen cell (one - in case of 1st, 2nd and 4th processes; two - in case of 5th; four - in case of 3rd) the chosen process can either occur or not. E.g., if the $CO$ adsorption is chosen then for the success of this attempt the randomly chosen cell ($*_{hex}$ or $*_{1\times1}$) must be empty; in case of the $O_2$ adsorption two randomly chosen neighboring cells must be in the $*_{1\times1}$ state; if according the adjusted probability $w_3$ the process of $(hex) \rightarrow (1\times1)$ is chosen, we randomly choose the block from four (2×2) neighboring centers of the lattice, and if all of them are covered with $CO_{ads}$, then they become state $CO_{ads}^{1\times1}$, etc. Otherwise the state of the chosen cell (cells) remains unchanged. This procedure reflects indirectly the dependence of the stage rates on the surface coverages by adsorbed substances and, in our case, on the surface coverages by the different surface phases. Diffusion is necessary for the spatio-temporal processes synchronization occurring on the different regions of the model surface. In our model after each of N×N trial to carry out one of the processes (1) ÷ (5) the inner cycle of $CO_{ads}$ diffusion is arranged. The cycle consists of $M$ attempts of random choice of two neighbor lattice cells (in our computations $M$ was varied from 20 to 100). If such pair is $\{CO_{ads}, *\}$, then $CO_{ads}$ and * interchange their position, i.e. diffusion happens (stage 7). For all other pairs except for

# OP-A-4

$\{CO_{ads}, O^{1\times1}_{ads}\}$, an attempt of diffusion is rejected. If the pair is $\{CO_{ads}, O^{1\times1}_{ads}\}$, reaction (stage 6) occurs with releasing of active sites and forming of $CO_2$ (reaction rate counter increased therewith by a unit). The type of active sites remains the same. Thus, the rate of $CO_{ads}+O_{ads}$ interaction is determined by a number of diffusion trials (i.e., by $M$ parameter): at large $O^{1\times1}_{ads}$ coverages and sufficiently intensive $CO_{ads}$ diffusion the reaction rate is practically "infinite", while at small $O^{1\times1}_{ads}$ coverages the reaction rate is limited by $CO_{ads}$ transfer to small oxygen clusters. Realization of the 6th stage indirectly assumes that for the interaction of surface species the diffusion of mobile $CO_{ads}$ is required to overcome the potential barrier, in such a manner that $CO_{ads}$ faced with $O_{ads}$.

The synchronous variations of the reaction rate, $O_{ads}$ and $CO_{ads}$ coverages and *hex* and 1×1 surface phases exhibited within the range of the suggested model parameters (under the conditions very close to the experimental observations). These oscillations are accompanied with the autowave behaviour of surface phases and adsorbate coverages. In the course of simulations the distribution of local intensity of $CO_2$ formation was calculated. The simulation shows that the intensity of $CO_2$ formation in the $CO_{ads}$ layer is low, and the highest intensity of $CO_2$ formation is related to a narrow zone between the growing $O_{ads}$ island and surrounding $CO_{ads}$ layer («reaction zone»). The presence of the narrow reaction zone with atomic resolution was found experimentally (field ion probe-hole microscopy technique with 5 Å resolution) in [4]. Inside oxygen island the intensity of $CO_2$ formation is intermediate. The peak of the integral reaction rate corresponds to the maximal perimeter of the oxygen island. At the sufficiently high rates of $CO_{ads}$ diffusion and $O_{ads}$ + $CO_{ads}$ reaction ($M = 100$) the oscillations are characterized by nearly constant amplitude and period. The shape of oscillations also remains almost unchanged, though the active zones with elevated concentration of free active centres appear every time on new regions of the model lattice. The lowering of $M$ parameter down to 50 does not influence the regularity and uniformity of the oscillations but results in some decrease of period and amplitude. The further lowering of $M$ down to 30 leads to the nonregularity (chaotization) of the period and amplitude of oscillations and even to intermittence phenomena. In this case the adsorbed oxygen is always present on the surface in a shape of moving spots (cellular structure, fragments of spirals, strips, etc.).

The competition of the mechanisms of $O_2$ and $CO$ adsorption in combination with the processes of the surface structure transition *hex* ↔ 1×1 are the driving force for self-oscillations. At a proper choice of model parameters $k_i$ on the surface regions with elevated concentration of the active centres $*_{1\times1}$ the oxygen adsorption dominates, needed two neighboring free centers $*_{1\times1}$. Carbon monoxide adsorption prevails in zones with low local concentration of the active centres. $CO_{ads}$ diffusion and surface reaction represented by $M$ parameter synchronize the situation on different local regions of the surface thus governing the oscillation regularity. The increase of the rate coefficient for structural phase transformation (*hex*) → (1×1) leads to the disappearing of the wave phenomena on the surface, however the reaction rate and surface coverage's continue to oscillate.

The dependencies of oscillation features *versus* reaction parameters (e.g., $CO$ partial pressure) has been studied by means of step-by-step changing of these parameters. The boundaries of oscillatory behavior and hysteresis effects are revealed. Furthermore, the kinetic model, as a system of ordinary differential equations corresponding to the above mentioned detailed mechanism of the reaction, has been studied using the continuation algorithm, which allows to provide the bifurcation analysis of solutions and simultaneous analysis of their stability [5]. The reasons for the similarity and distinctions between dynamics of both models (ODE's system and Monte Carlo) are discussed.

Hence, the statistical lattice model constructed for $(CO+O_2)$/Pt(100) reaction takes into account the change of surface properties due to the adsorbate-induced reversible surface transformation *hex* ↔ 1×1. The model demonstrates the synchronous variations of reaction rate, $O_{ads}$ and $CO_{ads}$ coverages, *hex* and 1×1 surface phases under the conditions close to the experimental ones. Self-oscillations of the reaction rate are accompanied by autowave processes on the model platinum surface. The existence of the reaction zone between the moving adsorbate islands has been shown. The results obtained make possible to interpret the surface processes on the atomic scale. The computer movies illustrating the spatio-temporal dynamics of the adsorbed layer distribution and the local intensity of the reaction rate at different rates of reaction and $CO_{ads}$ diffusion are available at http://ieie.nsc.ru/~latkin/

1. G. Ertl. *Adv. Catal.*, 37 (1990) 213; *Surface Sci.*, 299/300 (1994) 742.
2. A. Hopkinson, X.C. Guo, J.M. Bradley and D.A. King. *J. Chem. Phys.*, 99 (1993) 8862.
3. R. Imbihl, M.P. Cox, G. Ertl, H. Muller and W. Brenig. *J. Chem. Phys.*, 83 (1985) 1578.
4. V. Gorodetskii, W. Drachsel and J.H. Block. In: *11th Intern. Congr. on Catalysis*, June 30 – July 5, 1996, Baltimore, Maryland, USA. Posters, Catalyst Characterization, Po-138.
5. V.I. Dyatlov, V.V. Konyashkin, V.S. Potapov, S.I. Fadeev. Film Electromechanics, Nauka, Novosibirsk, 1991, p.140-246.

**OP-A-5**

# THE REACTION OF CO OXIDATION ON THE DISCRETELY NON-UNIFORM SURFACE

Savchenko V.I., Fadeev S.I.*, Berezin A.Yu.*, Kalinkin A.V.,
Efremova N.I., Gainova N.A.*, Pavlova S.N., Ivanov E.A.

*Boreskov Institute of Catalysis, SB RAS, Russia*
** Sobolev Institute of Mathematics SB RAS, Russia*

The surfaces of real catalysts are not uniform regarding their structure (different metal facets) and chemistry (metal on support, oxides mixture). Most likely, the reaction proceeds on the interface and/or individual reaction steps occur on the different surface patches (phases), kinetically conjugated by the surface diffusion of adparticles. The task is to assess the possible kinetic effects associated with the surface diffusion of adparticles.

In the present work the mathematical models of CO oxidation on the non-uniform catalyst surface were analyzed using numerical simulation of the respective autonomous systems. The discussed surface consisted of the patches of two types, conjugated by $CO_{ads}$ diffusion. On each patch the reaction proceeded via the same mechanism (three- or five-step) but with different constants. Homotopic method has been used to obtain the diagrams of stationary states depending on temperature, P(CO), and other parameters. The domains of stability of the obtained stationary states were determined. The $CO_{ads}$ diffusion between patches proved to change considerably the bifurcation picture of the stationary states and to give rise to isols (i.e., isolated branches of solutions). For the three-step mechanism, kinetic conjugation of different regions causes synergistic effect. This is very promising for the designing of the catalyst for the low-temperature oxidation of CO. With this respect, the systems precious metal//reducible oxide are the most important. The studies of the model heterophase systems $Pd/Fe_2O_3$, prepared in the cell of the XPS spectrometer, revealed that the high activity of the catalyst in the low-temperature CO oxidation correlated with the oxide reduction to $Fe_3O_4$. Under the reaction conditions the surface of Pd is covered by $CO_{ads}$ , that of $Fe_3O_4$ - by $O_{ads}$. The reaction proceeds on interface $Pd\text{-}CO_{ads}//O_{ads}\text{-}Fe^{2+}$ ($Fe_3O_4$) and/or is facilitated by the diffusion of adparticles between phases. Catalyst $Pd/Fe_2O_3$, showing excellent performance in the low-temperature CO oxidation (300K), was prepared by the impregnation of $\alpha\text{-}Fe_2O_3$.

It has been studied how $CO_{ads}$ diffusion affects the domains of periodic solutions (i.e., the reaction rate autoosillations) for the conjugated five-step mechanisms. The numerical results were obtained using software “STEP”. Since the construction of stationary solutions includes the assessement of their stability by the Godunov-Bulgakov criterion and the sign of Jacobian, it is possible to find such parameters that provide autooscillations. It has been shown that the movement of the reaction boundary over the non-uniform Pt-edge in FEM, as well as the broadening and shift of oscillation range in P(CO), are attributable to the conjugation of different patches by $CO_{ads}$ diffusion. Complex oscillations, double period oscillations, complete synchronizing of oscillations can occur depending on the speed of $CO_{ads}$ diffusion between patches.

This work is supported by the Russian Fund for Fundamental Investigations, grant N 96-03-34002

## OP-A-6

# KINETICS MODELING OF MULTICOMPONENT MIXTURES CONVERSION IN OIL PROCESSING

V.S. Beskov, S.V. Getmantcev, A.V. Kravtsov*

*Mendeleev University of chemical Technology, Moscow, Russia*
**Tomsk Polytechnic University, Tomsk, Russia*

Complex composition of reacting mixtures, the plentity of simultaneously proceeding reactions and mutual conversions of reagents are peculiarities of chemical technological processes of oil processing. Using of modern kinetic of chemical reactions has principal restrictions:

- Very large dimensionality of reacting system, containing tens and hundreds substances. The amount of reactions is much more.
- The experimental research of all reactions and their mutual influence is impossible during reasonable time.
- The composition of processed mixtures varies rather frequently because of change of initial raw material and conditions of primary processing. Necessity of the frequent complete analysis of a processed mixture results in impossibility of process control in time.

Therefore the special methods of the mathematical description of conversions in a multi-component mixture are necessary. At the moment such approaches to construction of kinetic models for complex mixtures are developed.

*Statistical methods* [1,2] use polinomial models, combined some generalized parameters. These models as a method of "black box" are poorly reasonable theoretically, and describe process only in narrow interval of parameters changing.

*All-component description* [3] is half-useful for practical using because of complexity of the operative and complete analysis of mixtures.

*Aggregation* [4, 5] has received the greatest distribution. In this method the components are united in groups (units) by definite signs. These groups react between themselves as pseudo-components. The group aggregation does not take into account change of intragroup composition.

*Mixture of continuous composition* [6, 7] means physico-chemical properties of a mixture, including reactivity, not as a set of their determinated values, but as a continuous change of these properties by some parameter of the mixture, for example by a number of carbon atoms in component moleculs. This method does not take into account different chemical groups (paraffin, olefin, aromatic hydrocarbons etc.) and results in methodical errors.

**Discrete model of continuous composition componens** [8, 9] was suggested to predict technological process proceeding (conversion, selectivity, temperature) and technological properties of products (boiling temperature, combustion heat, density, octane level and other). This method combines advantages of aggregation method for distinguishing chemical groups, of method of continious composition mixture for consideration of changing of a group properties and uses discretic distribution as reflection of individual components. It permits to:

- support physical chemistry ground of the scheme of conversion between groups and inside its;
- describe the conversion compactly;
- reserve information about hydrocarbon conversion when raw material composition and process condition change;
- reduce a volume of additional information that is necessary for process controll under changing of raw material composition and process conditions.

Modeling of a number of multicomponent processes in oil processing has shown validity and perspectivity of use of the developed method to modeling of multicomponent processes as applide to oil processing.

## References

1. Bel'tcov B.A. Chemistry and technology of fuels and oils, 1967, N 4, P. 31
2. Rubekin B.F. Chemistry and technology of fuels and oils, 1966, N 6, P. 40.
3. Hutter T. and other - Journal of Applied Chemistry, 1972, N 11, P. 2574.
4. Gureev A.A., Jorov Ju.M., Smidovich E.V. - Production of hihly-octant gasolines, M., Chemistry. 1981.
5. Wei J., Kuo J.C.W. - Ind. Eng. Chem., Fundam., 1969, v. 8, N 1, P. 114.
6. Aris R., Gavalas G.R. - Roy. Soc. London, Phil. Trans., 1966, V. 220, P. 351.
7. Flock W., Kuznezov J.I., Hoffman J., Beskov V.S. - Chem. Techn., 1976, N 3, P. 138.
8. Kravtcov A.V. and other - Physical-chemistry aspects of development of petrochemical processes, M., CNIITEneftekhim, 1983. P. 34.
9. Moskvin V.S., Beskov V.S. and other - Modeling of process of catalytic reforming of gasoils, M., CNIITEneftekhim. 1990.

# OP-B-1

## MATHEMATICAL MODELING OF CONVECTIVE HEAT AND MASS TRANSFER IN A CHEMICAL REACTOR WITH FLOW REGION VARYING IN TIME

I.V. Melikhov, A.M. Kutepov, A.Ya. Gorbatchevski, A.G. Churbanov

*Lomonosov Moscow State University, Chemical Dept., Moscow, Russia*
*E-mail Gorba@radio.chem.msu.ru*

Formation of incrustations and sedimentations on walls as well as construction elements of chemical reactors, pipelines and heat-exchangers were investigated in the present study. Deposition of salts on walls and accessories of heat-exchangers, sedimentation of side products on walls of catalytic reactors, formation of incrustations on accessories of crystallization facilities take place in such installations. To analyze these phenomena, mathematical models are developed and employed for predicting influence of depositions formation on hydrodynamics and heat transfer. A model chemical reactor for mixing of species is considered taking into account homogeneous reactions (endothermic and exothermic) and convective motion of components. Calculations can be performed for real installations too.

### Heat and mass transfer of species in a reacting mixture

A model reactor for mixing species injected through separate inlets is investigated numerically. A flow of the mixture is laminar, second order homogeneous reactions are taken into account. It is assumed that all components have the same viscosity, density and temperature. Convective heat and mass transfer in the mixture is governed by the Navier-Stokes equations taking into account heat generation due to exotermic reactions. Sinks/sources of concentration are governed by the kinetics of homogeneous and heterogeneous reactions whereas heat generation is induced by external heating as well as thermal effects of reactions.

### Crystallization on the walls of apparatus

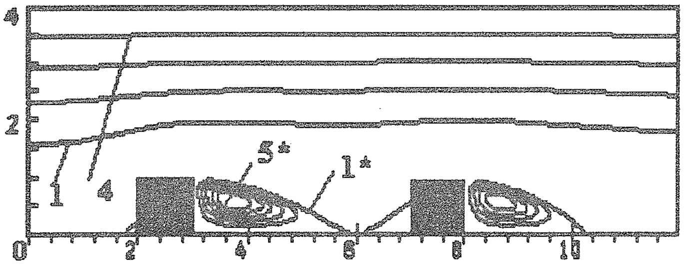
Origination and growth of crystalls AB takes place at each part of a wall contacting the solution. Initiation of growth points is treated as attachment or separation of molecules up to formation an element of surface being a face of an incrustation crystal. During the crystal growth on a wall there takes place overlapping faces growing along the wall.
This process is described by the following equation

$$\frac{\partial F_S}{\partial t} = \frac{\partial}{\partial l}\left[ b\frac{\partial}{\partial l}\left(G_{W0}F_S\right) - G_{W0}F_S \right] + \frac{\partial}{\partial l_1}\left[ b\frac{\partial}{\partial l_1}\left(G_{W1}F_S\right) - G_{W1}F_S \right]$$

where $F_s = \partial^2 A/\partial l_1 \partial l_2$, A- the number of crystals with the width lower then $l_1$, and height $l_2$ at the wall surface, b - the averaged scale of fluctuations, $G_{W0}$ and $G_{W1}$ – average rates normal and tangential with respect to the surface, respectively.

### Heat and mass transfer in a domain varying in time

Geometry and properties of the flow domain varying in time during growth or dissolution of incrustations. The following subdomains are involved in conjugate heat and mass transfer: a solution flow, a porous (permeable) medium and impermeable walls. Porous media can appear at soluting multi-phase incrustations (with various soluble properties of phases), growth of dendridic crystals etc. Porosity is lightly varying in time and in the reactor volume during this process.



Values of stream function contours:
0.444 (1), 0.889 (2), 1.334 (3),
1.778 (4), In vortex -0.006 (1*),
-0.012 (2*), -0.019 (3*),
-0.025 (4*), -0.031 (5*).
1-0.444, 2-.....

Fig.1 Flow pattern for two obstacles, Re=20

**Numerical experiment**

**Incrustation of a wall during crystallization**

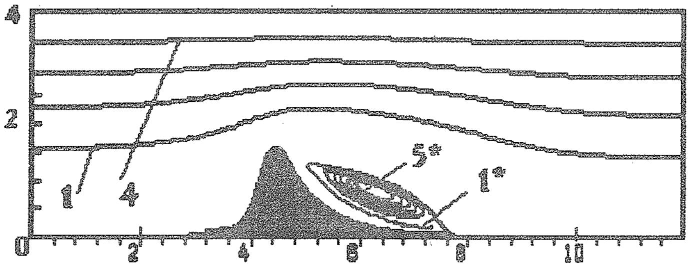
If a solution is injected into the reactor then crystals are growing on its walls. The incrustation process has two formation stages: island-like incrustations and continuous film of incrustation at the surface. The growth rate of incrustation crystals depends on the solution supersaturation, local characteristics of hydrodynamics, deposition of impurity particles etc.

**Flow about a system of obstacles**

A reagents flow over a number of obstacles is considered (see Fig.1). Primary characteristics of the flow field and detected conditions of transition from separate recirculation zones were studied at various flow regimes.

**Conjugate problem of incrustation growth and flow domain variation**

At the beginning of the process there is a rectangular obstacle on the wall. Two recirculation zones appear near the obstacle (in front and behind). This results in incrustation growth near the obstacle and, recpectively, in variation of the channel geometry.



Values of stream function
contours:0.444 (1), 0.889 (2),
1.334 (3), 1.778 (4), In vortex
-0.0001 (1*), -0.0003 (2*),
-0.0005 (3*), -0.0006 (4*),
-0.0008 (5*).

Fig.2 Flow pattern for a deformed obstacle with incrustation on it, Re=20

**Heat transfer in the region of incrustation growth**

Heat transfer in the system: moving solution - incrustation of varying width - rigid wall was investigated. Temperature fields and heat fluxes were determined for different flow regimes and governing parameters. It was shown that incrustation growth leads to decreasing heat transfer rate through the walls.

The following effects have been analyzed via numerical experiments:

*Peculiarities of incrustation deposition: formation of incrustation islands, formation of a continuous film of incrustation, roughness of incrustations, minimal, maximal and mean thickness of incrustation.*

*Hydrodynamics: the flow domain is varying in time, variation of primary flow characteristics at incrustation growth in the vicinity of obstacles*

*Dynamics of heat transfer change through inctrustated walls: the change of heat flow through the wall with variable geometry and coefficients of transfer.*

# SECTION B

## PHYSICO-CHEMICAL AND MATHEMATICAL FUNDAMENTALS OF PROCESSES IN CHEMICAL REACTORS

## OP-B-2

# THE MATHEMATICAL MODELING OF AEROMECHANIC PROCESS IN APPARATUS WITH POROUS INSERTION

Balakaeva G.T. , Zhapbasbaev U.K.
*Kazakh State University, address: Almaty, 480090,*
*Universitetskaya st., 30, 76, ph. (3272) 64-59-69*

Some applied problems, for example, waste gases utilization in industry, automobile transport exhaust gases after-burning defines the necessity of investigation of full aerothermochemical process on the base of combine examination of equation in each media with the use of conjunction boundary conditions on boundaries of media division.

Our mathematical model constitutes a set of hydrodynamic and heatmass exchange equations with usage of chemical transformations for reactor with axlial symmetry. Movement equations are solved combinely with heatmass transfer equations, which describe the transfer of heat in solid and gas phases and transfer of reactant substance.

Numerical method of solution allows to conduct combine solution of set equations in running parts of apparatus and in grained bed with usage of boundary conditions on boundaries of media division.

For description of turbulent movement in running parts of apparatus two-parameters k-ε model is used, the ratio of effective viscosity in porous medium is defined by algebraic model of turbulence.

We made calculating theoretical investigations with wide variation of regime parameters. The results are obtained, which show hydrodynamic and thermal characteristics distributions in industrial apparatus.

As a result of calculation the influence of different regime and constructive parameters on aerodynamic of apparatus is revealed, that is: intensisty of heat exchange with surrounding medium, wall nonuniformity, ..., etc.

The suggested mathematical model and method of aerothermochemical process calculation in apparatus with porous insertion allows to uncover aerodynamic and heatmass transfer regularities, and to estimate apparatus efficiency.

The result of that calculation allows to get not only full view of thermal and dynamic characteristics distribution, but methods to affect them with the aim to increase apparatus efficiency.

In more complex constructions to described above, other types of nonuniformity are added, that results in decreasing of main product output. Consequently in each case it is necessary to calculate airthermal process and then after getting information about flow parameters distribution, to find methods to increase reactor efficiency.

**OP-B-4**

# NONEQUILIBRIUM THERMODYNAMICS OF HEAT WAVES PROPAGATION IN A CATALYTIC FIXED-BED

A.P. Gerasev

*Boreskov Institute of Catalysis SB RAS*

*Novosibirsk, 630090, Russia, e-mail: gerasev@reverse.nsk.su*

The phenomenon of heat waves propagation in a catalytic fixed-bed is one of the vivid examples of derivation of spatiotemporal dissipative structure in fissile mediums. A key to understanding a nature of these structures is the determination of a common principle of a compounded course of physicochemical processes ensuring their spatiotemporal fastness.

The elementary mathematical model of a catalytic fixed-bed is created in approximation for two interpenetrating continuums filling the same volume. The model takes into account a convective stream of a reactionary admixture, chemical transformation of substances and effective thermal conductivity of a catalytic fixed-bed. The stationarity of the characteristics of heat waves allows to reduce the mathematical description of non-stationary process to the system of two nonlinear ordinary differential equations. The task contains the unknown parameter - rate of propagation of a heat wave, which is the subject for definition. In [1, 2] the existence of multiplicity of the autowave solutions of the first and second type is strictly shown at a course of a reversible reaction in a catalytic fixed-bed. The slow heat waves (SHW) (autowave solutions of the second type) can spread in a preliminary heated catalytic stratum at feed of a cold reactionary admixture and correspond to the only physically reasonable solution of the task. Therefore, it is not enough to know the conservation laws of mass and energy to choose this unique solution, additional suppositions are needed.

The second beginning of a thermodynamics, reflecting an irreversibility of all actual macroscopic processes, expresses the law of development of a substance. Accepting a condition of local quasi-equilibrium and using thermodynamic relations [3] the law of conservation of energy in a catalytic fixed-bed can be written as an entropy balance and terms matching to the local production of the entropy ($\sigma$) can be allocated. It is shown, that $\sigma$ is the positively defined function from temperature and concentrations of reagents, which by virtue of boundary conditions of mathematical SHW model aspires to zero at plus and minus infinity. The complete production of entropy in a catalytic fixed-bed $P$ is an integral from $\sigma$ on length. Let's mark, that by virtue of Curie's principle of reflection the thermodynamic forces and the fluxes of various tensor dimension can not be connected among themselves [3]. Therefore, Onsager's reciprocal relations in a considered case do not play a role.

The autowave solution of SHW model corresponds on the phase plane to a trajectory - a separatrix of a saddle connecting two singular points. First, defined by conditions at minus infinity, is nodal, second - the cross point of isoclines of thermodynamic equilibrium and thermal balance at plus infinity - is saddle. For arbitrary selected value of SHW propagation rate ($\omega$) it is possible numerically to construct an included in saddle point of trajectory, integrating a set of equations in return time. For each trajectory the values of $\sigma$ and $P$ were calculated. The computing experiment has shown, that the distribution functions of $\sigma$ on length of a catalytic fixed-bed have a brightly expressed maximum. At decrease of $\omega$ trajectories pass through the area of lower temperatures and $\sigma$ decreases in each point of a catalytic fixed-bed together with its maximum value. At the same time dependence of $P$ from $\omega$ wears an extreme character. The minimum of $P$ corresponds to an only trajectory - SHW image, for which the concentration of reagents practically equal to the entry values at higher temperatures, than temperature on an inlet in a catalytic fixed-bed.

Obtained outcomes have allowed to construct the formalized procedure of choice of the unique physically reasonable solution of the task of one-parameter family of the autowave solutions, by supplementing the mathematical SHW model with the equation for calculation of the complete entropy production.

Thus, the phenomenon of SHW propagation appeares as a result of coordinated stable course of physico-chemical processes in catalytic fixed-bed and complete entropy production in system is a functional of this autowave process (spatiotemporal dissipative structure).

*References*

1. Gerasev A.P., Chumakova N.A., *Phys. Goren. Vsriva*, 1997. V. 33, № 5, P. 53-62 (in Russian).
2. Gerasev A.P., Chumakova N.A., Matros Yu.Sh., *Chem. Eng. Sci.*, 1997, V. 52, № 5, P. 693-701.
3. De Groot S.R., Mazur P., *Nonequilibrium thermodynamics*, North Holland, Amsterdam, 1962.

# OP-B-5

# COMPARATIVE STUDY OF UNSTEADY STATE REACTION PERFORMANCE CONTROLLED BY SPATIAL REGULATION AND BY PERIODIC OPERATION: TWO SITES KINETIC SCHEME MODELING

**E.A. Ivanov, S.I. Reshetnikov , A.A. Ivanov**
*Boreskov Institute of Catalysis, Novosibirsk 630090, Russia*

**L. Kiwi-Minsker, R. Doepper and A. Renken**
*Swiss Federal Institute of Technology Lausanne (EPFL), Switzerland*

Experimental and theoretical studies during the last decades have given enough evidence that methods of unsteady state heterogeneous catalysis can lead to improvement in reactor performance compared to optimal steady state operation. Using surface dynamics it is possible to achieve and maintain the catalyst surface in an optimal state in order to increase the selectivity towards a specific product formation. This can result in an increased yield of the desired product.

The catalyst unsteady state can be controlled in two ways:

- by forced oscillations of reagents concentrations or flow reversal (regulation by periodic operations) [1-3];
- by spatial regulation when input and output parameters of the reactor do not change with time, but the catalyst moves in a field of variable reagents concentrations and temperature either in a fluidised bed or in a dual-reactor system [4-5].

This work is aimed on the comparative study of reaction unsteady state performance controlled by

(i) periodic operations of reactor and
(ii) spatial regulation in a dual-reactor system.

The modelling is based on the two kinetic schemes shown below:

| Scheme I | Scheme II |
|---|---|
| $A + S_1 \leftrightarrow AS_1,$ | $A + S_1 \rightarrow B + S_1,$ |
| $A + S_2 \leftrightarrow AS_2,$ | $A + S_2 \rightarrow C + S_2,$ |
| $AS_1 + S_2 \rightarrow B + S_1 + S_2,$ | $S_1 \leftrightarrow S_2,$ |
| $[S_1] + [AS_1] = 1,\ [S_2] + [AS_2] = 1.$ | $[S_1] + [S_2] = 1.$ |

These kinetic schemes are based on two types of active sites ($S_1$) and ($S_2$). The first scheme assumes that the reaction rate is proportional to the concentrations of occupied sites

($AS_1$) and empty sites ($S_2$) [6]. The second scheme assumes that the reaction rate is proportional to the concentrations of both empty sites ($S_1$) and ($S_2$) and suggests a transformation of one-type sites into another [7]. This transformation depends on the reaction temperature. At low temperature one type of sites predominates on the surface and at high temperature another. It is therefore possible to control the catalyst surface and consequently the reaction selectivity, since different products (B or C) are formed on the different active sites ($S_1$) or ($S_2$).

Based on the schemes of the reaction kinetics, the influence of various parameters like temperature, concentrations of reagents, period of forced oscillations, etc. on the reaction rate and selectivity was studied.

The model of forced concentration oscillations predicts mean reaction rates, which can exceed more than twice the maximum observed under optimal steady state conditions. A single analytical solution was found to describe the mean performance as a function of concentration, length of period and cycle split.

In the model proposed for the dual-reactor and scheme II the catalyst is supposed to circulate between two reactors with different temperatures. In the first reactor, with a low temperature, the catalyst surface would have mostly ($S_1$) type of sites. In the second reactor, with a high temperature the catalytic reaction takes place, followed by transformation of ($S_1$) to ($S_2$) sites. After the reaction the catalyst moves back to the first reactor for ($S_1$) sites regeneration. During circulation between the reactors the catalyst particles permanently change their catalytic properties, since they are in unsteady state with respect to the surrounding media.

It was shown that the main parameters influencing the state of the catalyst were the reaction temperature, the amount of the catalyst in each reactor and the rate of the catalyst circulation between two reactors. The rate of circulation is mostly determined by the rate of ($S_1$) to ($S_2$) sites transformation (see scheme II).

The optimisation of the above mentioned parameters allowed to increase the selectivity towards the desired product from 66.7% up to 83%.

The method of unsteady state regulation in dual reactor system is proposed for reactions of partial oxidation of hydrocarbons.

## ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support from the European Commission under the INCO-COPERNICUS Programme (Grant N° IC15-CT97-0709).

## REFERENCES

1. A. Renken, *Int. Chem . Eng.*, 24, N° 2 (1984) 202.
2. P.L. Silveston, R.R. Hudgins and A. Renken, *Catalysis Today*, 25 (1995) 91.
3. J.A. Moulijn, R.A. Sheldon et. al. in: *Catalysis: An Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis*, (eds. J. A. Moulijn, P.W.N.M. van Leeuwen and R.A. van Santen), Elsevier, Amsterdam, (1993) 23.
4. R.M. Contractor, A.W. Sleight, *Catalysis Today* 3, (1988) 175.
5. A.A. Ivanov, B.S. Balzhinimaev, in *Unsteady State Processes in Catalysis*, (ed.Y.S.Matros), VSP, Utrecht, (1990) 91.
6. J. Thullie, A. Renken, *Chem. Eng. Sci.*, 46, N°4, (1991) 1083.
7. S.I. Reshetnikov, E.A. Ivanov et al., *Chim. Prom.*, 80, (1997) 382.

# QUALITATIVE AND QUANTITATIVE $^1$H NMR IMAGING STUDY OF MASS TRANSPORT IN POROUS SOLIDS DURING DRYING

Igor V. Koptyug[1], Renad Z. Sagdeev[1], Valentin N. Parmon[2], Vladimir B. Fenelonov[2],
Ludmila Yu. Khitrina[2], Sergei I. Kabanikhin[3], Kazizat T. Iskakov[4]

[1]International Tomography Center, [2]Boreskov Institute of Catalysis,
[3]Sobolev Institute of Mathematics, Novosibirsk 630090, Russia,
[4]Karaganda State University, Karaganda 470012, Kazakhstan

Transport phenomena in porous catalyst grains are the processes of top importance for heterogeneous catalysis because very often these are determining the behavior of real industrial catalysts and their activity. Typically, transport coefficients are determined by measuring the concentration (or flux) of a diffusing substance on the outlet of particular model entities as a function of time or by measuring the spatial concentration distribution within the sample at a single time by sectioning the sample. The classical way for obtaining concentration profiles is the gravimetric method. However, it has two major disadvantages regarding concentration profiles. First of all it is a destructive method and therefore every profile has to be determined using different samples. Secondly, the method is not accurate in its spatial resolution. Slices which can be cut are of the order of 0.5-1 cm, depending on the type of material. Apparently, an experimental method for determining an evolution of concentration profiles should be non-destructive and give a high spatial resolution. NMR-imaging is method which satisfies such requirements.

In our experiments evaporation of water, acetone, benzene and other solvents from gamma-$Al_2O_3$ samples with varying porous structure and from industrial catalyst CRS-31 ($TiO_2$) was studied. The presoaked cylindrical samples (3.6 mm in diameter) were positioned inside the rf coil of the NMR probe and were subsequently dried at ambient temperature and various flows of dry nitrogen. One dimensional two-pulse spin-echo was optimized to yield an acceptable sensitivity for real-time monitoring of the drying process in the samples with very short $T_2^*$ times (0.5-2.5 ms), and was employed to obtain radial distribution of the liquid in the cylindrical samples. For quantitative analysis the profiles detected have been corrected for the inevitable $T_2$-weighting, employing a calibration curve obtained in a separate experiment.

# OP-B-6

We have found that for acetone, benzene and cyclohexane radial concentration profiles rapidly acquire a round-top shape immediately after the drying is initiated. This indicates that the drying proceeds in the rapid drying regime, implying that redistribution of liquid is not efficient enough to compensate for liquid losses at the sample periphery. The same is true for water at the late stages of drying, when about one half of the initial water content is removed, and a substantial decrease of the drying rate is observed. At the early stages of water evaporation, however, capillary flows compensate successfully for water losses at the periphery and maintain uniform water distribution across the sample, ensuring the constancy of the drying rate.

At the same time, we have demonstrated that the technique is sensitive to the fine details of the drying process. It has been observed that the transformations of the water concentration profiles depend on the pore size distribution of the sample under study. For alumina sample with a more pronounced "bimodality" in the distribution of pore sizes this leads to a peculiar rectangular, round-top, rectangular, round-top sequence of profile shape transformations. This indicates that capillary suction is efficient enough to maintain a quasi-equilibrium at each instant of the drying process. In the case of acetone evaporation, capillary suction is much less efficient due to much lower surface tension, and concentration gradients gradually increase with time throughout most of the drying process.

To obtain quantitative characteristics of mass transport in the course of drying, the process was modeled as radial diffusion in a quasi-homogeneous medium with appropriate boundary conditions. It is demonstrated that for liquids characterized by low surface tension, such as acetone, benzene and cyclohexane, transformation of concentration profiles can be adequately modeled assuming liquid content independent diffusivity. In contrast, the diffusivity for water in titania and alumina pellets substantially decreases with the decrease of water content. For alumina pellets with a pronounced "bimodality" in the pore size distribution the water concentration dependence of diffusivity is shown to be non-monotonous. It is argued that for liquids with high surface tension the shape of concentration profiles and the behavior of diffusivity as a function of liquid content are both related to the shape of the cumulative pore size distribution of the porous solid under study due to the existence of efficient capillary flows induced by capillary suction.

# SECTION C

## NEW TYPES OF CHEMICAL PROCESSES AND REACTORS

# Photocatalytic Reactors for Removal of Volatile Organic Air Contaminants

A.V.Vorontsov and E.N.Savinov
*Boreskov Institute of Catalysis*
*pr.ak.Lavrentieva 5, Novosibirsk 630090, Russia*

Photocatalytic oxidation of gaseous organic contaminants is a promising method of air purification. Oxidation can be fulfilled at room temperature and atmospheric pressure using sunlight. Besides organic contaminants removal, photocatalytic oxidation destroys microbes [1]. The rate of oxidation is limited by UV light flux from light source. Therefore, photocatalytic technology can be competitive in purification of air with low contaminants concentration, for example, of air in buildings. However, a row of problems have to be solved for successful use of this technology.

We have carried out photocatalytic oxidation of volatile oragnic solvents vapours by air oxygen in a static reactor with titanium dioxide photocatalyst deposited on honeycomb supports. $CO_2$ and $H_2O$ are final products of oxidation. Oxidation of acetone vapours did not result in any gaseous intermediates. Oxidation of ethanol and diethyl ether vapours led to formation of acetaldehyde. Of vital significance for air decontamination is to stop such hazardous intermediates from releasing.

This releasing can be avoided by using long residence time in flow reactors. Indeed, passing of acetone vapour-air mixture through quartz coaxial cylindrical reactor equipped with DB-15 lamp with residence time >1 min result in complete acetone degradation. Air flow was less than 1 l/min under these conditions.

To treat higher air flows it is necessary to use more powerful light source and change the reactor geometry to create a good contact of reagents and light with photocatalyst.

A reactor of this type has been developed at our Institute. Photocatalyst was deposited on ring nettings made of stainless steel. The nettings were arranged coaxially and perpendicularly to a cylindrical lamp DRT-1000. The apparent rate coefficient of acetone oxidation has proved to be directly proportional to light intensity of the lamp at air flow rate 14 $m^3/h$. Thus, the reaction rate is not limited by diffusion of reagents to the photocatalyst surface.

Test results of this reactor in oxidation of some organic compounds are shown in the table below for air flow rate 14 $m^3/h$.

| Compound | Initial concentration, ppm | Conversion, % |
|---|---|---|
| trichloroethylene | 78 | 45 |
| ethanol | 65 | 95 |
| acetone | 28 | 85 |

During the tests it has been revealed that the concentration of unreacted compound changes along reactor radius. This is due to non-uniform light consumption across the reactor. One can demonstrate easily that the highest conversion will be achieved under uniform light consumption across the flow of air in the reactor.

In order to optimize the light distribution in netting photocatalytic reactors mathematical models were created for calculation of conversion as a function of netting arrangement, netting parameter, rate coefficient and dimentionless sizes of reactor. Reaction was taken to be of first order in contaminant concentration and consumed light intensity. Diffusion was not taken into account. Three nettings arrangements were modeled: ring nettings coaxial and perpendicular to the lamp; truncated cone nettings coaxial to the lamp; cylindrical nettings coaxial to the lamp. Computer calculations demonstrated that the highest conversion can be achived in reactor with cylindrical nettings.

## References

1. T.K.Goswami, S.Hingorani, H.Greist, D.Y.Goswami, S.S.Block, Abstracts of The Third International Conference on $TiO_2$ Photocatalytic Purification and Treatment of Water and Air, Orlando, Florida, USA, September 23-26, 1997, p.32.

# OP-C-2

# APPARATUS FOR OXIDATIVE DEHYDROGENATION OF HYDROCARBONS

Ackhundov A.A., Alimardanov H.M., Shabanova C.M.

*Institute for Theoretical Problems of Chemical Technology, AS Baku, Azerbaijan*

## *Modelling processes of oxidative dehydrogenation of hydrocarbons on a surface of the catalyst*

Experimental research of the influence of convectional and diffusional thermo-mass transfer speed in a granular layer of the alumo-copper catalyst of an industrial type has been conducted.

Study of kinetic laws of oxidative dehydrogenation (OD) reaction of individual isomers of methylcyclopenten /MCPE/ in the presence of Al-Cu-Mo-O catalytic systems, immobilized on spherical pills, the average diameter of which is $d_4$ = 0,5-2,0 mm, were carried out in experimental tubes with fixed height of layer l = 0,6 m at various diameters of the apparatus $d_p$ = 0,45-1,8 cm.

The results of separate experiments were obtained in a wide area of process parameters (partial pressure of methylcyclopenten $P_{MCPE}$ varied from 12,7 to 15,5 kPa, $V_{MCPE}$ specific volumetric velocity from 63 to 426 $h^{-1}$, partial pressure of oxygen $P_{O_2}$ from 1,5 to 4,7 kPa, reaction temperature T from 623 to 723 K.

The model of OD MCP process of key components taking into account convectional and diffusional thermo-masstransfer is solved as system of the differential equations in partial derivatives with boundary conditions.

The effective coefficients of diffusion were found during the solution of reverse problem, that is were determined from condition of applicability of the diffusion and thermo-conduction equations in view of chemical reaction for the description of thermo-masstransfer processes on a pill of the oxide catalyst.

Numerical experiment allowed to construct profiles of concentration and temperature radial distribution for various times of contact and diameters of pill. The received structures are possible to consider practically constant on the whole section of pill (of the apparatus). Only the rather narrow layer of grain surface of the catalyst is considered to be responsible for sharp change of structures, that confirms the assumption, that just a thin boundary layer of the catalyst is responsible for oxidative dehydrogenation process of hydrocarbons, while deeper penetration of molecules into a pill of catalyst - for processes of aromatization, cracking and deeper oxidation.

Criteria estimations of thickness of concentration and thermal boundary layers are obtained, which should be taken into account at designing and intensification of OD processes.

### *Apparatus for oxidative dehydrogenation of hydrocarbons*

The oxidative transformation of hydrocarbons belongs to a perspective direction in a chemical industry, to a class of processes, for which methods of mathematical modeling, allowing to solve problems of optimization, are rather full developed. With this purpose concurrent system of reactors is offered.

The results of theoretical optimization of high-exothermal temperature profile of OD MCPE process are considered, which at the stage of designing allow to choose the reactor, in which the process in the best way approaches theoretically optimum mode, and for acting reactors - to establish limits of its intensification.

The solving of problems on theoretical optimization of a temperature profile is reduced to TOTP determination, providing maximum output of a target product with the greatest selectivity per volume unit of reactor, in view of technological restrictions. For this solution a method of TOTP search with the use of Pontragin maximum principle was chosen. With this purpose the program module, being updating of a Bycov-Jablonscky-Slinco method, was developed. Theoretically optimum nonlinear profile has been received.

The TOTP form, probably, is connected with the fact that the rates of reactions of partial oxidation MCPE to MCPD and destructive oxidation rise with increasing of contact time. It is shown, that such thermal mode can be realized in multi-shelf concurrent reactor at the account of heat emission intensification in intersection thermoexchangers, where quasi-stationary part is approximated by reactor with organized pseudoliquefied oxide catalyst layer. Initial and tail parts of TOTP are approximated by adiabatic reactors with intermediate heat emission and by-sectional submission of oxygen.

The final confirmation choice of technological designing of reactionary system is possible in view of technical and economic parameters during tests of process in integrated scale.

## *Dynamic modeling of oxidative dehydrogenation processes of hydrocarbons*

The research of transient modes of closed system "reactor-thermoexchanger" (R-T) was carried out with the purpose of definition of stability of oxidative dehydrogenation (OD) process of methylcyclopenten (MCPE) in multi-shelf adiabatic reactors with intermediate heat emission and by-sectional submission of oxygen at small deviations of entrance parameters (concentration, temperature) from stationary condition.

With this purpose gear function of (R-T) system reflecting dependence of outlet vector of system condition from vectors of condition (concentration and temperature) on its input, was synthesized.

Reactor system works in an automatic mode, at which a temperature of reactionary mixture on input in reactor is previously increased in thermoexchanger, located in the space between layers of the catalyst.

The similar catalytic system has a positive feedback on the temperature channel, is unstable and therefore cannot function without reliable system of automatic control (SAC), that is important to provide at the stage of designing.

The research of dynamic peculiarities of OD MCPE process assumes construction of gear functions on various dynamic channels, solving of questions of process dynamic stability and synthesis of (SAC) systems on their basis.

The dynamic model of adiabatic reactor was constructed on the basis of mathematical model of the process' static, in the assumption, that in reactor ideal replacement on raw material and heat takes place.

The program module of the numerical solution of the nonlinear differential equations system in partial derivatives is developed, gear functions on various dynamic channels are determined and on their basis complete gear function of "reactor- thermoexchanger" system is synthesized, peak-frequent characteristics, allowing to solve questions of dynamic stability of adiabatic reactor and synthesis SAC, are constructed.

## PP-C-3

# PLASMOCHEMICAL PROCESSES AND REACTORS

**A.G. Karengin**, **I.A. Tikhomirov, A.V. Merkulov, S.A. Sosnovskii**

Tomsk Polytechnic University, Tomsk, 634004, 30 Lenin avenue, Russia
Tel. (382-2)-419-143

## THERMODYNAMIC MODELING OF PLASMOCHEMICAL PROCESS FOR OBTAINING OF ULTRADISPERSIVE CATALYTICALLY ACTIVE MATERIALS

A.G. Karengin, I.A. Tikhomirov, A.V. Merkulov

Ultradispersive catalytically active materials on the basis of complex oxides of transition and rare-earth metals (UDCM), received in conditions of low temperature plasma, find practical application in processes catalytic purification of gaseous wastes of the industrial enterprises [1,2]. However, the process of obtaining of such UDCM in conditions of low temperature plasma is yet few investigated.

In the given work results of thermodynamic modeling of process of practical obtaining of UDCM from dispersed aqueous solutions of metal salts (Cu, Cr, Ni, Co, Ce) in air and reducing plasma are submitted. The accounts were carried out at P=0.1 MPa, T= 300-6000 K, for initial parity plasma heat-carrier : solution = 20-80 % at total concentration of salts of metals 5-20 %. Thus the initial share of reducer ($H_2$, $C_2H_2$, $C_4H_{10}$, or $CH_3COOH$, $C_2H_5OH$) in system did not exceed 15 %.

The analysis of received equilibrium composition shows that in air plasma in the whole range the change of initial parameters of UDCM composition in a condensed phase depends only on working temperature of process.

So, copper at T = 1200 - 2300 K is in a condensed phase, mainly as $Cu_2O$ and at T < 1100 K - as CuO. Nickel at T < 1700 K is in a condensed phase only as NiO. Cobalt at T=1300-1700 K is in a condensed phase, mainly as CoO, and at T < 1200 K to - as $Co_3O_4$. Chromium at T < 2200 K is in a condensed phase only as $Cr_2O_3$. Cerium at T=2300-3200 K is in a condensed phase, mainly, as $Ce_2O_3$, and at T < 2200 K - as $CeO_2$.

The replacement of a part of the air heat-carrier by 3 % $H_2$, 5 % $C_2H_2$, 5 % $C_4H_{10}$, or input of 10% $C_2H_5OH$ in an initial solution essentially change composition UDCM in a condensed phase in comparison with air plasma.

So, at T < 1700 K copper, nickel and cobalt are in a condensed phase, only as metal kind. Chromium at T < 2700 K is in a condensed phase, as well as in air plasma, only as $Cr_2O_3$. Cerium at T=2100-3200 K is in a condensed phase, as well as in air plasma, as $Ce_2O_3$, and at T < 2100 K to - as $CeO_2$.

Decrease of a share of these reducers in the system results in that in a condensed phase one and the same elements are as oxides and metals simultaneously.

The accounts of theoretical specific power inputs on obtaining of 1 kg of a target product as UDCM in air and reducing plasma for the specified above conditions have shown, that they poorly depend on a type of the plasma heat-carrier, decrease with increase of concentration of salts of metals in an initial solution and sharply grow with increase of working temperature of the process above 2000 K. In an interval of temperatures 1000 - 1500 K they make up 10-20 KW*hour per 1 kg UDCM.

Thus, selecting a type of the plasma heat-carrier, parity air: reducer, working temperature of plasmothermic process and applying "tempering" of products of plasmothermic processing of aqueous salt solutions of metals it is possible to receive purposefully UDCM of required structure.

## PLASMOCHEMICAL REACTOR FOR REGENERATION OF ETCHING SOLUTIONS

A.G. Karengin, I.A. Tikhomirov, S.A. Sosnovskii

In manufacturing of catalysts, absorbents, especially pure substances and divided materials, thermochemical processes in conditions of phases dispersing are widely spread.

There are many apparatus for thermal rendering safe and regeneration of industrial waste waters of metallurgical factories, that work by principle of chemical sputtering reactors, in particular, in contrary jets, where in quality of a high enthalpic gas-heat-carrier it is possible to use plasma of high frequency flare (HFF) and arc discharges [3]. As an example process of simultaneous obtaining synthetic $TiO_2$ and regenerated etching solution from fulfilled etching solutions. Highly dispersed oxide powders produced can be widely used as catalysts, pigments, fillers of polymeric and rubber containing products, and in other areas of a science and engineering. As an initial mixture, submitted on an entrance of the chemical reactor, real fulfilled muriatic-hydrofluoric mixtures were used that left after etching of a titanium and have the following structure: HCl - 6-8%; HF - 0,81%; $\sum$Ti - 20-30% g/l; $H_2O$ and pollution - other; temperature - 50-60°C.

Synthesis of highly dispersed powder of $TiO_2$ and regeneration of muriatic-hydrofluoric mixture have been conducted in a “sputtering reactor” test bench in temperature limits from 400 up to 700 °C with an interval 100 °C.

The structure of the titanium oxide was determined for each temperature of experiment. Regenerated muriatic-hydrofluoric mixture had the following structure: HCl - 6-8%, HF - 1-1,5%, Ti - 2,5 g/l, $H_2O$ -other.

The investigated process can be described by the following general equation:

$TiOF_{2\,(solution)} \xrightarrow{t} TiO_{2\,(solid)} + 2HF_{(gas)}$

Thus, received regenerated acid return back on etching and highly dispersed powder of the titanium oxide is realized as a commodity product. Investigations have shown that major factors, determining properties of products, are temperature in a zone of reaction and concentration of a solution.

Products have been estimated by two parameters: to the contents of the basic substance (liq., sol.) and specific surface (sol.)

The results of work give the basis to believe, that the regeneration of muriatic-hydrofluoric mixtures from fulfilled solutions, formed at etching of titanium, by thermochemical processing in sputtering plasmochemical reactor is technically possible. However it is necessary to solve a number of technological problems. First, it should be developed new or specified known methods of the chemical analysis, which would allow receiving the reliable information on chemical structure of initial substances, intermediate and final products of regeneration. Secondly, hardware processes require the serious study, among which choice of sputtering thermochemical reactor (contraflow, with partial ablation or direct-flow with complete taking out) are the most important. Here it is necessary to attribute problems of dust separation, connected, on the one hand, with a type of reactor, and on the other hand with the search of new means, promoting dust separation of highly dispersed products. Thirdly, more careful technological study of a question about use of firm products of regeneration is necessary.

In this work we consider an opportunity of regeneration of etching solutions and reception highly dispersed powders of titanium oxide and iron from fulfilled etching solutions in conditions of low temperature plasma. The scientific-reasonable recommendations for realization these plasmochemical processes are submitted.

## LITERATURE

1. Karengin A.G., Gubaidulina T.A., Arefieva R.A. Catalysts consume of departing gases enamel unit on the basis complex oxides of base metals. Cable Engineering, № 6,1995, c.1-42.
2. Tikhomirov I.A., Karengin A.G., Gubaidulina T.A., Arefieva R.A Clearing departing gases of furnaces enamel unit by ultradispersive catalysts. Materials of an International Conference "Ultradispersive powders, materials and nanostructuere", Krasnoyars, 1996, p. 17-19.
3. .Rodionov A.I., Klushin B.H., Torocheshnikov H.C."Engineering of protection of an environment", Moscow: Khimiya, 1989, p.512.

**OP-C-5**

# HETEROGENEOUS CATALYTIC REACTOR FOR CREATION OF AIR-AMMONIA MEDIA IN TECHNOLOGY OF STRENGTHENING THE METALS AND ALLOYS ARTICLES

V.Ya. Syropyatov, V.V. Barelko, V.M. Zinchenko, L.A. Bykov

*NIIT Avtoprom, Moscow, Russia*
*Institute of Chemical Physics RAS, Chernogolovka,Russia*
*JSC "Chemphyst", Chernogolovka, Russia*

The report is oriented to a development of notions connected with mechanisms and kinetic of the reactions proceeding when the ammonia-containing gaseous media interact with the surface of different metals and alloys. Such reactions constitute the base of the widely used in the machine-building technology processes, namely the low-temperature thermochemical processing of the metallic articles by the surface nitriding method. In spite of the fact that this problem concerns physical metallurgy and is not directly connected with catalysis, the authors succeeded on the base of new notions about the nitriding action mechanisms of the ammonia-air media on the metal surface to establish theoretically and to prove in actual practice the possibilities of the essential widening of the azotizing process applications field and to obtain articles with new properties by introduction into the muffle furnace a catalytic element which regulates the transformations of the nitriding ammonia-air furnace atmosphere at the in situ regime. The initial principle which served as a starting point of the study was non-traditional for the existing theory of the nitriding conception. The conception is based on an assumption, whereby the authors asserted that during the metal nitriding the active components of the gaseouse medium are not the stable, equilibrium products of the furnace atmosphere interaction (in the most typical case they are the products of ammonia oxidation by air oxygen), but the intermediate, labile and chemically high-active formations (the radicals containing nitrogen, hydrogen or oxygen, the ions and ion-radicals). Namely such non-equilibrium but sufficiently long-lived "fragments" (having the high activity, small size and ability to penetrate into the solid metal matrix and to react with it) make a decisive contribution to the real effect of the surface nitriding of the metal or alloy articles.

The natural next logic step was an idea that it is worthwhile to use during the process a catalytic factor influencing the ammonia-air medium transformations during its interaction with the metallic surfaces (in situ regime). The catalyst use allows to control in purposeful and selective fashion the parallel routes of the ammonia oxidation reaction, i.e. the whole spectrum of the intermediate and final reaction products formed during the process.

Even the first experiments realizing practically this idea verified the correctness of the initial premises: the nitriding process have changed its character very strongly both on the regime parameters and the qualities of the article treated. For example, when the reactor is equiped with the silica fiberglass woven catalyst having Pt content up to 0,1 mass % (designing and production of JSC "Chemphyst" ) was installed to the ammonia-air mixture the catalytic activity of the gaseous medium during the steel surface nitriding reflecting in realization of the next new peculiarities: the alpha-solid solution range was widened to much extent (the supersaturated alpha-solid solution was realized containing up to 1,4 % nitrogen with an abnormally great lattice parameter ); the control of the final nitrogen content in steel was realized in the range from 0,1 to 8,5 % which is inaccessible under the traditional nitriding; the corrosion resistance of constructural steels was increased; the hardness of the treated articles was increased to the depth more than 1 mm; the decarburizing process during the nitriding was strongly depressed; the nitriding process was sufficiently accelerated simultaneously with the multiply decrease of the ammonia consumption rate; the catalytic activity of the furnace atmosphere gave rise to the nitriding operations usage for the previously non-nitriding systems (the powder metallurgy articles, the high-speed tool steels, the cuprous, aluminium, titanum alloys).

The authors have performed the investigations cycle of the nitriding process regularities under the catalytic activation of the different types of the catalysts. The new catalytic systems designed by the authors on the silica woven materials base, doped with Pt, Pd and Cr, offer the greatest promise.

The more detail information on the given development was published in [1-3].

We are very grateful to RFBR for support of this investigation.

## REFERENCES

1. Zinchenko V., Siropiatov V., Safonova O., Barelko V. A New Way In Low-Temperature Chemical Heat-Treatment. Book of abstracts, p.175, "10th Congress of the International Federation for Heat Treatment and Surface Engineering", September 1996, Brighton UK.
2. V.M. Zinchenko, Siropiatov V.Ya., Barelko V.V., Bikov L.A. Metallovedenie i termicheskaya obrabotka metallov (russ) 1997, No7,pp 7-11.
3. Patent of Russia, No 97107097/02, 14.05.97

# MATHEMATICAL MODELLING OF THE REVERSE-PROCESS FOR VOC INCINERATION CONSIDERING ADSORPTION EFFECTS

A.N. Zagoruiko

*Boreskov Institute of Catalysis SB RAS*
*Pr.Lavrentieva, 5, Novosibirsk, 630090, Russia*
*Phone (3832)354591, fax (3832)357678, e-mail: zagor@caty.catalysis.nsk.su*

The reverse-process of catalytic incineration of volatile organic compounds (VOC), based on reverse-flow fixed-bed reactor operation, has found the wide application in purification of industrial waste gases [1,2].

The development of such processes is usually based on application of the steady-state kinetic models. However, the experimental studies [3] showed that in the area of low and moderate temperatures (below ~300$^0$C) the oxidation of VOC occurs via intermediate steps of adsorption and chemisorption of the oxidised compound, thus giving rise to the significant nonstationarity of the catalyst surface, which may significantly effect the incineration process technology.

The present paper is dedicated to the reverse-process of VOC incineration, the chemistry of which may be represented by the following scheme:

$$A + [O] \Leftrightarrow [AO] \quad (1)$$

$$[AO] \Rightarrow [P] \quad (2)$$

$$[P] + O_2 \Rightarrow CO_2 + H_2O + [O] \quad (3)$$

where A – a molecule of VOC, [AO] - substance A, reversibly adsorbed at the catalyst surface, [P] – irreversible chemisorbed compound at the catalyst surface.

The kinetic parameters of nonstationary kinetic model were defined on the base of experimental study [3] of cumene oxidation at alumina-copper-chromium oxide catalyst IC-12-8 [4].

Process simulation on the base of this transient kinetics showed that under low temperatures, which may be observed in the inlet part of the catalyst bed in the end of the operation cycle (before the flow reversal) the adsorption of VOC may occur, giving both reversibly and irreversibly adsorbed species. After the flow reversal this part of the bed becomes the outlet one and the temperature starts to rise here. As a result, some fraction of reversibly adsorbed VOC may desorb into outlet stream, thus sufficiently decreasing the total degree of waste gas purification.

Fig.1 shows the dependence of gas purification degree from relation of inert bed length to total bed length (at constant total bed length) for cycles of different duration. It is seen, that account for adsorption effects leads to the decrease of calculated process efficiency, while the decrease of purification degree is more expressed for shorter inert beds and for longer cycles.

One may conclude, that to avoid the decrease of purification efficiency it is necessary to use high enough inert beds. On the base of Fig.1 data the paradoxical conclusion may be made: in optimisation of the inert and catalyst loading of the existing reactor, when the total bed length is limited by existing vessel design, to improve the process efficiency sometimes it is necessary to increase inert loading with decrease of catalyst volume. Moreover, the inert material should be considered in the process not only as the cheap replacement of the catalyst in the bed ends, but also as an important process element, playing significant role in the process purification efficiency.

The decrease of the purification degree may be also avoided by application of reasonable process control strategy. The most effective way of process control here is performance of the flow reversal when the gas temperature at the catalyst bed inlet becomes lower some fixed value. Very important question is the choice of this "switching" temperature.

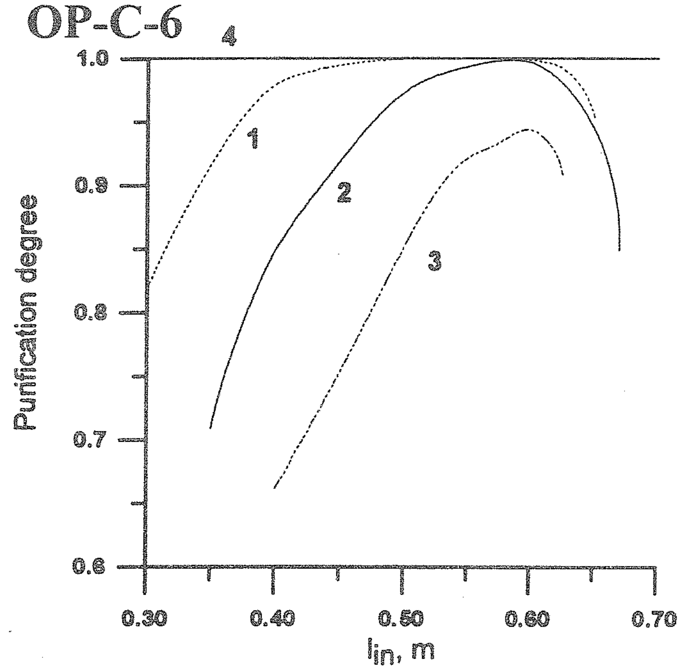


Fig.1
Influence of adsorption effects on the process efficiency.
Curves 1-3 – for cycles with duration 500, 700 and 900 sec respectively, 4 – no adsorption effects taken into account.

Fig.2 shows the dependence of purification degree from switching temperature $T_{sw}$ for the different lengths of inert beds. It is seen that for all cases the practically full purification is obtained for $T_{sw}$>200-250$^0$C.

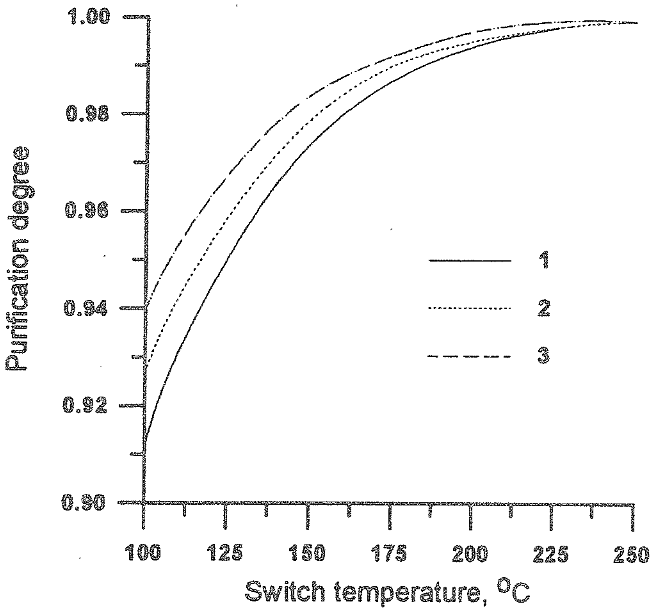


Fig.2
Dependence of purification degree from switching temperature for different lengths of inert bed.

All this may in larger or smaller extent have the relation to others catalytic reaction, performed in the reverse-flow operation mode.

### *References*

1. Yu.Sh. Matros, A.S. Noskov, V.A. Chumachenko. Catalytic abatement of industrial waste gases. – Novosibirsk, Nauka, 1991, 224 p.
2. Yu.Sh. Matros, G.A. Bunimovich. Reverse-flow operation in fixed bed catalytic reactors. - Catal.Rev.-Sci.Eng., 38(1), 1996, pp.1-68.
3. Yu.A. Kachurovskii. Deep oxidation of aromatic hydrocarbons admixtures in air at alumina-copper-chromium oxide catalyst IC-12-8. PhD Thesis, BIC, Novosibirsk, 1988.
4. A.N. Zagoruiko. Nonstationary kinetic model of deep oxidation of aromatic hydrocarbons on oxide catalysts. - React.Kinet.Catal.Lett., in press.

OP-C-7

# SYNTHESIS GAS PRODUCTION BY STEAM REFORMING AND CATALYTIC PARTIAL OXIDATION OF NATURAL GAS

G.F. Froment

*Laboratorium voor Petrochemische Techniek Universiteit Gent; B-9000 Gent, Belgium*

After an Introduction in which the characteristics and technologies of both types of processes are compared the paper deals with their kinetic modeling and reactor simulation.

The kinetic modeling of steam reforming, derived from extensive experimentation in a bench-scale unit, consists of a number of elementary steps starting from the feed hydrocarbon with gradual abstraction of hydrogen and introduction at a certain level of oxygen from water dissociation, leading to CO and $CO_2$.The water gas shift and coke formation by methane and ethane cracking are also included. The main pathway contains three rate determining steps leading to three Hougen-Watson type rate equations, one for CO-formation from methane, one for $CO_2$ formation from methane and one for the water gas shift. The coke formation, studied in an electro-balance unit, accounts for the gradual abstraction of hydrogen from methane, for dissolution/segregation of the carbon on the nickel-surface of the catalyst particle, for diffusion through the particle and for precipitation of the carbon in the form of filaments called whiskers. The kinetic model correctly separates the region in which there exists an affinity for carbon formation from that in which the affinity for gasification is prevalent. The experimental results with higher hydrocarbons were shown to fit into the schemes developed for methane.

The reactor model considered plug flow for the gas phase and accounted for the diffusional limitations inside the catalyst. The heat input for this strongly endothermic process was obtained by considering the heat generated by fuel gas combustion in the furnace containing the row of reforming tubes. The detailed model used for this simulation comprised heat transfer by radiation and convection. The furnace was divided into a number of zones, i.e. volume zones for the gas and surface zones for the tube-and furnace walls. The view factors entering into the radiant heat transfer were obtained by Monte Carlo simulation of the fate of beams emitted from the individual wall burners. Reflection on the wall zones and absorption of radiation by $CO_2$ and water were accounted for. The agreement between simulated and industrial results was excellent.

# OP-C-7

The kinetic model for the catalytic partial oxidation by oxygen or air on a nickel catalyst consisted of two parts: the first describing the combustion of methane into water and $CO_2$, the second - the steam reforming. The equation of Trimm and Lamm was adapted to a nickel catalyst, while the rate equations for the steam reforming and coke formation were those described above. Again the simulation of the reactor was based on a heterogeneous model with diffusion limitation inside the catalyst. The effect of operating conditions like the addition of steam. or $CO_2$ on the C/O and C/H ratio of the syngas and on the coke content of the catalyst along the reactor was simulated. In an attempt to reduce the operating cost the feasibility of catalytic partial oxidation in a reversed flow reactor was also studied. To avoid excessive temperatures at the solid surface and destruction of the catalyst, the flow rate of the feed and the $CH_4/O_2$ ratio have to be carefully selected. Also, steam should be added. Most of the coke deposited in a semi-cycle is removed after flow reversal.

# DESIGN OF CARBON MEMBRANE CATALYTIC REACTOR FOR HOMOGENEOUS LIQUID-PHASE REACTIONS

A.A.Lapkin*, S.P.Perera, S.R.Tennison, B.D.Crittenden, R.W.Field, W.J.Thomas

*Department of Chemical Engineering*
*University of Bath, BA2 7AY, UK, fax: (01225) 826894*
*(*E-mail: cesal@bath.ac.uk)*

In this paper a carbon membrane catalytic reactor applied to a gas-liquid homogeneous equilibrium reaction is described. A reactor of this type combines the principles of membrane catalysis and the supported liquid phase catalysis (SLP)[1].

The trial reaction is the direct hydration of propylene to 2-propanol catalysed by aqueous phosphoric acid solution. This is a typical example of homogeneous equilibrium reaction involving complex vapour-liquid equilibrium[2] which is also a major industrial chemical processes. Another potential application for the new reactor is the hydroformylation processes.

Present commercial technologies for the hydration reaction are based on the supported liquid phase (SLP) and trickle-bed reactors. In the SLP hydration process, concentrated phosphoric acid catalyst is distributed on a porous support. Reaction is homogeneous and involves absorption and desorption of vapour phase reagents and products into the liquid film-catalyst[3]. In the trickle-bed process solid acid catalysts are used, usually ion exchange resins[4]; it is a three-phase heterogeneous process. Being thermodynamically more favourable the trickle-bed process allows one to obtain higher product yields compared to the SLP process, but suffers from liquid phase mass transfer resistance[5].

In order to combine the thermodynamic advantage of the liquid phase reaction with the more favourable mass transfer of the SLP catalysts a carbon membrane catalytic reactor has been proposed. In the reactor configuration proposed for the hydration process, a porous membrane supports the liquid phase phosphoric acid catalyst, thus simultaneously acting as a catalytic medium and a phase separator. Favourable conditions for reaction and mass transfer are therefore created.

# OP-C-8

It was suggested in an early patent[6] on the direct hydration process that carbon is a suitable stable support for phosphoric acid. Furthermore, its porous structure can serve as a reservoir for the reaction product. Indeed, the flexibility of carbon membrane technology allows the design of a membrane with a porous structure that is required for the particular chemical process. Thus, in the case of the propylene hydration process two different types of carbon support could be suggested. The first possibility is a carbon-carbon composite with a thick macroporous support and a thin mesoporous layer in which the reaction takes place. In this case the liquid-phase resistance is minimum while the gas-phase resistance is complex as it involves diffusion and adsorption-desorption in the porous carbon support. The second possibility is a carbon composite with a microporous layer for which liquid-phase resistance becomes more dominant as it is the liquid phase which is contained in the macroporous support.

Adsorption of the reaction components in the carbon membranes and membrane preparation and characterisation will be covered in this presentation. The effects of gas-phase and liquid-phase resistance coupled with simultaneous reaction are considered in conjunction with carbon surface chemistry and membrane texture. This provides a background for the optimisation and design of a catalytic membrane reactor and evaluation of the process model.

---

[1] R.Datta, R.G.Rinker, Supported liquid-phase catalysis. I. A theoretical model for transport and reaction, J.Catalysis, 95 (1985) 181-192.

[2] Hancock, E.G., "Propylene and its industrial derivatives", Ernest Benn Ltd., London & Tonbridge, 1973.

[3] М.А.Далин, Состояние производства непредельных газообразных углеводородов и синтез этилового спирта прямой гидратацией этилена, Химическая наука и промышленность, 1 (1956) 259-272. (M.Dalin, in «Chemical Science and Industry» 1(1956) 259-272.)

[4] W.Neier, Direct hydration of propylene to isopropyl alcohol, Ion Exchange Techn., 1984, 360-366.

[5] J.R.Kaiser et al., Direct hydration of propylene over ion-exchange resins, I&EC Prod. Res. Dev., 1:4 (1962) 296-302.

[6] US Patent 3,232,997 W.Ester, Process for the production of alcohols by catalytic hydration of olefins, Feb. 1, 1966.

**OP-C-9**

# ANNULAR NUCLEAR-SAFE CATALYTIC REACTOR FOR DESTRUCTION OF MIXED ORGANIC WASTES CONTAINING RADIONUCLIDES

Z.R. Ismagilov, M.A. Kerzhentsev, V.N. Korotkikh
B.I. Lunyushkin*, Yu.V. Ostrovski*
*Boreskov Institute of Catalysis, Novosibirsk; Russia*
**NGPII VNIPIET, Novosibirsk, Russia*

At present a huge amount of hazardous radioactive wastes is accumulated on the Earth. One of the most dangerous types of the wastes are so-called mixed organic wastes, consisting of organic substances: oils, extractants, solvents contaminated by radionuclides of uranium, plutonium and their fission products. The particular hazard of these wastes is due to the combination of flammability, explosiveness, toxicity and radioactivity. The amount of these wastes in USA is about 200000 t, and in Russia, in particular at Siberian nuclear material processing plants in Tomsk-7, Krasnoyarsk-26, Krasnoyarsk-45 and Angarsk - thousands of tons. At Novosibirsk Chemical Concentrates Plant Ltd. (NCCP) each year several hundreds tons of mixed organic wastes are formed in the production of nuclear fuel (fuel rods) for power stations. The major part of the wastes is accumulated at NCCP. Previously a part of the mixed wastes was incinerated in flame or sent to storage to special basins. It is apparent that such methods of waste disposal are hazardous and can lead to the contamination of the environment with radionuclides.

Basing on the experience in the combustion of fuels and organic wastes in catalytic heat generators we have developed an environmentally safe process for the treatment of mixed organic wastes, based on total oxidation of organic components of wastes in a fluidized catalyst bed and transition of radionuclides to compact solid state, convenient for subsequent processing or burial. The process was studied at two pilot installations with a capacity of 1 kg/h both with model wastes and real wastes of NCCP containing radionuclides. The developed process in combination with the original off-gas treatment system was shown to decrease the emissions of radionuclides and gaseous pollutants below maximum allowable limits.

Basing on the experimental results design documentation for the construction of a prototype industrial plant for destruction of mixed organic wastes containing natural uranium with a capacity of 50 t/year was elaborated. The fabrication and assembly of this plant is now in progress at NCCP.

# OP-C-9

Recently we have started the development of the process for the treatment of mixed wastes containing enriched uranium (up to 90%) and plutonium-249, i.e. isotopes capable of fission. In this case, in order to prevent the development of self-supported chain reaction upon probable accumulation of the radionuclides in the installation units, the dimensions and shape of the equipment for waste treatment must meet nuclear safety requirements. In particular, the diameter of the cylindrical catalytic reactor should not exceed the certain value (ca 120 mm). For the increase of the installation capacity one should use many such reactors or create a single nuclear safe reactor of the annular shape, i.e. with a cross section as a ring with a definite breadth. We have designed such annular reactor. The reactor is comprised of two coaxial cylinders with a working annular space between them, the breadth of this space along the radii not exceeding a certain value defined by the requirements of nuclear safety. In addition, for the reliable prevention of the development of the self-supporting chain reaction a neutron absorbing material, e.g., boron carbide can be installed into the inner cylinder. This allows some increase in the breadth of the working space and the increase the overall size (outer diameter) of the reactor.

For efficient removal of heat from the catalyst bed a tubular water cooled heat exchanger is immersed in the upper part of the bed. Excess heat is extracted by heating or evaporating of water. A non-isothermal wire grid is installed before the heat exchanger. The grid is permeable for the catalyst, but it has a certain resistance to the catalyst vertical movement. Therefore it controls the vertical heat transfer in the bed and divides the bed in two zones: a lower one - zone of heat evolution with a temperature of 600-750°C and an upper one - zone of heat extraction with a temperature of 250-400°C. The decrease of temperature in the upper part of the bed results in reduction of gas velocity and therefore in less bed elutriation.

A model installation with the annular catalytic reactor was successfully tested at Boreskov Institute of Catalysis in combustion of diesel fuel.

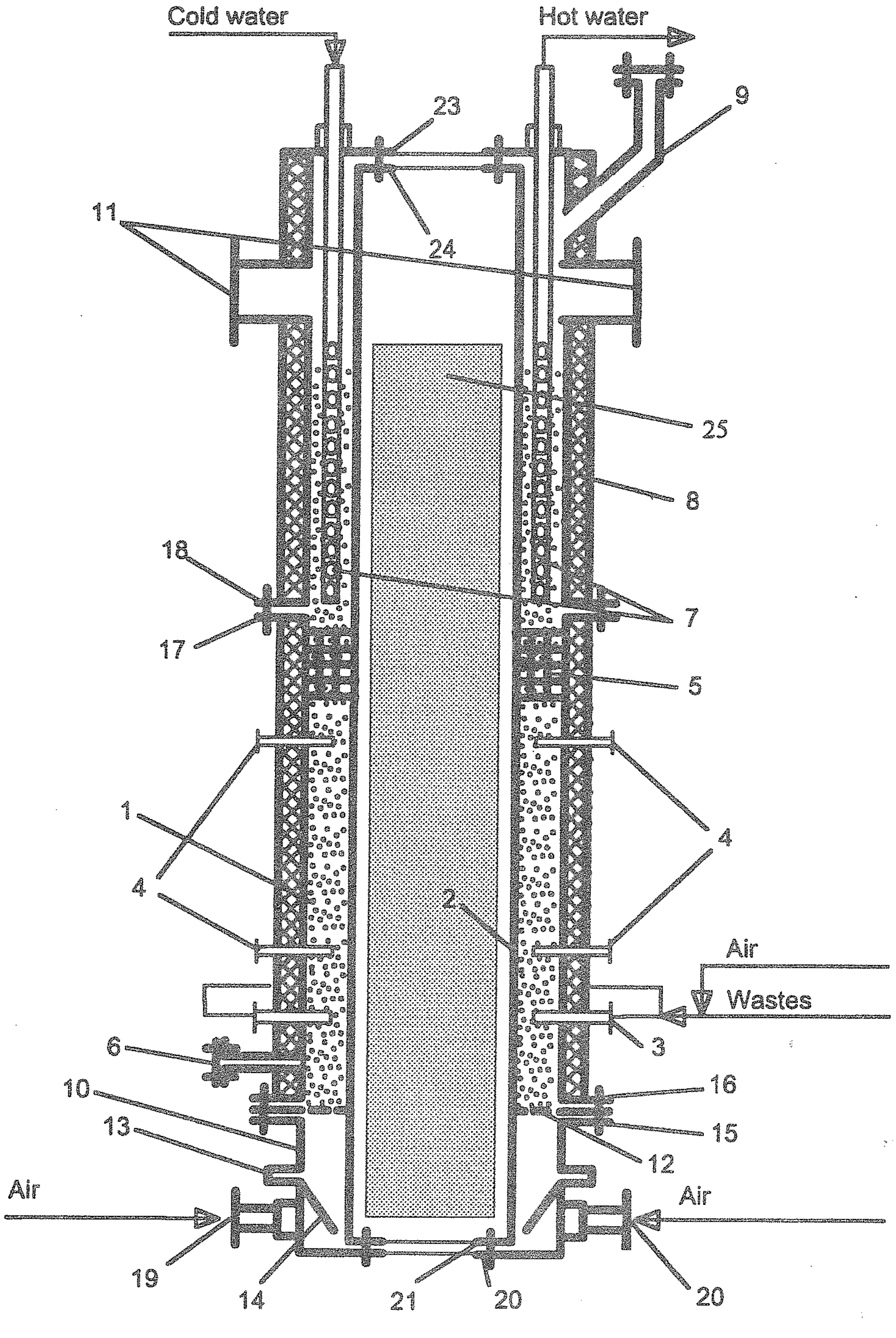


Fig. 1. Longitudinal cross section of annular catalytic reactor for destruction of organic wastes containing fissionable radionuclides:

1 - outer wall, 2 - inner wall, 3 - nozzles, 4 - thermocouples, 5- non-isothermal grid ,

6 - catalyst unloading connection, 7 - heat exchanger, 8 - thermal insulation, 9 - catalyst loading connection, 10 - annular air collector, 11 - exhaust gas discharge connections,

12 - air distributing grid, 13 - bellows, 14 - diffuser, 15-24 - flange connections,

25 - filling made of neutron-absorbing material

## OP-C-10

# MODELLING TWO-STAGE AMMONIA OXIDATION PERFORMANCE WITH THE NON-PLATINUM HONEYCOMB CATALYST

I.A. Zolotarskii, V.A. Kuzmin, E.S. Borisova, L.N. Bobrova, N.A. Chumakova, E.A. Brustein[1], T.V. Telyatnikova[1], A.S. Noskov

*Boreskov Institute of Catalysis, Novosibirsk*

*[1] JSC GIAP, Moscow*

Recently a non-platinum honeycomb catalyst IK-42-1 developed by Boreskov Institute of Catalysis was applied in ammonia oxidation at several high-pressure nitric acid plants. The usage of the IK-42-1 catalyst at a second stage of ammonia oxidation allows to decrease a number of Pt alloy gauzes loaded and operational Pt losses, gauzes life time being increased significantly without NO yield reduction /1/.

The present report deals with a simulation of two-stage ammonia oxidation with application of non-platinum honeycomb catalyst. On the literature information there has been developed a mathematical model of ammonia oxidation on Pt gauzes and honeycomb catalyst accounting for gauzes deactivation caused by metal losses. For ammonia oxidation the following reactions are considered in the model:

$NH_3 + 1.25O_2 = NO + 1.5H_2O(1)$ (1)

$NH_3 + O_2 = 0.5NO + 1.5H_2O$ (2)

$NH_3 + 1.5NO = 1.25N_2 + 1.5H_2O$ (3)

$Pt + O_2 = PtO_2$ (4)

Reactions (1) and (2) are heterogeneous, their summary rate is determined by limiting step of mass transfer between gas flow and the surface of gauzes or honeycomb catalyst. Reaction (3) is homogeneous. Kinetics obtained in /2/ is used for its description. Under commercial conditions the rate of reaction (4) is substantially higher than that of diffusion of $PtO_2$ vapors and is limited by mass transfer /3/. The model gives due consideration for change of geometrical characteristics of Pt gauzes as the metal is lost. Herewith mechanical platinum loss is considered to be proportional to its chemical one.

Parametric analysis of the model of two-stage ammonia oxidation with usage of non-platinum honeycomb catalyst is made for typical Russian nitric acid plant UKL-7 with annual capacity of 120,000 ton of $HNO_3$. Analysis of the calculated data has shown substantial influence of reaction (3) at the second oxidation stage.

Simulation results show that the non-uniformity of gas flow velocities stipulated by reactor design is an essential factor for unit operation. Herewith the non-uniformity of gas flow increases in the course of gauzes run since at local sites the elevated gas flow rate initiates an increased platinum loss, reduction of gauzes pressure drop and therefore even higher local gas flow rate. It has been shown that the usage of honeycomb catalyst along with prevention of ammonia slip assists in alignment of the field of gas flow rates due to the stable friction factor intrinsic to the honeycomb structure.

Comparison of the calculation data based on the developed model with the commercial data for one- and two-stage schemes of ammonia oxidation has shown a good agreement in gauzes life time.

References:

1. V.A. Sadykov, E.A. Brustein, L.A. Isupova, T.V. Telyatnikova, A.A. Kirchanov, I.A. Zolotarskii, A.S. Noskov, N.G. Kozhevnikova, V.Yu. Kruglyakova, O.I. Snegurenko, Yu.N. Gibbadulin, A.A .Khazanov, Khim. prom., 12(1997)819.
2. A.M. Vashkevich, Intensification of nitric acid production in a closed circulation system. PhD thesis, Dnepropetrovsk, 1967.
3. E.J. Nowak, Chem. Engng. Sci., 24(1969)421.

## OP-C-11

# CONTINUOUS PRODUCTION OF FILAMENTARY CARBON IN THE FLUIDIZED CATALYST BED

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

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

At present, the process of catalytic filamentary carbon (CFC) formation on hydrocarbon decomposition is treated as a nontraditional way to produce novel carbon materials. Commercial production of the material is determined by its unique properties as a catalyst, catalyst support, adsorbent, and material for electrodes.

In our earlier works [1-3], we have shown that the CFC granules can be obtained in a vibrofluidized heavily-loaded-nickel bed reactor of ideal mixing. As found, the process of CFC formation is accompanied by catalyst deactivation. Moreover, the initial catalyst particles transform into the CFC granules, whose volume is hundred times greater. In [4], we have reported the data on the process, performed in the pilot reactor with fluidized- and vibrofluidized catalyst beds and laboratory reactor with ideal mixing, which are significantly different. Thus, one must allow for non-ideal gas mixing in designing large-scale reactors.

With mathematical modeling of CFC formation processes over Ni-containing catalysts in a fluidized bed reactor, the following assumptions are customary :

(1) reaction is described by equation $CH_4 \leftrightarrow C + 2H_2$

(2) CFC formation follows the kinetic equation allowing for the catalyst deactivation

(3) reactor operates under steady-state isothermal regime with a continuous catalyst loading and CFC unloading

(4) relation between gaseous component concentrations and 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 catalyst bed;

(b) solid particles are ideally mixed through the height of the fluidized catalyst bed of the dense phase;

(c) gas flow rate in the dense phase is constant and equals to the rate, which is required to generate fluidization of solid particles. Moreover, the gas excess, resulting from various chemical conversions in the dense phase, moves instantaneously to the bubble phase;

(d) dimensions of the reactor are so big that one can neglect the changes in bubble sizes through the height of the fluidized catalyst bed, and assume that bubbles become maximum in size immediately after their formation near the gas-distribution plate.

(e) hoisting speed of bubbles in the fluidized catalyst bed was calculated which accounts for their hydrodynamic interaction.

Introducing the function of particle distribution regarding the CFC concentration permits one to write the CFC equation for the above conditions:

$$d(rf)/dC = (G_0 f_0 - Gf)/V \qquad (1).$$

where f and $f_0$ are functions of particle distribution regarding the CFC concentration (kg $_{cat}$/kg) in them at the inlet and inside the reactor, respectively, V is reactor volume ($m^3$), G is catalyst consumption ($m^3/s$), C is specific concentration of CFC (kg/kg$_{cat}$), r is rate of the CFC generation (kg/(kg$_{cat}$*s)).

On inserting the equations of methane balance for the dense and bubble phases in the fluidized bed and equations for calculations of bubble hoisting speed in the fluidized bed, bubble portion in the bed, gas space velocity with respect to methane conversion and rate of methane conversion, as well as boundary conditions into eq. (1), we have described the process of CFC generation which meets the above assumptions.

The mathematical model in concern permitted us to analyze the process of CFC production in the fluidized catalyst bed, when the reactor is continuously loaded with fresh catalysts. Basing on the calculation data analysis, one can choose optimal parameters and regimes of the reactor operation with respect to maximum conversion of methane and maximum amount of the CFC formed. Besides, the model permits one to determine regime parameters that might lead to formation of stagnation zones in the reactor and catalyst ablation from it.

## References

1. Kuvshinov G.G., Avdeeva L.B., Goncharova O.V. and Mogilnykh Yu.I. //Extended Abstracts of International Meeting on Chemical Engineering and Biotechnology. Thermal Process Engineering. ,ACHEMA`94. 1994. P. 96.
2. Avdeeva L.B., Kuvshinov G.G., Goncharova O.V., Mogilnykh Yu.I. and. Likholobov V.A. //Proceedings of the 1st World Congress on Environmental Catalysis, Pisa (Italy). 1995. P. 459.
3. Kuvshinov G.G., Mogilnykh Yu.I., Kuvshinov D.G., Zaikovskii V.I., Avdeeva L.B., //Khim. Prom., 1997. No4. p. 270.
4. Zavarukhin S.G., Kuvshinov G.G., Mogilnykh Yu.I., Kuvshinov D.G., //Khim. Prom. (in press).

OP-C-12

# PURIFICATION OF INDUSTRIAL WASTE WATERS BY CATALYTIC WET AIR OXIDATION

Dobrynkin N.M., Batygina M.V. and Noskov A.S.

*Boreskov Institute of Catalysis, Novosibirsk—90, 630090, Russia*
*Fax: +7 (3832) 357678 E—mail: DOBR@reverse.nsk.su*

In recent years the growing interest to environmental protection makes more topical the development of a cost—effective and environmentally friendly technology for the treatment of variety industrial wastewater. So called "wet air oxidation" (WAO) is one of the most effective methods for wastewater purification from dissolved organic compounds. WAO is accomplished by oxygen/air at T= 473 – 598 K and P=50 –150 bar. The process is applied successfully for wastewater with organic admixture content up 10 to 100 $g \cdot l^{-1}$. Another methods based on the routine burning or use of strong oxidizers such as ozone or chlorine are not effective for mentioned interval of concentrations. The biofiltration methods are not applied as a rule for the treatment of (i) high toxic pollutants and (ii) deep purification of wastewater with large content of organic compounds. The use of catalysts for WAO is capable of signicantly reducing the temperature and pressure, and providing the processes commonly unrealized in the absence of catalyst. So the catalytic WAO application for the treatment of wastewater will allow deep oxidation of O—containing organics to $CO_2$ and $H_2O$ and conversion of N—containing organics to $N_2$, $CO_2$ and $H_2O$. In recent case the formation of typical toxic compounds (as $NO_x$ – usually formed during conventional combustion of wastewater, or $NH_3$ that is main product of non—catalytic WAO) is excepted.

This paper is dedicated to the design of high—effective catalysts for WAO of N—, and O—containing organics, and to define the optimal process conditions for the treatment of industrial wastewater under use of developed catalysts. The static setup used in experiments consisted of high—pressure catalytic reactor of complete mixing. Variety of catalysts based on Ru—, Pt—, Pd— and transition metal oxides supported on $\gamma-Al_2O_3$, $\alpha-Al_2O_3$ and carbon were used. The complex mixture of low—boiled alcohols and aldehydes, alcohols mainly: 2—pentanol (0.009 vol. %) and ethanol (0.005 vol. %) , so called "*Luther water*" was used as O—containing organics, while water solutions of acetonitrile, carbamide and dimethyl formamide were used as N—containing compounds. Main test conditions are listed below: initial oxygen pressure – 10 bar, regime oxygen pressure – 20÷45 bar, process temperature – 403÷533 K, catalyst load – 1g.

The conducted experiments for wet air oxidation of N–, and O–containing compounds are resulted in determination ruthenium supported on the carbon as most active catalysts. So it is found that the alteration of total organic carbon content (ΔTOC) is equal 97.5 % after 1 h of Luther water oxidation at 473 K when Ru/carbon catalyst is used. Besides, the application of Ru/C and $Ru/C/Al_2O_3$ catalysts allows to conduct the oxidation of N–containing compounds completely to $N_2$, $CO_2$ and $H_2O$ (Table).

Table. Catalytic oxidation of N containing compounds by oxygen.

| Compound | Catalyst | T, K | t, h | Total conversion, % | Selectivity $CO_2$ formation, % | Selectivity $N_2$ formation, % |
|---|---|---|---|---|---|---|
| $CO(NH_2)_2$ | Ru/C | 473 | 2 | ~100 | ~100 | 71 |
| $(CH_3)_2NCHO$ | $Ru/C/Al_2O_3$ | 493 | 1 | ~100 | 61 | ~100 |
| $CH_3CN$ | Ru/C | 493 | 1 | ~100 | ~100 | 75 |

To establish optimal process conditions the dependencies of intermediates and products as functions of temperature, pressure and reaction period are defined for oxidation of water solutions of acetonitrile, dimethyl formamide and low–boiled alcohols ($C_1 - C_5$) and aldehydes over Ru/C and $Ru/C/Al_2O_3$.

**Conclusion**. Therefore the conducted research is resulted in creation of water–stable solid catalysts for effective treatment of industrial wastewater from solved organic compounds by use WAO at comparatively mild conditions: T~ 493÷513 K, $P_{O_2}$=10 bar. No toxic compounds are formed during oxidation of variety N– and O–containing organic substances. The obtained results may be applied for the design of the commercial plants for water purification at industrial enterprises of Nitrogen, Chemical and Alcohol Industries.

## OP-C-13

# MATHEMATICAL SIMULATION OF THE GAS-LIQUID PROCESS IN A CONTINUOUSLY OPERATED REACTOR

E.F. Stefoglo, O.P. Zhukova, Yu.V. Romanov, S.N. Albrecht*, A.T. Nagirnjak*
*Institute of Coal, Rukavischnikov St.,21, Kemerovo, 650610, Russia*
**KAOOT «Azot», Kemerovo, 650099, Russia*

One of the way to intensify gas-liquid processes is keeping a high gas concentration in the liquid (or a suspension of the catalyst) during the reaction. This leads to the increase of the reactor performance and the catalyst life extension. One of the promising equipment for gas-liquid processes is a loop-ventury reactor (LVR). The mathematical simulation of LVR batch and continuous reactors was investigated for the reaction engineering of a gas-liquid (suspended catalyst) process. A new model describing the LVR system for different operation modes is proposed. The model allows to calculate the liquid and gas dissolved concentration in the reaction mixture during the reaction.

Usually the ejector works like a saturator for the reaction mixture before the reaction in the main holding vessel. For a fast reaction with an optimal (minimum) liquid (suspension) flow circulation rate over the ejector the main holding vessel the reaction can be finished already within the ejector volume. Normally the initial reactant is converted in the main vessel. In such a situation it is possible to pump a liquid continuously through the reactor with a volumetric flow rate of the same magnitude as internal circulation rate. In this case the original batch LVR starts to operate like a normal continuous reactor. Until now there are no modeling data or experimental published data concerning such a reactor system. The mathematical model is more complex than the previous batch model which was published. [1] The new model has been analyzed for a commercial process of diphenilamine nitrosation in trichloroethylene. The experiments were executed in a pilot reactor with a volume of 18 liters. Concentration of dissolved $N_2O_3$ in the solvent was measured separately. The reaction kinetic studies allow to describe adequately experimentally obtained data with the proposed model. It was found the higher is the reaction internal liquid circulation flow rate and pressure the more effective is Loop-Ventury reactor's use.

The mole quantity of $N_2O_3$ used for nitrosation was calculated taking into account the stoichiometry of the reaction and then the concentration of nitrogen oxides was defined. The obtained values are 0.54; 1.05; and 1.9 *kmol/m*$^3$ for 10, 20 and 30°*C* respectively. The Henry's law constant is: $He = 2.4\cdot10^9\exp(-33070/RT)$, $Pa\cdot m^3/kmol$. During the kinetic experiment in a batch stirred reactor it was found that the rate of DPHA nitrosation did not depend on its concentration and it was the first order with respect to nitrogen oxides dissolved concentration $r = k\cdot C_{GL}$. The reaction constant is $k=296.5\cdot10^5\exp(-E/RT)$, $E=41500$ *kJ/kmol.* The r, k and $C_{N2O3}$ absorption values are presented in Fig. 1. The pilot LVR characteristics are: $V_E = 2.30\cdot10^{-5}\ m^3$, $L_E = 0.281\ m$, $V_R = 0.018\ m^3$, $d_{nozzle} = 2.6\ mm$. The experiments were carried out at corresponding parameter values: $Q_{Lc} = (0.55\div9.72)\cdot10^{-4}\ m^3/s$, $Q_G = (1.83\div4.17)\cdot10^{-4}\ m^3/s$, $Q_{Lo}=(1.67\div3.33)\cdot10^{-6}\ m^3/s$, $u_l=(10.46\div18.3)\ m/s$, $u_g=(8.45\div18.3)\ m/s$, $(k_La)_E \approx 2\ s^{-1}$ and $(k_La)_R \approx 0.01\ s^{-1}$.

In Fig. 2 the data of experiments in a pilot reactor with a volume of 0.010 $m^3$ are shown. Due to technical difficulties the ratio of $Q_{Go}/Q_{Lc} \approx 3\div5$ was not optimal, equal to 1, and the $k_La$ values were less than those usually exist in LVR system ($5\div10\ s^{-1}$). Nevertheless the model calculations reflect the real gas and liquid change concentrations in LVR contour. After finishing the batch step process it starts to function as continuos one with given degree of conversion.

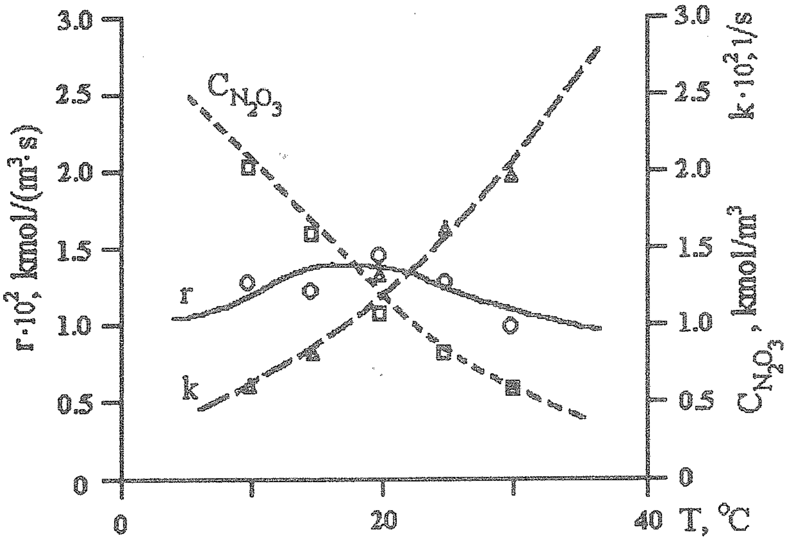


Fig.1. Dependencies of the rate of reaction of nitrosation of diphenylamin, reaction constant and concentration of $N_2O_3$ in thrichloroethylene from the temperature.

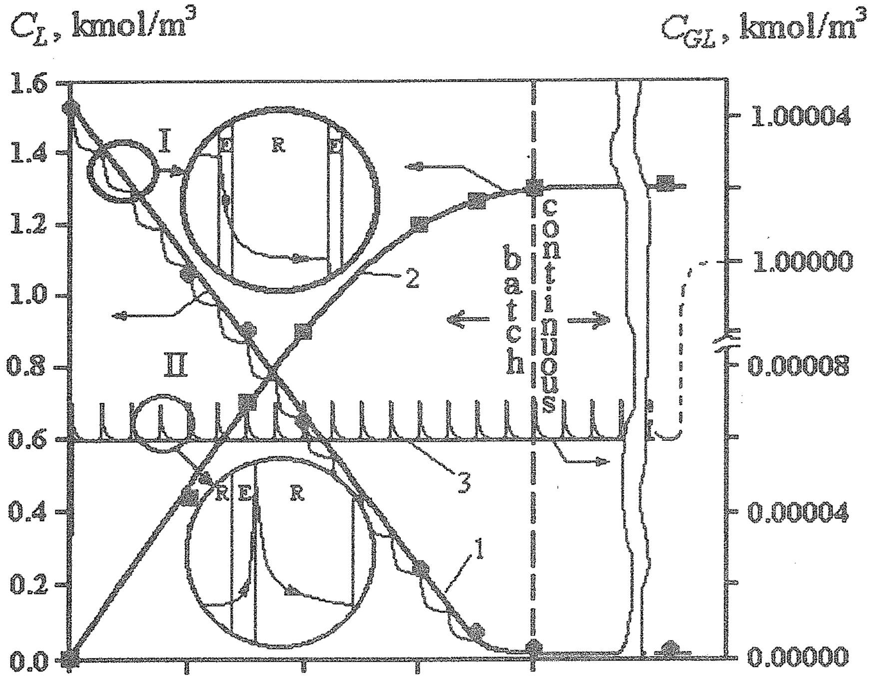


Fig.2. Pilot experiments and data calculated for diphenylamine nitrosation by $N_2O_3$ with the proposed model.

I - liquid substance concentrations dependencies in the ventury tube-main reactor.

II - gas dissolved in a liquid concentration through the ventury tube-main reactor.

1 - DPHA; 2 - NDPHA; 3 - $N_2O_3$.

$Q_{Lo}=2.5 \cdot 10^{-6}$ m$^3$/s; $Q_{Lc}=5.55 \cdot 10^{-5}$m$^3$/s; $Q_G=1.67 \cdot 10^{-4}$m$^3$/s; $(k_La)_E=2$ s$^{-1}$; $(k_La)_R=0.01$ s$^{-1}$.

## LITERATURE

1. Stefoglo E., Bortnikova I., Zhukova O. (1994) Pilot testing and mathematical simulations of loop-reactors in comparison with stirred vessel operations. European Symposium: Catalysis in Multiphase Reactors. Lyon, France: pp.41-48.

## OP-C-14

# MATHEMATICAL MODELING OF A COMBINED REACTOR TO PRODUCE FORMALDEHYDE ON Fe-Mo CATALYST

V.N. Bibin, N.A. Chumakova, I.A. Zolotarskii, V.I. Drobyshevich(1), A.S. Smirnov(2)

Boreskov Institute of Catalysis, SB RAS, Novosibirsk;

(1)Institute of Computational Mathematics and Mathematical Geophysics SB RAS, Novosibirsk;

(2)"Sibkhimproekt" Inc., Novosibirsk

Some industrial tubular reactors to oxidize methanol to formaldehyde over iron-molybdenum catalyst were modernized by adding adiabatic bed installed inside the reactor shell after the tubular section [1]. Their operation shows adiabatic bed to be rather sensitive to the process parameters.

The present study discusses the detailed mathematical modeling of catalytic fixed-beds regarding various apparatus design for a two-step methanol oxidation to formaldehyde over iron-molybdenum catalyst using tubular reactor at the first step and adiabatic bed at the second step. The comparison of reactor operation for various designs is performed and ways how to improve industrial process reliability are suggested.

The mathematical description of process occurring in a tube with the catalyst considers radial heat and mass transfer, and cooling agent temperature gradient along the catalyst bed under co-flow and counter-flow regimes. Plug flow model is applied for the process occurring in the adiabatic catalyst bed. In all cases pressure gradient along the bed and reaction mixture volume changing during the reaction were taken into account. The apparent kinetic model of the reaction rates on the industrial catalyst grains was used considering catalyst deactivation on operation.

The numerical analysis of mathematical models is performed using a modified dialog software "REACTOR" [4] designed at ICMMG.

Specified example of a combined reactor with the capacity of 15ths metric tons of formalin per year is presented. Numerical analysis of the model shows that:

- consideration of the cooling agent temperature distribution along the catalytic tube increases the hot spot temperature by ~15°C, and makes the process more sensitive to parameters;
- counter flow regime of the cooling agent in the tubular section is favorable regarding the parametric sensitivity;
- the hot spot temperature as well as the temperature at the tube outlet increase by 15°C when real pressure profile in the bed is simulated.

The following two main variants of industrial process apparatus design are compared:

1. Tubular section and adiabatic bed are installed in the same reactor shell. The adiabatic bed inlet temperature is equal to that at the tubes outlet.
2. Temperature at adiabatic bed inlet is regulated with additional heat exchanger.

The modeling shows that the second case is characterized by essentially lower sensitivity to parameters variation, and thus by a higher reliability allowing to work with higher inlet methanol concentrations (that means to reach a larger capacity), or with a lower hot spot temperature (a longer catalyst operation life is possible then).

References:

1. Boreskov G.K., Matros Yu.Sh., Nakrokhin V.B., Popov B.I., Vorobyov Yu.A. Khim. Prom., 1977, № 1, p. 48. (In Russian)
2. Bibin V.N., Popov B.I. Kinetics and Catalysis, 1969, 10, № 6, p. 1826. (In Russian)
3. Bibin V.N., Popov B.I., Lugovskoi V.I. In: Hydrocarbons partial oxidation. Methodological and mathematical aspects of kinetics. - Novosibirsk, 1973, p. 56. (In Russian)
4. Drobyshevich V.I., Rapatskii L.A., Yausheva L.V. Khim. Prom., 1989, № 6, p.460. (In Russian)

# OP-D-1

## DEVELOPMENT AND MODELLING OF THERMO-CHEMICAL IMPACTING ON AN OIL-GENERATING LAYER

A.G. Anshits, V.I. Bykov*, V.A. Nizov**

*Institute of Chemistry and Chemical Process Engineering SB RAS, Krasnoyarsk, Russia*
**Institute of Computer Modelling SB RAS, Krasnoyarsk, Russia*
***Section of Chemical Process Engineerings SB RAS, Krasnoyarsk, Russia*

The raise of degree of extraction of petroleum and magnification of efficiency of maintained deposits is one of priority problems of Russia connected with technological safety.

Three basis types of methods are applied to raise petroleum extraction: thermal, gas and physico-chemical. The analysis of a global structure of use of different methods to raise petroleum extraction shows, that the domestic practice has obvious accent on application of physico-chemical methods of handling of layers with water.

The passage to thermal methods to raise petroleum extraction, widely used abroad, puts before domestic petroleum industry new serious problems, as the operating slits where not design for a thermal method of extraction and, in overwhelming majority of cases, do not withstand the requirements on a design of columns and other technological equipment. Therefore strategically important is the problem on development of a radiant of a thermal energy with a local type of action, that would allow to refuse from installation of a special thermal equipment on a surface and trunk of a slit and to remove thermal voltages in a column of pipes.

The chemical radiants based on interaction of some metals with water relate to power sources with local zone of action.

Basis of a new process engineering to raise petroleum extraction is the reaction of specific metals (lithium, sodium, aluminum, magnesium ets.) with water, that allows to create compact and completely autonomous devices for generation high power parametric vaporgase mixture in active zone. Magnitudes of thermal effect and specific gase production for some hydro reacting metals are given below.

| Metal | Density, kg/m$^3$ | Temperature of melt, °C | Thermal effect*, $10^7$ | | Specific gase production | |
|---|---|---|---|---|---|---|
| | | | J/kg | J/m$^3$ | m$^3$/kg | m$^3$/m$^3$ |
| Lithium | 534 | 186 | 2,83 | 154,5 | 1,61 | 860 |
| Sodium | 970 | 96 | 0,61 | 60,7 | 0,49 | 470 |
| Potassium | 860 | 62 | 0,36 | 32,9 | 0,29 | 245 |
| Calcium | 1500 | 850 | 1,03 | 163,2 | 0,56 | 870 |
| Aluminum | 2750 | 660 | 1,55 | 426 | 1,24 | 3220 |
| Magnesium | 1740 | 651 | 1,39 | 248 | 0,92 | 1600 |

# SECTION D

## CHEMICAL REACTORS FOR SOLVING THE FUEL AND ENERGY PRODUCTION PROBLEMS. OIL AND GAS PRODUCTION AND PROCESSING

For comparison, the thermal effect of condensation of a water vapor widely used in thermal methods of influencing on a layer, is 2-2,5·$10^6$ J/kg.

Main prerogative of an offered mode is the localization of thermal action directly in reactionary zone without the transport communications and intermediate working mediums, that allows to avoid essential lose of heat, velocity shoks and energy of generated oscillations. Thus there is a possibility of creation in reactionary zone sub- or supercritical conditions, where solubility of hydrocarbon in water mediums will shurply increase.

Outcome of such action are:

- Realization of process of dissolution and hydrocracking of hydrocarbon in sub- and supercritical conditions;
- Recompression in active zone up to 10,0-15,0 MPa at the expense of formed vaporgase mixture;
- Heavily warm-up of containing breeds ensured, apart from a vapor, diffusion of hydrogen formed in reaction;
- Generation of impulses of pressure of a vertical column of fluid in a split by its modulation by an ejection of a mixture.

Other advantages of a method concern:

- High ecological safety and intensity of working processes;
- Simplicity of an operational upkeep and minimum expenditures on transporting of a production equipment;
- Independence from exterior energy sources.

With the purpose of an evolution of effectiveness of action on a layer of thermal charges the mathematical model is developed which is based on representation of a layer as dispersive medium, where the processes of a filtration, heat transfer and physico-chemical processes of extraction of hydrocarbon proceed. Milestone of modelling is the calculation of a characteristic velocity of propagation of thermal front in volume of a productive layer. The warm-up of a layer is accompanied by heavily physico-chemical action on it of other factors ensuring a raise of petroleum extraction. The model allows to evaluate best value of frequencies of a dumping of charges in a slit and potency of a single charge for a specific structure of a layer.

## OP-D-2

# COMPUTERIZED FORECASTING OF THE PROCESSES FOR BENZINE PRODUCTION

A.V. Kravtsov, E.D. Ivanchina
*Tomsk Polytechnic University, Tomsk, Russia*
*E-mail: TPU@TPU.EDU.RU. Fax 22-39-95*

At present the oil refining industry feels pressure from the part of the defence counsels of an environment. The manufacturers should correctly and rather quickly estimate current and potentially possible variants of motor fuels manufacture, to satisfy the requirements of ecologists and to keep volume of manufacture. The system analysis with use of computer methods and artificial intellect allows operative and correct definition of the optimum technological decisions in the field of manufacture, which should be correct and effective. In this connection during the last years new information technologies, based on knowledge and receptions of artificial intellect, heavily take root, that has defined qualitatively other level of systems of modeling, designing, forecasting and management of technological processes, and also has opened a way for creation the computer training programs. On the whole, new information technologies, scientific basis of which is a combination of methods of mathematical modeling and artificial intellect turns the computer into the basic tool for the user at the decision of the important technological problems.

The approach offered to development intellectual systems represents consecutive set of stages of formation of the adequate circuit of the mechanism of chemical-technological process with subsequent its kinetic description, on the basis of which non-stationary generalized model of contact apparatus and all chemical-technological system as a whole are formed. This model allows not only operative estimation of optimum modes of processes for the given raw material, but also to predict activity of the catalyst during the period between regeneration and general service life, to decide a problem of complex processing of petroleum raw material on ORF and modernization of working plants.

Thus it is necessary to take into account, that the prevailing part of industrially important processes of hydrocarbons raw materials processing proceeds on catalysts, which under the influence of an environment change their activity. The physico-chemical regularities of change of catalyst activity are a basis for construction of non-stationary models of industrial processes, which are established at the first stage of work.

The second stage of construction of intellectual systems consists in development of kinetic model of heterogeneous process and in estimation of kinetic parameters of hydrocarbons on various catalysts depending on their adsorption properties.

On the given stage joint consideration of the basic mechanism and reactions deactivation of the catalyst is necessary, that allows to consider work of industrial units in dynamics.

The third stage - drawing up of models of the contact apparatus, realization of accounts of particular plants, estimation of adequacy of mathematical models to real processes in view of the temporary factor.

The fourth stage - accounts of complex technologies of processing of hydrocarbon raw materials with optimization not only of target technological parameters, but technological parameters CTS as well.

The fifth stage of modeling of complex technological processes - forecasting of effective modes of functioning of the enterprises during long-duration period of time in view of varied initial structure of raw material and catalytic activity level.

Thus, at forecasting of production as system of the cumulative phenomena, the information is enriched and is realized as generalized mathematical model CTS of the industrial process.

The examples of practical application of intellectual systems for the analysis and forecasting of manufacture of ecologically pure motor fuels on ORF are submitted.

## OP-D-3

# An Experience of Modeling of Naphtha Reforming Process. Thermodynamics, Kinetics, Deactivation, Catalyst Design

N.M. Ostrovskii, A.S. Belyi

*Boreskov Institute of Catalysis, Omsk Department. Omsk, Russia*

Naphtha reforming process is one of the most science-intensive processes in modern chemistry. Its characteristic features are:

1. Naphtha fractions are composed of 30-40 hydrocarbons at least.
2. The major reactions (dehydrogenation, isomerization, cyclization, and hydrocracking) have rather different rates, ca. 10-100 times.
3. The catalysts (Pt/$Al_2O_3$, Pt-Re/$Al_2O_3$, Pt-Sn/$Al_2O_3$ ) are bifunctional in nature of active centers.
4. Catalyst deactivation plays an exceptional role in the process technology.

That is why the reforming process is extremely complicated for the physical and mathematical modeling and optimization.

On the other hand, the problems variety and their mutual influence became the reasons for many publications on reforming catalysts and process. This provides a continuous development of the process. The reforming process features that assisting to solve the more common scientific problems especially is of interest. Some of them are discussed in this report.

***The equilibrium of lumping components.*** The major reactions in reforming process reach the equilibrium. So in lumping of naphtha fractions the problem of calculation of equilibrium constants for lumped components ($K_p^*$) is coming up. The analysis of this problem using graph theory allows to derive the simple rule for $K_p^*$ calculation in terms of equilibrium constants for initial mixtures ($K_p$).

***Reaction kinetics.*** In order to develop the kinetic model several investigations were carried out. The individual reactions kinetics were studied in gradientless condition. Then conversions of some model and real mixtures of hydrocarbons were examined in the integral reactor. Finally, the lumping of components and formulation of model were made based on pilot tests simulation. Only those complete investigations allow us to obtain the model that is invariant to the reactor scale and suitable for the process analysis.

***The role of platinum state.*** The elucidation of metallic ($Pt^{o}$) and ionic ($Pt^{\sigma}$ ) platinum roles, as well as role of acid centers ($H^{+}$, $Al^{3+}$) was principal for understanding of reforming catalyst. For measuring of $Pt^{\sigma}$ quantity the adsorption method was developed, that allows to obtain a number of fundamental characteristics of $Pt^{\sigma}$. For investigation of $Pt^{o}$ and $Pt^{\sigma}$ roles in a complex mechanism of reforming reactions, the method of mathematical simulation was used. Combination of the kinetic experiments (pulse and integral) and calculations gives a possibility to establish the reactions in which $Pt^{\sigma}$ plays a principal role.

***Active component distribution.*** The optimal distribution of Pt along the pellet radius (macrodistribution) was determined. Their influence on the intrinsic reaction kinetics due to the changing in surface Pt concentration was established. In turn, this affects the adsorption properties of Pt, and it's specific activity. A new characteristic of supported catalysts was proposed, namely microdistribution (among the pores with different size), and the method for it measurement was developed. The area of microdistribution influence on catalyst activity, selectivity, and stability was estimated using mathematical modeling.

***Catalyst deactivation.*** Deactivation of catalyst in the reforming process is greatly complicated by polyfunctional nature of catalyst, by several deactivation phenomena occurring simultaneously, and due to the self-regeneration of catalyst by hydrogen. The experiments and simulations allow to understand the features of different active sites deactivation and to propose the correspondent models.

Simultaneously, the method of derivation of the equations has been developed. Quite common equations were obtained for linear and some nonlinear deactivation mechanisms, including coking.

***Catalyst testing.*** Pilot-scale testing of the catalysts is carried out as usual in the integral isothermal reactors. A considerable error in stability parameters arises from the poor information about activity profile in the catalyst bed. Based on reforming catalysts testing, the method and a set of models have been developed for correct estimation of catalyst stability. The method gives a possibility to evaluate the deactivation parameters using integral reactor data independently on the activity profile.

## OP-D-4

# INFORMATION - SIMULATING SYSTEM FOR TECHNOLOGY OF OIL PRIMARY PREPARING

A.V. Kravtsov, N.V. Usheva, O.E. Moizes, V.I. Reizlin, V.I. Chudinov

*Tomsk Polytechnic University, Tomsk, Russia*

At present using of mathematical simulation methods for oil primary preparing processes (OPPP) and creation of information-simulating systems (ISS) is the most perspective direction for :

- oil processing units (OPU) analysis, optimization and efficiency increase
- CAD development.

General principles of hybrid expert systems and knowledge of OPPP are to be placed in the basis of ISS development.

Separation, dropping, settling and other processes are main modules of created ISS. Herewith, mathematical models of these processes are based on their detailed physico-chemical regularities. Only in this case mathematical modeling is a source of new knowledge and efficient facility for OPPP forecasting.

We have designed mathematical models which allows to calculate:

- one - and multistep separation,
- dropping,
- settling

and forecast the influence of technological parameters -temperature, pressure, raw material composition, number of separation steps, etc. on main indexes of processes described above.

Mathematical models of the process of separation, reflected physico-chemical regularities, are built on the combination of theoretical equations and dependencies obtained by experimental data processing. Such combination is inevitable since separation is a complex multicomponent process by its physico-chemical essence. Experimental data, received from "Tomskneft" company oil fields: Luginetskoe, Igolsko-Talovoe, Zapadno-Poludennoe have been used for the model development and checking the models on adequacy. Besides, we have conducted research of physicist-chemical oil characteristics and gas composition on OPU of Vasiugan oil and gas obtaining headquater (Pervomaiskoe oil field).

Mass exchange and coalescence kinetics equations and also empirical equations for the liquid flow parameters, water globule sizes calculation and so on have been placed in the basis of dropping and settling mathematical models.

Influence of different parameters

- temperature,
- pressure,
- number of separators,
- physico-chemical characteristics of raw material,
- watering,
- concentration of chemical reagent

on OPU technological factors have been explored by means of ISS.

Herewith it was revealed that temperature and pressure are the main control parameters of separation process. It is possible to obtain a required quality of oil and gas combining process modes.

ISS has a module structure with suitable for the user interface (system of menu, dialog data input from keyboard and magnetic sources, results in different forms, graphic images).

For effective experimental data processing tools for source parameters and results databases have been included. They allow to

- keep enormous information volume,
- sort and search of necessary data,
- add new values with the purpose of including in algorithms as a source kit and following analysis of results.

Thereby, complex information-simulating system, appropriated for the material flows calculation, optimization and forecasting of OPU work and CAD creation have been designed.

# OP-D-5

# KINETIC MODEL OF HYDROCARBONS $C_2$-$C_4$ AROMATIZATION PROCESS ON MODIFIED ZEOLITE CATALYST OF ZSM-5 TYPE

O.Y. Belousova, A.V. Balaev, B.I. Kutepov, N.N. Khusnutdinov, A.F. Akhmetov

*Ufa State Petroleum Technical University,*
*Institute of Petrochemistry and Catalysis of Academy of Sciences of Republic Bashkortostan*
*450062, Ufa, Kosmonavtov street, 1, UGPTU*
*Phone: 347 2 43 15 35 Fax: 347 2 43 15 35 E-mail: root @ ink. ufanet.ru*

One of the variants of rational use of light hydrocarbons is their processing to aromatic hydrocarbons $C_6$-$C_9$ on zeolite catalysts of ZSM-5 type.

In the work the researches of kinetics laws of hydrocarbons $C_2$-$C_4$ aromatization on zeolite catalyst of ZSM-5 type, modified by zinc are carried out.

All experimental results on study of kinetic of this process were carried out in an isothermal mode on laboratory installation of a flowing type. During experiements the following parameters were varied: temperature, volumetric speed of submission and structure of raw material. Experiments with submission in reactor of hydrogen and inert gas (nitrogen) were carried out. The qualitative composition of reaction products is identical for all kinds of raw materials. The analysis of the obtained products of reaction was carried out by chromatography and showed that light products contain hydrogen, $CH_4$ and other hydrocarbons $C_2$-$C_4$. Aromatic hydrocarbons $C_6$-$C_9$ and higher are present in liquid products of reaction.

From the analysis of experimental kinetic dependence and available literature items of information the following chemical reactions proceeding in investigated process are allocated: hydrogenation - dehydrogenation, cracking, olygomerization, dehydrocyclization, isomerization, disproportionation and hydrocracking of aromatic hydrocarbons. On the basis of the chosen chemical reactions kinetic model of hydrocarbons $C_2$-$C_4$ aromatization is developed, including 26 basic stages of transformation. Besides them, in the circuit of chemical transformation the stage of formation of coke from olefin of hydrocarbons is included.

The experimental researches have shown, that for reception of an output of aromatic hydrocarbons $C_6$-$C_8$ of the order 35-40 (%wt) and higher, it is necessary to carry out process in temperature interval 520-550 °C. At decrease of temperature conversion to raw material and target products sharply decreases, at increase of temperature - the share of light paraffins $C_1$-$C_2$, aromatic hydrocarbons $C_9$ and higher grows and the selectivity of process decreases.

The decrease of volumetric speed promotes increase of a degree of transformation of raw material, formation of aromatic hydrocarbons $C_6$-$C_8$, $CH_4$, hydrogen and decrease of olefins concentration.

The analysis of influence of raw material structure has shown that use of $C_4H_{10}$ is more preferable, than propane or ethane, as the range of technological parameter values is extended and the higher outputs of target products are reached.

The search of kinetics parameters - front-exponents and activation energies - was carried out on the basis of mathematical model of ideal replacement. The system of the equations of the mathematical description takes into account also that the process of aromatization proceeds with change of reactionary volume (mole number of a reactionary mixture). Then the equations of material balance may be presented as follows:

$$dN/dt = F_N = \sum \delta_j W_j, \quad \delta_j = \sum \nu_{ij}$$

$$dX_i/dt = (\sum \nu_{ij} W_j - X_i F_N) / N, \quad i = 1,\ldots,n; \; j = 1,\ldots,m \qquad (1)$$

$$t = 0: \; X_i = X_i^0, \; N = 1$$

Where: $X_i$, $X_i^0$ - concentration of components and their initial content; Wj - speed of chemical reactions; N - relative change of moles number of reaction mixture; t - time; n, m - number of components and stages of chemical transformation.

With the help of the mathematical description (1) the inverse kinetic problem is solved and the numerical values of kinetic parameters are found.

The comparison of experimental and calculated values of component concentrations shows, that offered kinetic model adequately describes process aromatization of light hydrocarbons $C_2$-$C_4$ on the zeolite catalyst of ZSM-5 type modified by zinc.

## OP-D-6

# COMPUTER ANALYSIS OF CHEMICO-TECHNOLOGICAL SYSTEM OF METHANOL PRODUCTION FROM NATURAL GAS AS FEEDSTOCK

A.V. Kravtsov, A.A. Novikov, P.I. Koval, D.V. Ivolgin

*Tomsk Polytechnic University, Tomsk, Russia*

The methanol manufacture on the basis of natural gas is a chemico-technological circuit, consisting of branches of natural gas conversion and methanol synthesis. Modules "Conversion" and "Synthesis", specially generated by authors [1,2] on the basis of adequate determined models of basic processes and set-up on a current data of real operation of M-750 units accordingly cooperate in the computer analysis.

The basic problem of the analysis and optimization of the methanol manufacture is formulated as a whole as follows: to determine technological parameters of work of branches of conversion and synthesis, appropriate to a maximum of an methanol output per unit of used raw material - natural gas,

$k = G_{M,,} \cdot н_{M} /(G_{NG} + G_{FNG})$ =Max

$G_{MC}$ – raw methanol output, kg / h,

$H_M$ - mass share clear methanol in raw methanol, % of weights,

$G_{NG}$ - natural gas for conversion, normal $m^3$/h,

$G_{FNG}$ - fuel natural gas, normal $m^3$/h.

The decision of this problem is possible in many variants of its statement, determined by the technologists of a factory. Here results of the computer analysis of quantitative influence of the major factors: the charge of fuel natural gas, total gas pressure, structure of initial natural gas on parameter ‘k’ are resulted.

According to the calculations the maximum temperature of a wall of a pipe (on design given and data of real operation), is less than extremely allowable, i.e. there is the certain reserve of its increase. Results of calculations show, that increase of the charge of fuel natural gas up to a determined limit (up to 10 000 $nm^3$/h) results in more complete processing of initial raw material - to reduction of methane concentration in convention gas and to increasing of productivity of the furnace. This in turn results in improvement of parameters of work of branch of synthesis: raw methanol output increases, mass part of pure methanol in raw methanol raises, share of carbon oxides in deduced gas decreases, and as a whole the degree of natural gas processing to methanol (k) is increased to a maximum from 1.195 up to 1.235 kg $_{(CH_3OH)}$/m$^3$ $_{(CH_4)}$. However, the further reduction of methane concentration in converted gas (lower 1 %) is unprofitable, as far as:

- degree of natural gas processing to methanol is decreased. For this more significant expenses of fuel natural gas are required,
- maximum temperature of pipes wall of the furnace of conversion sharply raises and exeeds allowable limits.

As the activity of the catalyst is rather great, one of variants to increase an overall performance of installation is to increase total gas pressure. At increasing natural gas pressure higher than 90000 normal m$^3$/h the methanol output ($G_{MC}$) is increased, and the degree of natural gas processing to methanol (k) decreases. Difference of pressure in pipes of the furnace in conversion process increases. The increase of natural gas pressure from designed 85 216 normal m$^3$/h up to 90 000 normal m$^3$/h except an economic benefit at the expense of reducing of accounted norms on natural gas (≈2.5 %) gives common increase of productivity of units from 750 000 up to 870 000 tons of pure methanol per year.

Results of the computer analysis of quantitative influence of structure of natural gas on an overall performance of methanol manufacture shows following. The reduction of the methane content (concentrations of other hydrocarbon components are proportionally increased) in complete conformity with physico-chemical and thermodynamic bases of process of conversion results in reduction of the contents of residual methane and therefore to increase of efficiency (output of raw methanol) as a whole. Thus (in allowable limits) temperature of a wall of pipes of the furnace of conversion raises.

On the basis of the analysis it is possible to recommend profound study of the project on directed change of structure initial methane containing gas with the purpose to increase methanol production efficiency.

1. Koval P.I., Novikov A.A., Kravtsov A.V. Optimization of process of methanol synthesis in units of large individual capacity. // Chemical Industry.—1995, N3, p. 139-145.
2. Novikov A.A., Koval P.I., Kravtsov A.V. Optimization of the process of conversion of natural gas in methanol manufacture. // 13th International Conference on Chemical Reactors. Novosibirsk, 1996. Abstracts, v.2., p. 114-118.

## OP-D-7

# RUSSIAN OIL REFINING IN COMPARISON WITH WORLD TENDENCY

N.M. Ostrovskii, V.K. Duplyakin

*Boreskov Institute of Catalysis, Omsk Department, Omsk.*
*Tel. (3812) 66-44-74, Fax. (3812) 64-61-56, E-mail ostr@incat.omsk.net.ru*

The oil and oil refining industries in Russia are going through a long slump in oil recovery and refinery. Therefore, no considerable variations are observed in refinery configuration. It is concerned depth of refining, range of products, and especially the development of catalytic processes.

The major worldwide tendencies in oil refining during last 5-10 years are:

1. The increasing depth of refining on account of the heavy residues processing.
2. Stable grows of production of environmental friendly motor fuels and its components.
3. The increasing of fraction of petrochemical products in total oil refining.
4. The lowering of energy consumption in refining industry.

The analysis presented in the report includes:

1) the volume of oil refining in Russia for the last 10 years,
2) production indices,
3) demand and supply balance for motor fuels and furnace fuel oil.

In addition, demand/supply balances in another world regions are reported.

The refinery configuration in CIS, Russia and in Siberian region is analyzed. It differ significantly with the refineries of Europe, South-East Asia and USA in principal refining processes - hydrotreating, reforming and catalytic cracking. An important indicator is the fraction of vacuum gas oil treated in catalytic processes. It reaches in CIS only 30-50% of potential value.

The relative analysis of motor fuels quality, produced in Russia and in the world, is presented. Such characteristics as octane number and Pb concentration of gasoline, sulfur content in diesel fuels etc., are compared.

The typical schemes of refinery in Russia and in other countries have been analyzed, including set of processes, their combinations etc. The possible variants of modernized schemes are considered, taking into account the new capacity and revamps for treatment of vacuum gas oil and residuals.

From the processing economic point of view a good viability have schemes that include process of fuel oil hydrotreating following by catalytic cracking or delayed coking.

The analysis of Russian and worldwide gasoline pool is carried out. The major difference is in low fraction of cracking and alkylation products in Russian gasoline pool, and in the absence of light fraction isomerization. The biggest contribution in gasoline production in Russia comes from naphtha reforming process.

The positive tendency is the increasing of unleaded gasoline fraction, and the growing of ecological diesel and jet fuels production. In order to maintain this tendency the new capacities for several processes should be introduced: alkylation, isomerization, selectoforming, and production of oxygenating high octane additives. Some data are reported about the present level of production of high octane additives in Russia.

A brief analysis of the present state in the field of oil refining catalysts is reported. It includes the information on catalysts production and its operation in the processes of cracking, reforming and hydrodesulfurization. The dramatic drop in production of Russian home catalysts is marked that will prevent oil refining development.

# POSTER SESSION

# SECTION A

## PHYSICO-CHEMICAL AND MATHEMATICAL FUNDAMENTALS OF PROCESSES ON CATALYSTS SURFACE

# PARAMETRIC ANALYSIS OF MATHEMATICAL MODELS DESCRIBING CSTR

V.I. Bykov, T.P. Pushkareva

*Krasnoyarsk's State Technical University, Russia*
*Institute of Computing Modelling, Krasnoyarsk, Russia*

The detailed parametric analysis of the models of CSTR for the reactions A→B and $A+O_2 \to B$ is carried out. The bifurcation curves are obtained explicitly. The phase portraits and time dependencies are analyzed.

Let us consider the following scheme of the reaction

$$A \to B \qquad (1)$$

Dimensionless mathematical model of Volter-Salnikov [1] for this mechanism is of the form

$$\begin{aligned} x' &= -x\exp(-1/y) + \lambda(x_0 - x), \\ y' &= x\exp(-1/y) + \mu(y_0 - y), \end{aligned} \qquad (2)$$

where x and y are the phase variables: $0<x<1$, $1<y<y^{\infty}$, and $\lambda$, $\mu$, $x_0$, $y_0$ are the dimensionless parameters.

The steady states (st. s.) of the system (2) are the solution of the system

$$P(x, y, \lambda, \mu) = Q(x, y, \lambda, \mu) = 0$$

Or

$$G(y, \lambda, \mu) = 0 \qquad (3)$$

where besides y two more parameters, for example, $\lambda$ and $\mu$ are resolved; P, Q – the right hand parts of the system (2), G – the stationary equation obtained by excluding of variable x.

By virtue of the specificity of the equation (3) (linearity on parameters $\lambda$ and $\mu$) we can obtain dependencies of st. s. on parameters $\lambda$ and $\mu$:

$$\lambda g_1(y, \mu) = g_2(y, \mu)$$

or

$$\lambda(y, \mu) = g_2(y, \mu)/g_1(y, \mu) \qquad (4)$$

A similar procedure is valid for another parameters.

For the bifurcating st. s. multiplicity curve $L_\delta$ to be constructed in the plane $(\mu, \lambda)$ we need to solve the system

$$G(y, \mu, \lambda) = 0, \quad D(y, \mu, \lambda) = 0, \qquad (5)$$

where $\Delta$ is the determinant of Jacobi matrix of the right hand parts of the system (2) in st. s. Substituting the explicit expression of $\lambda(y, \mu)$ obtained in (4) into the second equation of (5) one can write the equation of the boundary of the st. s. multiplicity region in parameter plane $(\mu, \lambda)$:

$$L_\Delta(\mu,\lambda): \qquad \mu=\mu_\Delta(y) \qquad \lambda=\lambda(y, \mu_\Delta(y)).$$

The st. s. neutrality curve L allow the change of st. s. stability type to be analyzed. It is defined by the system

$$G(y, \mu, \lambda) = 0, \qquad \sigma(y, \mu, \lambda) = 0, \tag{6}$$

where $\sigma$ is the trace of Jacobi matrix of the system (2). Similar to above one can obtain the explicit form of equation of the neutrality curve $L_\sigma$:

$$L_\sigma(\mu,\lambda): \qquad \mu=\mu_\sigma(y) \qquad \lambda=\lambda(y, \mu_\sigma(y)).$$

The bifurcation curves $L_\sigma$, $L\Delta$ divide the parametric plane into six regions, which are distinguished by the number and stability type of st. s. For each of this regions the corresponding phase portraits are constructed.

The time dependencies are analyzed. The influence of the various parameters on the amplitude and period of the oscillations is studied.

Such parametric analysis is carried out for Aris-Amundsen's model for the general scheme $nA \rightarrow B$:

$$x'= f(y)(1-x)(1-\alpha x)^n-x,$$
$$y'= \beta f(y)(1-x)(1-\alpha x)^n-(s+1)(y-y^*), \quad f(y)=Da\exp(y(1-1/y)). \tag{7}$$

The oxidation reaction $A+O_2 \rightarrow B$ is also analyzed. The parametric analysis of one of the basic models of combustion theory – Zeldovich–Semenov's model [3]:

$$x'=(1-x)\exp(y/(1+\beta y)-x/Da,$$
$$\gamma y'=(1-x)\exp(y/(1+\beta y))-y/Se, \tag{8}$$

is also carried out, where Da, Se, $\beta$, $\gamma$ – dimensionless parameters.

The usage of the explicit form of the bifurcative curves $L_\sigma$, $L_\Delta$, obtained in the various combinations of dimensionless parameters, allows the most full analysis of st.s. local bifurcations to be carried out without difficult calculations.

## REFERENCES.

1. B.V. Volter, I.E. Salnikov. The stability of the regimes of chemical reactors work. M., Khimiya, 1981.
2. R. Aris. Introduction to the analysis of chemical reactors. Prentice-Hall, INC., New Jersy, 1965.
3. D.A. Frank-Kamenetskiy. Diffusion and heat transfer in chemical kinetics. 3-th publ.,M., Nauka, 1987.

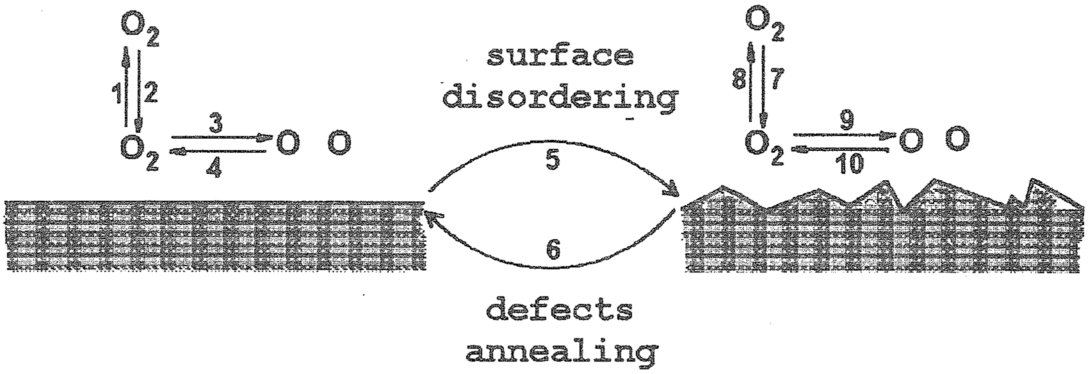
# MECHANISM OF THERMALLY STABLE OXYGEN STATES FORMATION ON SILVER

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

*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

Different adsorption forms of oxygen on silver are discussed. 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], ( $\beta$ - $O_2$) - 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], ($O_\gamma$ ) - 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. Two blocks determine adsorption-desorption and dissociation of oxygen on regular and disordered surfaces, respectively. The third 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 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 in a wide range from 0.01 to 1000 mbar.

The calculated curves are described 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 of 10 and 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 and atomic oxygen is observed on the regular ordered surface, whereas at $T > 700$ K similar forms exist on the defect surface. In the intermediate region at $T = 500$-$700$ K, a quasi-molecular thermally stable form 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 ($\alpha$ - $O_2$) -form and thermally stable states 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, N 111(1997).
3. X. Bao, M. Muhler, Th. Schedel-Niedrig and R. Shlogl, *Phys. Rev.* B. **54**, N3, 54 (1996).

# ADSORPTION PROPERTIES OF METHANE AND ETHANE OVER CARBON MICROPOROUS ADSORBENTS

V.N. Kashkin, M.S. Mel'gunov, I.A. Zolotarsky, S.A. Pokrovskaya,
N.A. Chumakova, V.B. Fenelonov and N.A. Baronskaya

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

On developing a pressure swing adsorption (PSA) process, the first step is to choose an adsorbent and to investigate its adsorption properties [1]. The adsorption properties for a number of carbon microporous adsorbents with respect to model methane-ethane system have been studied in the present report. The choice of this system is governed by the idea to isolate methane homologs from natural gases by the PSA method and to use them as a feedstock.

The adsorption characteristics of methane and ethane over carbon microporous adsorbents WS45, TOG, TL830 (produced by «Chemviron Carbon») and SKT-6A (produced by Join Stock Company «CHMZ», Elektrostal') were measured by pulse chromatography under low pressure and temperature ranging from 50 to 120°C. A pulse of the gas mixture with a methane or ethane concentration ranging from 1 to 8 vol.% was injected into a carrier gas (helium) flow, that was blown through a glass column filled with an adsorbent. The height of the adsorbent bed was varied from 10 to 40 cm, and the column diameter - from 0.4 to 1.5 cm. At column outlet the gas mixture was controlled with a flame-ionization detector.

The modeling of chromatographic peaks at adsorbent bed outlet was carried out to determine the adsorption characteristics from experimental data. A new IMPULSE program was used for modeling. The program was developed to calculate parameters of adsorption nonlinear isotherms and coefficients of intraparticle diffusion. We used apparent Henry constant (adsorption equilibrium constant), that corresponds to the slope of linear adsorption isotherm as an initial approximation. This parameter was determined from the first absolute moment of the chromatographic peaks [2]. The calculated chromatographic curves agree well with the experimental ones.

The values of initial heat of adsorption for methane ($Q_{CH_4}$) and ethane ($Q_{C_2H_6}$) were evaluated for all adsorbents using the temperature dependence of adsorption equilibrium constants. Textural characteristics of the adsorbents were measured by $N_2$ adsorption (77 K).

# PP-A-3

Textural, adsorption and intraparticle diffusion data allowed us to suppose that the separation of methane-ethane system by PSA would be proceed under equilibrium regime over the samples studied. The adsorbents have a microporous structure and the rates of methane and ethane diffusion inside of adsorbent granules are very close.

The separation coefficient of the methane-ethane mixture $K_s = K_{C_2H_6} / K_{CH_4}$ was calculated, where $K_{CH_4}$ and $K_{C_2H_6}$ are adsorption equilibrium constants for methane and ethane, respectively. At 50°C $K_s$ ranges from 23 to 42.5 for the adsorbents studied (see Table 1).

Table 1.

| Sample | Pore volume, $cm^3/g$ | $Q_{CH_4}$, kJ/mol | $Q_{C_2H_6}$, kJ/mol | $K_s$ |
|---|---|---|---|---|
| WS 45 | 0.51 | 20.1 | 32.7 | 23 |
| TOG | 0.39 | 19.3 | 31.7 | 42.5 |
| TL 830 | 0.554 | 18.9 | 31.0 | 28 |
| SKT-6A | 0.99 | 14.6 | 32.1 | 30.6 |

The data on the pore volume and the separation coefficient allows us to estimate the efficiency of adsorbents for mixture separation by the PSA method. According to our data, TOG has the highest coefficient of separation. The adsorbent SKT-6A has a larger volume of micropores, however a lower separation coefficient.

We express sincere thanks to V.D. Al'pern (Chemviron Carbon) and N.K. Kulikov (Join Stock Company «CHMZ», Elektostal') for supplied adsorbent samples.

## References

1. D.M. Ruthven, «Pressure swing adsorption», VCH Publishers, Inc., 1994.
2. K.Kawazoe, M.Suzuki, K.Chihara. Chromatographic study of diffusion in molecular-sieving carbon, J.Chem.Eng.Japan, vol. 7, № 3, c.151-157, 1974

## PP-A-4

# A PROGRAM FOR SIMULATION THE MULTIPLICITY OF STEADY-STATES IN CATALYTIC REACTIONS

I.V. Kozhevnikov, B.V. Alekseev, N.I. Koltsov

*Chuvash State University, Cheboksary, Russia*

The program of the investigation of multiplicity of stationary states (MSS) for isothermal catalytic reactions under the conditions of stable concentrations of main substances and changing concentrations of intermediate ones has been worked out in ref. [1]. However, in reality it is necessary to take into account also the changing of temperature and concentrations of main substances. Therefore we have developed the computer program which considers these changes and permits to automatize the MSS search for concrete reactions. The basic criterion idea is the existence of two different stationary states (SS) [2] which is necessary condition of MSS. This is equivalent to the solvability of equations system of stationary states which are recorded for each SS. These equations are linear with respect to the pre-exponentials of the constants of stage rates. This task leads to the system of linear inequalities. The sufficient condition of MSS criterion is an alternating vector which components are connected with the coordinates (temperature, concentrations of main and intermediate substances) of two different SS. The program in MapleV is developed with the help of this criterion for the automatization of the MSS search. The program permits to analyze the possibility of the existence of MSS for stage schemes of reactions. The program has three subprograms: the generation of all the systems of linear inequalities which connect reaction stoichiometry with different SS coordinates; inequality schemes solution; the calculation of pre-exponentials of rate constants and energies of stage activation. The program is used for MSS analysis in reactions of the oxidation of carbon monoxide and hydrogen on the metals of group VIII.

References

1. Alekseev B.V., Kozhevnikov I.V., Koltsov N.I. // Intern. Conf. "ChemReactor-13". Abstracts, Novosibirsk, 1996, part 2, p.196-197.
2. Koltsov N.I., Fedotov V.Kh., Alekseev B.V. // Reports of Acad.Sci., 1991, v.317, №2, p.401-406.

## PP-A-5

# MATHEMATICAL MODELING OF THE SIZE CLASSIFICATION OF MOISTENED FREE-FLOWING BULK MATERIALS

D.V. Kritonov, V.S. Moskvin, M.A. Samborskaya

*Tomsk Polytechnic University, Tomsk, Russia*

The process of classification of free-flowing bulk material is a critical preparatory stage in various branches of chemical and food industries. The main role of the process of classification is in quick and effective material grading on classes, the quality of which significantly affects their further technological application. That's why a choice of the optimum apparatus and processes for the stage of classification constitutes an important practical task.

One of the most effective procedures of free-flowing bulk material grading is a process of grading through sieves. At present there are a lot of sieves and apparatus designs for free-flowing bulk material classifying.

However the knowledge obtained from existing published works demonstrate that at present there is no mathematical description of the classifying process, using which one can count up the majority of factors influencing the process and analyze the possible ways to optimize the process - calculation of optimum basic parameters, designing of sieve structures adequate to the operation, that makes it possible to use the sieve area effectively, to reduce their wear, and so on.

In this work on the example of narrow grade classifying process on inclined vibrating sieves mathematical model of classifying process is suggested, which takes into account the relationship of process efficiency and dynamic model, material physical and geometric properties and technological process parameters.

When classifying free-flowing bulk material in any classifying apparatus the following pattern of classifying process kinetic is observed - the efficiency (E) in the first moment of classifying process is quickly grows up, then its growth retards and follows the equation:

$$E = 1 - \exp(-k1 * t)$$

k1 parameter takes into account the influence of final process parameters: material grading speed through the sieve (Vpr) and material layer thickness on the sieve (h):

$k1 = Vpr/h$

On the basis of summarized researching results the classifying speed is the following:

$Vpr = Vtr(1 - (d / n)^{k2})$

Vtr-material moving speed through the sieve, d - grain diameter, n - mesh size, k2 - material possibility factor determined by the equation of grain size characteristics.

Then for the periodic process:

$$E = 1 - \exp(-Vtr(1 - (d / n)^{k2}) * t / h),$$

for the continuous process with capacity Q, material density $\rho$ and sieve area S:

$$E = 1 - \exp(-Vtr(1 - (d / n)^{k2}) * S * \rho / Q)$$

In the course of kinetic process development the following assumptions were used: a) material particle is globe-shaped; b) material is uniformly spread over the sieve surface; c) layer thickness and granulometric characteristic do not change; d) grading speed is constant.

The main distinguishing feature of classifying apparatus is in the method of material advance through the sieve. Material advance speed trough the sieve is set up and determined by the apparatus dynamic operation mode. So, for apparatus of different designs when calculating material advance speed through the sieve it is required to take into account all dynamic factors affecting it. On the basis of experimental data for the vibrating inclined screen the following equation for speed calculation was proposed:

$$Vtr=k3*Am*Ch*\sin(\alpha)$$

parameter k3 takes into account the friction and material humidity effect and has its own value for each material.

When material advance speed through the sieve is set up it is required to take into account the possibility of grain overshot through the mesh. That is why the following condition restricting excessive speed of material advance through sieve, based on the condition of one grain advance was proposed:

$$Vmax = [\ n - 1/2*d(1+\mathrm{tg}\ \alpha)]\ \sqrt{\frac{g}{d*(\cos\alpha + \sin\alpha\ \mathrm{tg}\ \alpha)}}\ .$$

For mechanical operation mode it is required to observe the condition $Vtr \leq Vmax$.

The researching result are given on Fig. 1-2

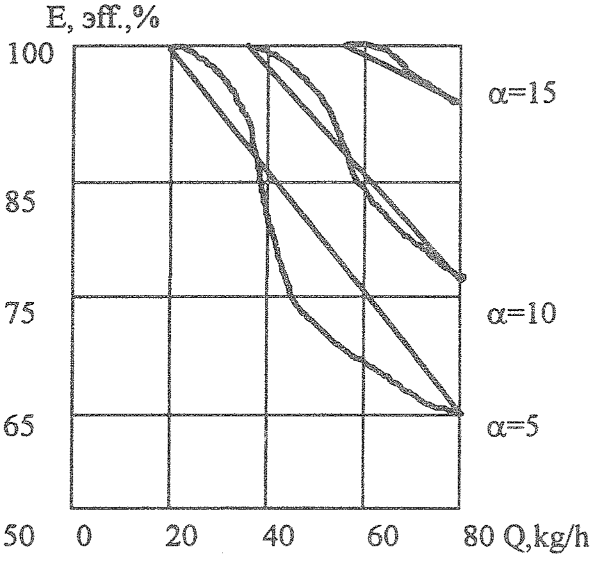


Fig.1 Output - Efficiency relation

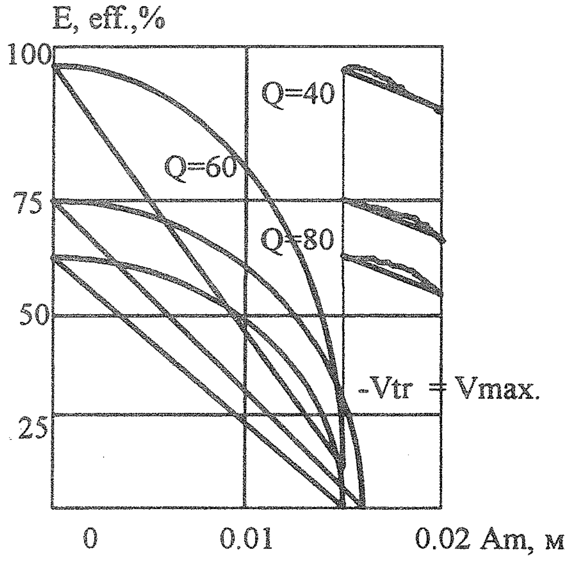


Fig.2 Amplitude-Efficiency relation

The calculation of classifying process on inclined vibrating screen according to the mathematical model proves that it is advantageous to select such dynamic mode of sieve operation with which the maximum possible speed of material advance through the sieve is achieved with correspondence to the maximal process efficiency.

## PP-A-6

# PATTERN FORMATION IN FOUR-VARIBALE MATHEMATICAL MODEL OF NO+CO REACTION ON Pt(100)

**E.S. Kurkina**, **A.V. Malykh**
*Moscow State University, Department of Comput. Mathematics*
*$ Cybernetics (BMK), Moscow, 119899, Russia.*

Recent investigations with the photo-emission electron microscope (PEEM) showed the spatio-temporal patterns formation during the NO+CO reaction over a Pt(100) single crystal surface [1]. A four-variable mathematical model of the reaction-diffusion type has been studied to describe variety of self-organization phenomena which should be experimentally verified. This model is based on the realistic space-independent model previously developed [2] to describe the temporal behavior of the NO+CO/Pt(100) system. The space-independent model provides excellent agreement between simulation results and various experimental data measured on a macroscopic level [2,3]. It consists of four ordinary differential equations upon the variations of NO, CO, oxygen and nitrogen coverages.

$$
\begin{aligned}
d\Theta_{NO}/dt &= V_1 - V_3 - V_5 + V_9 = f_1,\\
d\Theta_{CO}/dt &= V_2 - V_4 - V_6 = f_2,\\
d\Theta_{O}/dt &= V_5 - V_9 - V_7 - V_6 = f_3,\\
d\Theta_{N}/dt &= V_5 - V_9 - V_8 = f_4,
\end{aligned}
\qquad (1)
$$

The rates $V_\alpha$ of elementary reaction steps ($V_1$)-($V_9$) are expressed as:

$$
\begin{aligned}
&V_1 = P_{NO}K_1\,\Theta_*, && V_2 = P_{CO}K_2\,\Theta_*,\\
&V_3 = K_3\,\Theta_{NO}l_3, && V_4 = K_4\,\Theta_{CO}l_4,\\
&V_5 = K_5\,\Theta_{NO}\,\Theta_* l_5, && V_6 = K_6\,\Theta_O\,\Theta_{CO}l_6,\\
&V_7 = 2K_7\,\Theta_O^2 l_7, && V_8 = 2K_8\,\Theta_N^2 l_8,\\
&V_9 = K_9\,\Theta_N\,\Theta_O l_9;
\end{aligned}
$$

where

$$\Theta_* = 1 - \Theta_{NO} - \Theta_{CO} - \Theta_O - \Theta_N;$$

$$k_\alpha = \nu_\alpha \exp(-E_\alpha/(RT)), \qquad \alpha = 3,\dots,9;$$

$$l_\alpha = [\Theta_* + \sum_{p=1}^{4} \Theta_p \exp(\varepsilon_{\alpha p}/(RT))]^{m\alpha}.$$

The factors $l_\alpha$ determine the influence of lateral interactions on the rates of elementary reactions by means of energetic parameters $\varepsilon_{\alpha p}$ ($m_\alpha$ is the number of the nearest neighbor sites). Lateral interactions in the adlayer are an essential feature of the model and play a crucial role in the adequate simulation of the experimental data.

To study the spatial behavior of the system, the diffusion terms which take into account the influence of site-blocking on the diffusion rates, were included in the model. The spatially distributed model can be written in the vector form:

$$\partial\Theta/\partial t = f(\Theta) + D\cdot S(\Theta)\nabla^2\Theta. \qquad (2)$$

Here $D = diag(D_1,...,D_4)$ is the constant diffusion matrix; $S(\Theta)$ is a $4 \times 4$ matrix with elements $s_{mn}$ are given by $s_{mn} = \delta_{mn}\Theta_* + \Theta_m$, ($\delta_{mn}$ stands for the Kronecker delta).

We focus on the occurrence of stable inhomogeneous spatial patterns in the reaction-diffusion model with a spatially uniform medium. Nonuniform initial conditions were used to initialize spatial patterns. Existence conditions for Turing instability are defined for a class of four-variable reaction-diffusion type systems. It was found, which features the diffusion and stable Jacoby matrixes should exhibit to make spatially uniform stationary solution be unstable. It was shown, that stationary dissipative structures may appear in certain parameter regions as a result of such instability. Another type of stationary stable structures which was discovered and was investigated in this model is localized stationary structures (or stationary pulses). These spatial patterns coexist with a stable spatially uniform solution and don't branch off it.

The simulation results were obtained by numerical integration of the system (1)-(2) for one-dimensional or two-dimensional cases using different values of external parameters: pressure $P_{NO}$, pressure $P_{CO}$ and temperature $T$.

Linear-stability analysis of the homogeneous stationary states and extensive numerical simulations of the one-dimensional problem were carried out to construct the bifurcation maps in the $(P_{NO}, T)$ and $(P_{NO}, P_{CO})$ - planes revealing regions of different patterns. This model also describes spatiotemporal patterns under excitable and bistable conditions such as traveling pulses and propagating waves. The excitation of these patterns demands a perturbation with amplitude exceeding a certain threshold.

It is demonstrated that the new reaction-diffusion model actually describes the some main features of the experimental PEEM observations. In addition the simulation predicts various interesting phenomena such as formation of localized pulses (stationary, oscillating and chaotic) which have not yet been discovered during experimental studies.

**References**

1. G. Veser and R. Imbihl, J. Chem. Phys. **100** (11), 8483 (1994).
2. A.G. Makeev, J. Math. Modelling 8 (2), 115 (1996), in Russian.
3. E.S. Kurkina, A.G. Makeev , in the book «Reverse problems of Natural science» /Eds. D.P. Kostomarov, V.I. Dmitrieva -Moscow.: depart. BMK MSU, 52 (1997).

## PP-A-7

# «MIXED-MODE», QUASIPERIODIC, AND CHAOTIC OSCILLATIONS IN THE MODEL OF *CO* OXIDATION REACTION ON *Pd*-ZEOLITE CATALYST

*E.S. Kurkina*(1), *N.V. Peskov*(1), *M.M. Slin'ko*(2), *E.D. Tolstunova*(1)

(1)Department of Computational Mathematics and Cybernetics, Moscow State University, Moscow 119899, Russia
(2)Institute of Chemical Physics, Kosygina str., 4, Moscow 117334, Russia

The distributed mathematical model of *CO* oxidation reaction on *Pd*-zeolite catalyst was developed to describe the experimentally observed self-oscillations presented in [1]. The model describes the reaction on the surface of *Pd* clusters, homogeneously distributed in zeolite matrix and accounts *CO* diffusion in zeiolite pores. The model consists of the reaction-diffusion type equations:

$$\frac{\partial p}{\partial t} = D_0 \Delta p - \sigma G(X,p), \quad \dot{X} = F(X,p), \quad p(R_{cr},t) = P_{CO}, \qquad (1)$$

where $p = p(r,t)$ is the internal CO pressure, $D_0$ is the CO diffusion coefficient, $X = X(r,t)$ is the 3D vector of dynamic variables of the point, $P_{CO}$ is the CO pressure outside of zeolite crystallite, the function $G$ accounts the *CO* pressure variation due to the reaction, the coefficient $\sigma$ is proportional to the square of clusters surface per unit of volume. The system (1) is considered either for single crystallite of spherical form, or for thin layer of zeolite. In the first case the $R_{cr}$ is the radius of crystallite, in the second case it is the thickness of layer. The point model was constructed on the basis of oscillation mechanism including oxidation-reaction of the *Pd* surface. The parameters were fitted to describe the regular oscillations, observed experimentally.

The discrete version of the model (1) represents the system of ODE, which describes a chain of local coupled oscillators. The oscillatory process in the corresponding spherical or plane layer of a zeolite is considered to be a local oscillator. The main peculiarity of this chain is the type of coupling which is a parametric one, because the neighbor oscillators are coupled via *CO* diffusion in the gas phase - the parameter in the point model.

As the result of numerical analysis of the model (1) the phase diagram on the plane of external parameters $P_{CO}$ and $D = D_0/R_{cr}^2$ has been constructed. The oscillation region is bounded by two lines $P_b(D)$ and $P_t(D)$ of supercritical Andronov-Hopf bifurcation. It may be divided into four areas with different type of oscillations. At large values of $D$ ($> 10^7 s^{-1}$) the coupling between oscillators is weak and oscillations of individual oscillators looks like independent with almost equal natural frequencies. With decreasing $D$ ($\sim 10^5 \div 10^7 s^{-1}$) the coupling becomes stronger, the difference between natural frequencies of oscillators increases, and the global reaction rate oscillations begin to look like quasiperiodic oscillations with an amplitude modulation. At small values of *D, CO* pressure in the central layers diminishes to the level, where the natural oscillations disappear and the reaction proceeds in the regime of driven oscillations induced by oscillations in the outer layers. When $D$ is near to zero the oscillations are not excited. Passing through the boundary inside the oscillation region during $P_{CO}$ decrease firstly oscillations in the central layers of zeolite are excited, and then the outer layers are excited successively. Chaotic oscillations in the transition region may be explained by complex dynamics of the reaction in the outer layers and the large sensitivity of the oscillations to the $P_{CO}$ variation near the right point of supercritical Ahdronov-Hopf bifurcation.

Quasiperiodic and chaotic oscillations are observed in the chain of $N$ oscillators including large ($N = 40$) and small ($N = 2$) number of oscilations. The resonance phenomena are observed at the small and medium value of $N$ ($N < 15$). In this case the oscillations of individual oscillators have the typical form of «mixed-mode» oscillations.

The results of simulation demonstrate, that the origin of complex and chaotic oscillations may be due to the internal diffusion limitation in the zeolite crystallite. The presented model qualitatively describes the transition from regular to chaotic oscillations with $P_{CO}$ increase observed in experiments.

[1] M.M. Slinko, N.I. Jaeger, P. Svensson, J. Catal., 118 (1989) 349-359.

[2] E.S. Kurkina, N.V. Peskov, M.G. Slin'ko, M.M. Slin'ko, Doclady RAN, 351 (1996) 497-501.

## PP-A-8

# MODELLING OF SELECTIVE HYDROGEN SULFIDE OXIDATION IN A FLUIDIZED CATALYST BED PRODUCING THE CONDENSED PHASE

A.G. Kuvshinov, Yu.I. Mogilnykh, M.Yu. Lebedev

*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

Here we discuss a fluidized catalyst bed reactor with a catalyst particle circulation, where selective oxidation of hydrogen sulfide is accompanied by liquid sulfur deposition on the catalyst. The activity of the catalyst particle depends on the sulfur concentration $\varphi$ $(0 < \varphi < \varphi_m)$. The state of particles in the bed is described by a function of their distribution with respect to sulfur, which depends on the flow rate of catalyst particles through the reactor and on the function of particle distribution with respect to sulfur concentration at reactor inlet. Particle distribution with respect to sulfur concentration in reactor section x is set by function [1]:

$$(1)\ \rho(x,\varphi)=\frac{\partial(n/n_x)}{\partial\varphi},\ \int_0^{\varphi_m}\rho(\varphi)d\varphi=1$$

where n is the number of sulfur-carrying particles in a unit bed volume at height x, with sulfur concentration ranging from $\varphi - 1/2d\varphi$ to $\varphi + 1/2d\varphi$, $n_x = n_x(x)$ is the number of particles per a unit bed volume at height x, $\varphi = V_s/V_s^{max}$ is a ratio between the actual sulfur concentration in a catalyst particle and the maximal probable concentration.

For an isothermal two-phase system, assuming that the properties of the fluidized bed change lengthwise only [2], the model is presented by equation for the particle balance, equation of the i-th component material balance for the bubble and emulsion phases, relation for the sulfur content change in the particle, boundary and starting conditions. According to [3,4], we assume as mostly important reactions

$$(2)\ H_2S+\frac{1}{2}O_2\rightarrow\frac{1}{n}S_n+H_2O$$

$$(3)\ 1/n\,S_n+O_2\rightarrow SO_2$$

$$(4)\ H_2S+\frac{1}{2}SO_2\leftrightarrow\frac{3/2}{n}S_n+H_2O$$

Reactions (2) and (3) proceed at a rate that obeys the mass action law with the coefficients $k_1$ and $k_2$, respectively. For reaction (4), the rate is determined by the following equation [5]:

(5) $$w_3 = \frac{k_{31} c_{eH_2S} c_{eSO_2}^{1/2} - k_{32} c_{eH_2O} c_{eS}^{3/2n}}{(1+kc_{eH_2O})^2}$$

where $k_{31}$ and $k_{32}$ are the coefficients of the direct and reverse reactions, respectively, $c_e$ is the concentration of materials in the emulsion phase.

Assuming that reactor operates under the steady-state regime, the gas-and-particle mixing is ideal in the solid-phase, and gas volume changes insignificantly as a result of the reaction, the model equations will become:

(6) $$\frac{\partial(\dot{\varphi}\rho)}{\partial\varphi} = \frac{(\rho_o - \rho)}{\theta}, \quad \int_o^{\varphi_m} \rho(\varphi) d\varphi = 1$$

(7) $$U\frac{\partial(c_b^i)}{\partial x} + \beta_g\left(c_b^{\,i} - c_e^{\,i}\right) = 0, 0 < x < L/\left(1-f_b\right), x = 0: c_b^{\,i} = c_{bo}^{\,i}$$

(8) $$\int_0^L \beta_g\left(c_b^{\,i} - c_e^{\,i}\right)dx = \overline{W}^i L$$

where U is the gas rate related to the total reactor section, $c^i_b$ and $c^i_e$ are the concentrations of the i-th material in the bubble and emulsion phases, $W^i$ is the rate of change of the i-th material concentration, $W_j$ is the rate of j-th reaction, $\beta_g$ is the coefficient of mass exchange, L is the height of the fixed bed (m), index o is reactor inlet, $f_b$ is the fraction of bubbles in the bed.

Assuming that 1 stands for $H_2S$, 2 - $O_2$, 3 - $S_2$, and 4 - $SO_2$, one can write $\overline{W}^1 = -\overline{W}_1(x) - \overline{W}_3(x)$, $\overline{W}^2 = -1/2\overline{W}_1(x) - \overline{W}_2(x)$, $\overline{W}^3 = 1/n(\overline{W}_1(x) - \overline{W}_2(x) + 3/2\overline{W}_3(x))$, $\overline{W}^4 = \overline{W}_2(x) - 1/2\overline{W}_3(x)$

The model permits one to analyze how gas flow rate, catalyst consumption, mass-exchange coefficients, reagent concentration, reaction rate coefficients etc., affect the process parameters such as conversion, selectivity, and product yield. The numerical solutions for the system were obtained by the quasi-Newton gradient method. The relations between the process selectivity and kinetic characteristics have been established. We have obtained the kinetic parameters, mass exchange coefficients, gas flow rates, catalyst consumption, which correspond to the extreme process selectivity.

On varying $k_1$, a decrease in the rate constant provides a more slow oxygen burning and a less drastic selectivity decrease. This agrees well with the theoretical assumption. However, the plots show that functions decrease gradually in both cases. One can not exceed the equilibrium product yield though the selectivity at the initial step is higher than the equilibrium one, which is determined by relatively low rates of side-reactions. As $k_2$ increases, conversions of oxygen and hydrogen sulfide increase more intense but the product yield does not increase. This is determined by large constant $k_1$ and poor selectivity which is lower than equilibrium at the initial step. A decrease in the mass exchange coefficient results in process inhibition. As a result, the functions become more equilibrium. A decrease in the catalyst consumption provides a drastic decrease in conversion and product yield, because sulfur deposition increases on the catalyst particles. The qualitative curves agree well with the experimental ones.

The data obtained can be used for designing the processes of natural gas purification using the direct selective oxidation at high pressures, which is characterized by high-intensity heat release and sulfur decomposition on the catalyst.

**References**

1.G.G. Kuvshinov, Yu.I. Mogilnykh, A.G. Kuvshinov et al. Promising Environmentally Safe Technologies, 1998, Novosibirsk, NGTU, p. 21-27.

2. G.G. Kuvshinov, Yu.I. Mogilnykh, //Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Techn. N., vyp. 2, 1990, p. 17-24.

3. T.C. Alkhazov, I.M. Virzoev //Soviet-French Sem. on Catalysis, 1990, Novosibirsk, p. 9-11.

4. T.G. Alkhazov, N.S. Amirgulin //Kinet. Katal., 1982, v. 23, No 5, p. 1130-1134.

5. A.N. Zagoruiko, A.S. Noskov, B.Y. Drobyshevich // TOChT, 1993, v.23, No3, p. 209-215.

**PP-A-9**

# KINETICS OF DISPERSED PHASE DISSOLUTION

I.V. Melikhov, A.Ya. Gorbatchevski

*Lomonosov Moscow State University, Moscow, Russia*
*Phone 7 095 9393449, FAX 7 095 9328846, Gorba@radio.chem.msu.ru*

A mathematical model is proposed to describe the dissolution of a polydisperse solid substance with a distributed number of crystal defects under kinetic conditions, with the fluctuating dissolution rate and the mean dissolution rate depending on the number of crystal defects. A relation was found between the number of defects in crystals and their dissolution rate. Dissolution of dispersed solid substances is a common industrial process. Later, these models were refined by taking into account possible fluctuations of the dissolution rate and the presence of structural defects in the crystals. Dislocations were shown to have a major effect on the dissolution rate. Therefore, the model to be presented in this paper is constructed with regard to the influence of dislocations.

A solvent and a dispersed substance in which crystals differ in size L and in the number of dislocations $\chi$ are introduced into a reactor for dissolution. The dissolution is a slow Markovian process. The state of the suspension is determined by the local solution concentration C(t) and by the function of distribution of crystals over their properties $\varphi(L, \chi,t)=\partial^2 N/\partial L\partial\chi$, where N is the concentration of crystals which size and number of dislocations are less than L and $\chi$, respectively. The behavior of the function $\varphi(L, \chi,t)$ is governed by the equation

$$\frac{\partial\varphi}{\partial t} = -\mathrm{div}\,\Im_k + \frac{\partial}{\partial L}\left[G_L\varphi + \frac{\partial}{\partial L}\left(D_L\varphi\right)\right] - \frac{\partial}{\partial\chi}\left[G_\chi\varphi + \frac{\partial}{\partial\chi}\left(D_\chi\varphi\right)\right] \qquad (1)$$

where $\Im_k = v_k\varphi - \mathrm{grad}\,\varphi$, $D_L$ and $D_\chi$ are the decrease in crystal size and the change of the number of dislocations in time $\Delta t$ respectively. As every crystal is edged, $G_L = 2\sum_j G_j\alpha_j$, where $G_j$ is the rate of dissolution of face $G_j$ (or its displacement parallel to its original position toward the center of the crystal) and $\alpha_j = S_j/\pi L^2$. The value of $G_L$ depends on the frequency $\omega_k$ of transfers of molecules from the crystal to the solution. The molecules occupying the positions at vertices (k = 0), edges (k = 1), in the surface layer of faces (k = 2), at sites of dislocation "outcrops" (k = 3), at monomolecular steps (k = 4), and at fractures of the steps (k = 5) differ in frequency $\omega_k$ mainly because of the difference in number of the nearest neighbors $n_{k1}$ and of those next to the latter $n_{k2}$ in the crystal lattice. In this case, $\omega_k = \omega_k^0 \exp\left[-E_k/RT\right]$. If the step is chosen as a reference position

## PP-A-9

$$\omega_k = \omega_4 \exp\left[ -\frac{E_1^0(n_{k1}\gamma_k - n_{41}) + E_2^0(n_{k2}\gamma_k - n_{42})}{RT} + \mathit{ln}\frac{\omega_k^0}{\omega_4^0} \right] \tag{2}$$

When condition (2), along with $E_1^0./RT > 10$, $E_2^0./RT > 2$, $\omega^0{}_k \sim \omega^0{}_4$ and, $\gamma_k \sim 1$, is valid, crystals are dissolved layer by layer. The removal of each molecule from a crystal edge causes a sharp increase in the frequency of transitions of its neighbors at the edge. A train of molecules leaves the edge, giving rise to a step of monomolecular height extended along the edge. The steps are formed one after another, and a dissolving face is formed at the edge. Away from the edge, after the first molecule of the surface monolayer has passed into the solution, its neighbors also pass into solution, one after another. As a result, a recess is formed, outgrowing tangentially to the surface. In addition to the major faces (100) ($j = 1$) in originally cubic crystals, the dissolution gives rise to dissolving faces at edges ($j = 2$) and vertices ($j = 3$). The faces (100) in fine crystals ($l < a\omega_4/\omega_2$) are dissolved without the overlapping of recesses, so that the size of these faces can be determined from the geometrical relations

$$G_1 \equiv A_1 = \alpha\left\{ 4\omega_0 q_0 + 4l_1\omega_1 q_1 / a + \omega_2 q_2 \left[ \left( \frac{l_1}{a} \right)^2 - \chi_1 \right] + \omega_3 q_3 \chi_1 \right\} \tag{3}$$

In large crystals, each recess enlarges until it touches the neighboring recesses, and etching pits can develop at the dislocations. In this case, we have

$$G_1 \equiv G_0 \left[ 1 + \left( \frac{\alpha q_3 \omega_3 \alpha_T}{G_0} - 1 \right) \left( \frac{1 - e^{-t/\tau}}{1 + e^{-t/\tau}} \right)^2 \right] \equiv B_1 \tag{4}$$

where $G = f^{2/3} (\alpha q_2 \omega_2)^{1/3}$, $f = \alpha q_4 \omega_4$, $\alpha_T$ - is the ratio of the area of the side surface of the pits to the area of their bases, and $t = l_1/(2\alpha q_3 \omega_3 \sqrt{2})$. The simplest interpolation formula including cases (3) and (4) is written as

$$G_1 = A_1 + (B_1 - A_1)\exp(-2\alpha f / G_0 L) \tag{5}$$

The translational velocity $G_2$ is determined by the occurrence and movement of fractures at monomolecular steps. Fractures in fine crystals are formed mostly at vertices ($\omega_0 >> \omega_4$) and travel away from the vertices at a velocity $\alpha\omega_5 q_5$, so that the face translational velocity $A_2 = \sqrt{2}\,\alpha\ \omega_5 q_5$. In large crystals, fractures are formed with a frequency $2\omega_4 q_4$ far from their vertices, that is, almost everywhere. Each fracture travels along the step at a velocity $f_u = \alpha\omega_5 q_5$ until it comes into contact with the neighboring fracture and annihilates. Over time $\tau_1$, which satisfies the condition $f_u\ \tau_1 = (2\omega_4 q_4 \tau_1)^{-1}$, all the fractures formed within the given monomolecular chain (their number per unit length of the step is equal to $2\omega_4 q_4 \tau_1/\alpha$) annihilate. As a result, the translational velocity of an infinitely large dissolving face is

$B_2 = \sqrt{2}\,\alpha\tau^{-1}{}_1 = 2\alpha(\omega_4 q_4 \omega_5 q_5)^{1/2}$. Interpolation formula including the velocities $A_2$ and $B_2$ is written as

$$G_2 = A_2 + \left(B_2 - A_2\right)\exp\left(-\alpha^2\omega_5 q_5 / G_0 L\right). \tag{6}$$

The probabilities $q_k$ are related to the solution concentration C because the faces not only give up molecules to the solution but also take them up in an amount that depends on C. If the nucleation and outgrowth of the layer is caused by the sequential removal of single molecules, then

$$q_k = q_k^0\left(1 - \frac{C}{C_L}\right) \quad \text{for} \quad C_L = C_\infty \exp\left(\frac{L_k}{\left(L + \alpha_0\right)}\right). \qquad L_k = \alpha V_m \sigma / RT \tag{7}$$

Formulas (3)-(7) characterize the mean dissolution rate of crystals $G_L = G - \Delta G$, which differs from the instantaneous rate G because of fluctuations of $\omega_k$. The behavior of the local concentration of the solution is governed by the mass-balance equation

$$-\frac{\partial \varepsilon C}{\partial t} = \operatorname{div}\left[\varepsilon\left(vC - D_s \operatorname{grad} C\right)\right] + \pi V_m^{-1}\int_0^\infty L^2 \int_0^\infty G_L \varphi \, d\kappa \, dL, \quad \text{where } \varepsilon = 1 - \pi/6 \int_0^\infty L^3 \int_0^\infty \varphi \, d\kappa \, dL \tag{8}$$

For stirred-tank reactors, integrating equations (1) and (8) over the suspension volume V with regard to the fact that the volume integral of the divergence of the flux is equal to the integral of the flux taken over the suspension surface, we obtain

$$\frac{\partial \Psi}{\partial t} = \frac{\partial}{\partial L}\left[G_L \Psi + \frac{\partial D_L \Psi}{\partial L}\right] + \frac{\partial}{\partial \chi}\left[G_\chi \Psi + \frac{\partial D_\chi \Psi}{\partial \chi}\right] - \oint_S J_\Psi dS \qquad \frac{\partial M}{\partial t} = \pi V_m^{-1}\int_0^\infty L^2 \int_0^\infty G_L \Psi \, d\chi \, dL \tag{9}$$

Equations (1)-(9) can be solved when data on parameters a, $\omega_k^0, E_1^0, q_k^0, \overline{\kappa}_1, \overline{\kappa}_2, \Omega_1, \Omega_2$ are available. However, these parameters are generally unknown, although their orders are evaluated and special methods for their experimental determination are developed. This model has been used for calculation of dissolution phenomenon on full agitation apparatus under varying temperature. The methods of measure of granulometric composition of dispersed phases by the method of partial dissolution have been developed.

## PP-A-10

# KINETICS OF TOPOCHEMICAL PROCESSES IN A MULTIPHASE SYSTEM

I.V. Melikhov, A.Ya. Gorbachevski, I.S. Sirota, S.V. Dorozskin

*Lomonosov Moscow State University, Moscow, Russia*
*E- mail Gorba@radio.chem.msu.ru*

The most processes of dispersed phases preparation consist of many stages. The recrystallyzation route has been considered during the dispersion product formation [1] and the model of route of solid phase transformation changing under influence of impurity has been studied.

The next processes are taking place under interaction of solid phase with reagent dissolved in the medium:

(1) the solid phase and reagents is adsorbed on solid phase surface and diffuses into its volume;

(2) the medium and solid phase are supersaturated relatively to product of interaction ;

(3) the nucleation centers of product crystallyzation are generated in the medium and solid phase volumes and are grown up to the end of transformation.

Usually some of these processes are much faster than others, and, hence the conversion occurs by one of the following routes:

- The predominant process in the system is the dissolution of the parent phase and crystallyzation of the product in the medium bulk (recrystallyzation route)
- product crystals are generated and growth preferably on the surface of initial solid phase (topochemical process)
- product crystallyzation proceed in the bulk of the parent phase (solid phase route)

It was shown that the transformation route could be changed by injection of impurities.

To determine the causes of the route change, we consider the following model. The parent solid phase A with reactant B by the scheme

$$A(\text{solid}) + B(\text{media}) \leftrightarrow AB(\text{media}) \rightarrow AB(\text{solid}) \qquad (1)$$

The solid reactant A, which consists of a multitude of crystals with similar composition and form, comes into contact with a solution of reagent B. This is accompanied by the dissolving of crystal A in solution B; as a result, the solution reaches saturation with product AB. Upon saturation of the solution, AB crystals nucleate in the solution bulk and on the surface of crystals A and they continue to grow until the complexion of the process. As a result, at any moment after solution saturation, two types of crystals are present in the solution: (1) crystals that are generated in the medium bulk and remain there until the end of process, and (2) crystals that are generated on the surface of crystals A and growth, remaining attached to them. The composition of both types of crystals is the same, but their shapes are different. Crystals A and both types of AB crystals have inherent size distribution function L that satisfy the condition:

$$N_i = \int_0^\infty \varphi_i dL, \quad v_i = \int_0^\infty \alpha_1 L^3 dL, \quad V_i = \int_0^\infty \alpha_1 L^3 dL, \qquad (2)$$

where $N_i$ is the number of crystals A (i=1) or AB (i=2) in the bulk of the solution, or AB on the surface of the A phase (i=3); $\varphi_\varnothing = \partial N/\partial L$, N - is the number of crystals smaller than L; $V_{01}$ is the initial volume of the solid reactant; $V_i$ is the overall volume of crystals of type i at a given moment; $\alpha_i$ - is the shape factor; and $\varphi_i$ is the size distribution of the parent reagent crystals. The changing of medium composition determined by mass balance

$$-\frac{dC_1}{dt} = \Phi + \frac{3}{Vv_i}\int_0^\infty \alpha_1 G_1 L\varphi_1 dL, \quad -\frac{dC_2}{dt} = \Phi, \quad -\frac{dC_3}{dt} = \Phi - 3\sum_{i=2}^{3}\frac{1}{Vv_i}\int_0^\infty \alpha_i G_i L\varphi_i dL \qquad (3)$$

$\Phi = k_1C_1C_2 - k_2C_3$, where $C_j$ - concentration of A (j=1), B (j=2) and AB (j=3) in medium; V is the volume of the medium; $v_i$ is the molar volume of the i-th phase; $k_1$, $k_2$ - are the constant for the forward and reverse reaction (1) in the medium respectively.
The distribution function are established by Fokker- Planck equation:

$$\frac{\partial\varphi_i}{\partial t} = -\frac{\partial}{\partial t}\left[G_i\left(\varphi_i - p_i\frac{\partial\varphi_i}{\partial L}\right)\right] \quad \left[G_i\left(\varphi_i - p_i\frac{\partial\varphi_i}{\partial L}\right)\right]_{L\to 0} = J_i, \qquad (4)$$

where $G_i$ , $J_i$- are the rates of crystal growth (or dissolution) and nucleation; $p_i$ is the fluctuation length; and $C_0$ is the initial B concentration in the medium. The solution contains a dissolved impurity that undergoes quasiequlibrium adsorption on the crystals in agreement with the Langmuir isotherm equation. In the accordance with Langmuire sorption equation there is equation for impurity adsorbed by the surface of phase A

$$G_i = \left[\beta_{i0} - (\beta_{i\infty} - \beta_{i0})\frac{K_{Ai}C_p}{1+K_{Ai}C_p}\right](\xi_i - 1)\chi_i \qquad (5)$$

where $\beta_{i0}, \beta_{i\infty}$ are the kinetic coefficients for growth in the absence of the impurity and when the surface of the crystals in saturated with it, respectively; $K_{Ai}$ is the adsorption coefficient; $C_{im}$ is the impurity concentration in the medium; $\xi = C_i/C_{i\infty}$, $C_{i\infty}$-is the solubility of i-th type crystals; and $\chi_i$ is a factor that accounts for hindrance by neighbors growth ( dissolution) of the crystals. The nucleation in the medium is spontaneous on the colloidal particles:

$$J_i = \gamma_i(\xi_i^{m_i} - 1)\Delta + N_{in} f_i(t) \qquad (6)$$

where $\gamma_i$ и $m_i$ - are the kinetic coefficient and the reaction order of spontaneous nucleation, $\Delta=0$ if $\xi_i<1$ and $\Delta=1$ if $\xi_i\geq1$, $N_{in}$ is the number of impurity particles in the medium or on surface of crystals A; and $f_i(t)$ is the intensity of transformation of colloid particles into conversion centers. The conditions for the maintenance of the number of atoms are:

$$\frac{V_{01}}{v_1}=\sum_{i=1}^{3}\frac{V_i}{v_i}+V\sum_{j=1,3}^{3}C_j,\quad C_0V=\sum_{i=2}^{3}\frac{V_i}{v_i}+V(C_2+C_3) \tag{7}$$

Relation (2)-7) determine the degree of the recrystallization and topochemical processes realization, including the value of the route factor,

$$q=V_2/(V_2+V_3) \tag{8}$$

The properties of model (2)-(8) have been studied in refer to concrete cases: the retardation of crystallyzation, local recrystallyzation process and intermediate mixed processes.

The results of model studies have been examined on the example of calcium phosphate dihydrate transformation during reaction

$$2CaSO_4\cdot 2H_2O \rightarrow 2CaSO_4\cdot 0.5H_2O+H_2O,$$

carried out under conditions similar to those used in the commercial extraction process for phosphoric acid production [2].

The experiment with powders prepared from the materials with different impurity content shows the possibility to realize the retardation and the local recrystallyzation processes as well.

---

1. I.V.Melikhov, A.Ya. Gorbatchevski, P.N. Vabishchevich. Mechanism of successive formation of phase during crystallization in multiphase system // Theoretical foundations of chemical engineering, 1994, Vol. 28, No. 6, pp. 578-581.

2. Becker P. Phosphates and phosphoric acid. Fertilizer Science and technology series. Vol. 6, N. Y.: Dekker, 1989, P. 156

PP-A-11

# AUTOMATICALLY CONTROLLED MULTI-REACTOR INSTALLATION FOR CATALYST ACTIVITY STUDIES

V.A. Rasulov, A.M. Aliev, R.M. Kasimov, E.M. Mamedov

*Institute for Theoretical Problems of Chemical Technology, Azerbaijan AS, Azerbaijan, Baku*

The optimize in searching and carrying out investigations of catalyst systems activity of technological processes defines the necessity of formation the automotive test stands connected with electronic computer.

With this aim the automotive multi-reactor device was created at the Institute of Theoretical Problems of Chemical Technology of The Academy of Sciences of Azerbaijan.

It is intended for investigation of catalyst activity which is used in processes of oxidative transforming of lowest paraffin hydrocarbons. The device contains ten monotype integral flowing reactors located in one thermostat and completed with measuring devices and with devices for measurement of reagents expense; for last one were used flowmeters. They have a high exactitude, reliability and allow the transmission of the measured information.

The chromatographs "LCM-80" were used as analyzers of reaction product's composition. In this case the input of the product for analysis from each reactor is doing step by step using the temporary programming device. The treatment of results of analyses is provided on personal electronic computer of IBM type.

The system of modal blocks including accumulators, local memory and analog-to-digital converters were used for its connection with chromatograph, temperature transducers and expense transducers.

The automated changing of work regime of some reactors was carried out at the necessity; it was realized when setting codes entered on temperature and expense regulators of chosen reactor.

The developed technical means were applied for selection of optimal compositions of synthesizing metal-zeolite catalysts, which were used in reaction of oxidative transforming of methane to ethylene and the oxidation of propane to acetaldehyde and formaldehyde.

The results of investigations and economical efficiency of used means are discussed in comparison with well-known methods of selection of active catalyst.

# PP-A-12

# ISOTOPIC TRANSIENT KINETICS IN PLUG-FLOW REACTOR

E.M.Sadovskaya and B.S.Bal'zhinimaev

*Boreskov Institute of Catalysis, Novosibirsk , Russia e-mail: iccct@catalysis.nsk.su*

The Steady-State Isotopic Transient Kinetic Analysis (SSITKA) is a very powerful technique for *in-situ* studies of heterogeneous catalytic reactions [1,2]. It implies a stepwise change in the isotope composition of an input reagent under steady-state reaction conditions. In the absence of kinetic isotope effects, concentrations of the gas phase- and surface species and elementary reaction rates remain unchanged. Isotopic-transient rates for each elementary step depend linearly on the isotope label concentration. So, the isotopic-label substitution method, used in SSITKA, provides a linear system. If the gas-phase concentrations are known, the analysis of isotope responses permits one to determine the reaction mechanism and estimate intermediate concentrations [3,4].

With plug-flow reactors (no gas-phase backmixing along the catalyst bed), the SSITKA technique is favored, as it allows the mathematical definition of the model isotope-transfer function, which is not influenced by gas dynamic effects [5]. The problems of numerical analysis of isotope responses, observed in the plug-flow reactors, are associated with the changes in reagent concentrations along the catalyst bed. Usually, investigations are carried out at low conversions as in this case the changes are negligible.

Our study proves that isotope responses are almost invariable with the concentration distribution along the catalyst bed, even if conversion is rather high. For the particular reaction scheme and different kinetic dependencies, the isotope responses are practically identical at invariable average concentrations. Thus, the SSITKA technique permits one to determine the reaction scheme for the unknown concentration distribution along the catalyst bed.

The model of isotope label transfer in plug-flow reactor:

$$\frac{\partial C_k^{st} Z_k}{\partial t} + \frac{1}{\tau}\frac{\partial C_k^{st} Z_k}{\partial \xi} = \beta \sum_{i=1}^{N_k} r_i^{st} Z_i$$

$$\theta_j^{st} \frac{\partial Z_j}{\partial t} = \sum_{i=1}^{N_j} r_i^{st} Z_i$$

Where $Z_i$ – are the relative concentration of isotope label, $C_k^{st}$ - are the steady-state concentrations of reagents in the gas phase and surface species, $r_i^{st}$ – are elementary reaction rates, $\tau$ - is the time of the reactor purging, $\beta$ - is the relation between catalyst active sites and reagent concentration in the gas phase, $\xi$ - is the dimensionless bed length.

For $r_i = const$ , the solution of this system of equations is the sum of exponents. In general, for any functions $r_i = f(\xi)$, the solution converges to exponential dependencies for long times. To estimate the influence of functions $r_i = f(\xi)$ on the behavior of solution within the temporal interval, we have numerically studied some model reactions. The isotope responses for the simplest catalytic scheme

$$A + [z] \rightarrow [zA]$$

$$[zA] + B \rightarrow C + [z]$$

are given in Fig.1. At considerable gradients of intermediate concentrations (conversion is about 70%), the curves differ by a few percent, which does not exceed the experimental error. Similar results were obtained for more complex mechanisms.

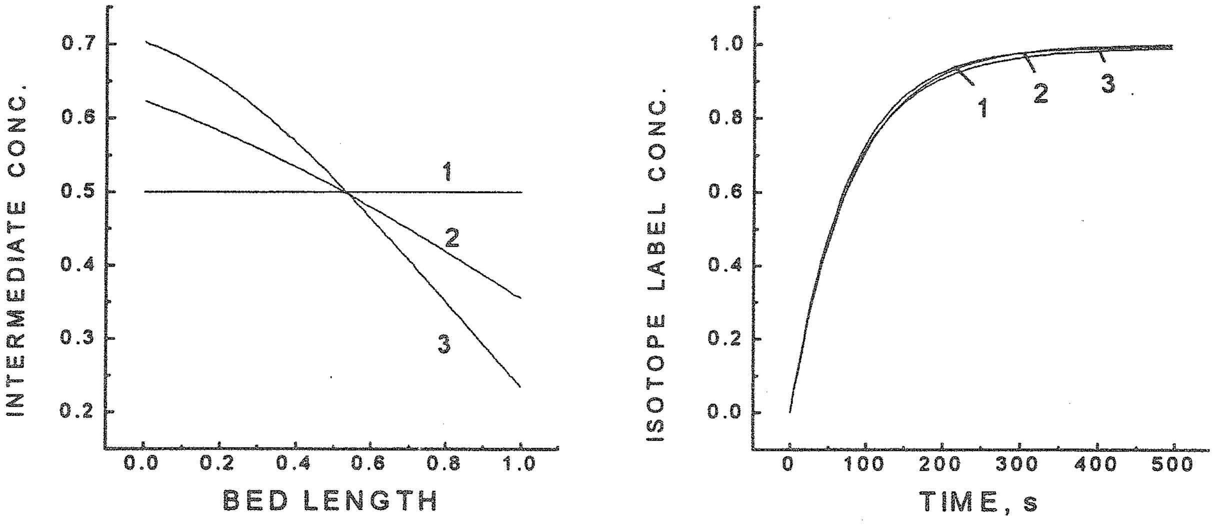


Fig.1. a) - Simulated profiles of intermediate concentrations and b) - Isotope responses for simplest model reaction. Curves 1 and 2 are the Langmuir kinetics (for different initial concentrations) , and curve 3 is arbitrary assigned.

Thus, the isotope response curves which are obtained for a wide range of conversions in the plug reactor can be expressed as a sum of exponents and retain the peculiarities characteristic of particular mechanism. To analyze isotope response curves, we have developed a program package which permits one to choose the most adequate reaction scheme and to estimate the coverages of intermediate products, averaged over the length.

**References**

1. *Tamaru K.* // Adv. Catal. 1964. V. 15. № 1. P. 65.
2. *Happel J.* // Isotopic Assessment of Heterogeneous Catalysis. Academic Press., Orlando, FL. 1986.
3. *Mirodatos. C.* // Catal. Today. 1991. V. 9. № 1. P. 83.
4. *Happel J., Walter E., Lecourtier Y.J.* // Catal.Today. 1990. V. 123. № 1. P. 12.
5. *Shannon S., Goodvin J.* // Aapplied Catalysis A: General 151.1997. P. 3

# PP-A-13

## KINETIC MEASUREMENTS PLANNING BY LINEAR PROGRAMMING METHOD

Salimonenko D.A., Spivak S.I., Salimonenko E.A.

*Ufa State Aviation Technical University, Russia*
*Bashkirian State University, Russia*

The purpose of this work is the developing of kinetic measurements planning for sharpening the kinetic model parameters.

Experimental data and results on kinetics of catalytic reactions is resolving of inverse problem. The later is connected with the fact that not all elemental processes taking part in reaction are known, and rates are unknown, too. That's why it is conveniently to approximate the reaction by model with only «macroscopic» parameters - initial concentrations of substances reacting, rate constants (for all reaction as a whole) of each substance separately and net reaction rate [1]. Linear connection of model between unknown parameters is considered.

A reaction model is represented as follows: $r_i=k_1c_{i1}+k_2c_{i2}+\ldots+k_Mc_{iM}$, where $r_i$ is chemical reaction rate, $c_{ij}$ - initial concentration of reacting substance, for i-th measurement, j-th substance, $i=1,\ldots,N$ - a measurements number, $j=1,\ldots,M$ - a reacting substances number.

Taking into account experimental accuracy $\Delta r_i$ a reaction rate $r_i$ lies in interval: $r_i-\Delta r_i\le r_i^o\le r_i+\Delta r_i$ , $i=1,\ldots,N$. Numerical calculation on computer on example of polypropylene oxidation reaction on the basis of values $c_{ij}$ and $\Delta r_i$, $i=1,\ldots,N$, $j=1,\ldots,M$ have shown that the experiment may be described by the above-mentioned linear model.

An intervals $(k_j^{min};k_j^{max})$ for each constant desired are determined. One can reach an intervals restricting, undetermination decreasing by two ways: experiment accuracy $\Delta r_i$ decreasing or planning new additional measurements. Experiment accuracy decreasing is impossible because of technology reasons.

Let us enter into consideration fictitious accuracy $\Delta r_i^*=\delta\cdot\Delta r_i$, $i=1,\ldots,N$ under condition of minimum $\delta$. (Note, initially $\delta$ was equal to 1). Then the constants values intervals will restrict. Obviously, there are some measurements caused value $k_j$ , j-1,...,M range from minimum value $k_j^{min}$ to maximum $k_j^{max}$.

These will be the measurements having calculated rate values under $\delta=\delta_{min}$ nearly to boundary values $r_i^o$ ($r_i-\Delta r_i^*$ or $r_i+\Delta r_i^*$). So further experiments one ought to carry out under any set of initial parameters (concentrations $c_{ij}$), excepting above-mentioned ones (which led to boundary constant values).

It was shown by us that in case of three variables (constant values) a number of such measurements will not be less than 6. For example, the polypropylene oxidation reaction was considered, in which three substances took part. There were carried out 20 measurements; a number of measurements giving boundary values of reaction rate was equal to seven.

The method considered allow to solve one question more. Some of constants (when finding minimum value) can get zero value; it means the appropriate substance (may be) not take part in reaction. The constant intervals narrowing allows to know it more correctly.

Literature:

1. Spivak S.I., Timoshenko V.I., Slinko M.G. //Himicheskaja promyshlennost, 1979, N3, c.33-36.

## PP-A-14

# THE OXIDATIVE DEHYDROGENATION OF n – BUTANE OVER Ti – P CATALYSTS

Ioan Sandulescu, Aura Matei, Cezar Ioan Marcu

*University of Bucharest, Faculty of Chemistry, Department of Chemical Technology and Catalysis, Bd. Carol I No. 13, Bucharest, Romania*

Several $TiO_2$ - $P_2O_5$ catalysts, with different Ti:P molar ratios, were prepared by impregnation of $TiO_2$ with phosphoric acid 85 %. The catalysts were characterised by physico - chemical methods: XRD, thermal analysis, acidity, texture, etc.

The Ti:P catalysts were tested in the oxidative dehydrogenation reaction of n - butane with air at atmospheric pressure. The influence of the reaction parameters on the conversion of n - butane and the selectivity to butene and butadiene was studied.

The catalytical properties, determinated by the Ti: P molar ratio are shown in the table:

| Molar ratio Ti : P | Conversion (%) | Molar ratio $C_2'/C_2$ | Selectivity $C_4'+C_4''$ | Selectivity $CO_2$ |
|---|---|---|---|---|
| 1:2 | 34.0 | 3.2 | 27.0 | 10.5 |
| 1:1 | 17.0 | 1.0 | 55.0 | 23.0 |
| 3:2 | 16.0 | 1.0 | 39.0 | 22.5 |

The selectivity in n - butane oxidation reaction is determined by the composition of the catalysts. At low Ti concentrations, higher conversions are obtained, but the selectivity to butenes and butadiene is low.

It is interesting to observe the fact that the ethene/ethane molar ratio of 3.4 suggests a possible oxidative cracking reaction on the Ti: P = 1: 2 catalyst.

A higher selectivity for the oxidative dehydrogenation of the n - butane was observed for the Ti: P = 1.0 : 1.0 catalyst.

The selectivity of the catalysts is also determined by the temperature, space velocity, molar ratio n - butane: air, steam.

We tried some correlations between the chemical composition, the physico - chemical properties of the catalysts and their selectivity in the selective oxidation of n- butane.

# SURFACE INTERACTION OF ETHYLENE GLYCOL WITH COPPER CATALYST

O.V. Vodyankina, G.A. Izatulina, L.N. Kurina
*Tomsk State University, 634050, Tomsk, Lenina str.,36, Russia*

Glyoxal (the valuable product of petroleum utilization) is widely used in industry for the production of polycondensational materials, synthelic resins, filins, medicine, heterocyclic compounds et al. Vapourphase ethylene glycol (EG) oxidation on Cu, Ag catalysts is the most perspective method of glyoxal synthesis. The knowledge of physical - chemical regularities of this process, of the glyoxal and by-products formation mechanism is necessary for realization of this process in industry. Analysis of literature data displays the absence of works concerning the studies of the glyoxal synthesis process mechanism, the absence of investigations such as determination and elimination of reasons leading to the loss of catalyst activity in this process.

The present work is devoted to the study of surface regularities of the process of ethylene glycol oxidation into glyoxal on massive copper catalyst by the methods of thermal programmed desorption (TPD) and thermal programmed reaction (TPR) for the mechanism detalization of the glyoxal and other reaction products formation.

It is shown that unlike Ag on the clean Cu surface the chemosorption and transformation of ethylene glycol (at $T_{ads}$EG ~ 200°C) are observed. TPD spectrum contains 3 peak with T max ~ 250°C (reversible desorption of ethylene glycol), 410°C (desorption of glyoxal and hydrogen), 550°C (of ethylene glycol desorption). According to the obtained data it can be assumed, that on clean Cu surface the process of ethylene glycol dehydrogenation occurs according to scheme:

$HOCH_2CH_2OH\ (g) \rightarrow HOCH_2CH_2OH\ (a)$ (1),

$HOCH_2CH_2OH\ (a) \rightarrow HOCH_2CH_2O\ (a) + H\ (a)$ (2),

$HOCH_2CH_2O\ (a) \rightarrow OCH_2CH_2O\ (a) + H\ (a)$ (3),

$HOCH_2CH_2OH\ (a) \rightarrow HOCH_2CH_2OH\ (g)$ (4),

$OCH_2CH_2O\ (a) \rightarrow O{=}CHCH_2O\ (a) + H\ (a)$ (5),

$O{=}CHCH_2O\ (a) \rightarrow O{=}CHCH{=}O\ (g) + H\ (a)$ (6),

$H\ (a) + H\ (a) \rightarrow H_2\ (g)$ (7).

Treatment of Cu surface by oxygen sharply changes the desorption picture. TPR spectrum at $T_{ads}$ $O_2$ and EG = 200°C contains 4 peaks Tmax ~ 220°C (water), 330°C (formaldehyde), 410°C (glyoxal), 440°C ($CO_2$). In this case the formation of glyoxal results along oxidative route predominantly.

Simultaneously, a part of ethylene glycol in such conditions is able to adsorb on the Cu surface dissociatively that leads to the formation of by-products. While increasing of ethylene glycol $T_{ads}$ to 300, 400°C the reaction transition from the copper catalyst surface to the volume is observed. The analysis of the ethylene glycol conversion products at the moment of adsorption showed the presence of the large number of compounds such as formaldehyde, glycol aldehyde, CO, $CO_2$ et al. It is evidence of a volume way of their formation.

Thus, the interaction of ethylene glycol with the clean surface of copper catalyst leads to the glyoxal formation along the dehydrogenation reaction; on oxidative surface of copper the glyoxal formation occurs along oxidative route and, simultaneously, the dissociating interaction of ethylene glycol with the Cu surface leads to the appearance of by-products: formaldehyde and $CO_2$. The increase of $T_{ads}$ EG up to 300, 400°C evokes a heterogenous - homogeneous trasformations of ethylene glycol to the formation of the large number of by - products.

PP-A-16

# SOFTWARE FOR TASKS OF DIFFERENTIAL EQUATIONS SYSTEMS REDUCTION IN CHEMICAL KINETICS

**A.M. Vaiman, S.I. Spivak***
Institute of Petrochemistry and Catalysis of Academy of Bashkortostan, Ufa, Russia
*Bashkir State University, Ufa, Russia

The problem of the differential 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 kinetics models [1].
- compounds gathering in group components. (lumping) [2-3];
- reducing methods based on the theory of asymptotic proximity [4].

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 sceme exists. It is described with the help of stehiomethric matrix $G\ (M \times N)$, where $M$ - reactions quantity, $N$ - quantity of compounds, which take part in reactions. Then differential 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 ; $\omega=(\omega_1 .. \omega_M)$ - reactions speed; $\gamma_{ij}$ - elements of matrix $G$.

Consider matrix with $\{N \times (M+1)\}$ dimentions : $F(t)=\left(\frac{X_j(t)}{t};\gamma_{ij}\omega_i\right)$, $i=1..M;\ j=1..N.$

Here the first matrix column consists of absolute values of concentrations and time ratio, other columns - elementary stages speed or zero, if any speed is 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 $i<>j$; $i=1..M$ , $j=1..N$;

By every $t$, matrix $F^*(t)$ determines significant level for corresponding members in differential equations system : the closer $f^*(t)$ to 1, the bigger the $j$-reaction investment in $i$-equation.

Algorihm of differential equations system simplification is built on assumption, that if $f^*_{ij}$ is small in any time interval, then reduction of the corresponding member in differential equations system will have a small influence on it's solving in this time interval.

# PP-A-16

Significance matrix *F*(t)* is considering at the moment t and all members of original differential equations system are setting to the zero, if their corresponding components in *F*(t)* less than value level. As a result, time intervals are assigned, and on every intervals the original system is being approached by the system with smaller dimention. Time moments, when one subsystem changes to another, determine as switch points.

This method was realized in the program for Windows 3.1/95 .

Income data :

- ■ - elementary stages speeds constants.
- ■ - stehiometric 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.

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.L., Spivak S.I., Yablonskii 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-A-17**

# CATALYTIC DECOMPOSITION OF NITROGEN OXIDES IN OXIDATIVE MEDIUM

Xu Yunlong, A.S. Savenkov, M.A. Sibirtseva
*Kharkiv State Polytechnic University, Kharkiv, Ukraine*

Catalytic nitrogen oxides decomposition on the catalysts based on transfer metal oxides in non-stationary chemosorptive-regenerative regime is most simple and economically profitable way. High activity of iron and aluminium oxides for nitrogen oxides decomposition in exhausted gases of commercial plants was ascertained earlier. Besides these oxides have high heat resistance and strength for oxygen poisoning. Taking into account all this the investigations on making more precise the catalysts compositions, the influence of technological parameters and kinetics of $NO_X$ decomposition in oxidative medium were carried out.

The activity of catalysts was studied under atmospheric pressure at nitrogen oxides concentration 0,1-3 vol.%; ratio $NO/NO_2$=0,5-2; oxygen content 3-18 %; water vapour content 5-10 vol.%. The tests were carried out in quartz reactor of the plant of flowing type. The catalysts were prepared with wet mixing of corresponding oxides with next formation, drying and burning.

The technique of catalysts preparation was maximally similar to one of industrial conditions.

Kinetic investigations were carried out on $Fe_2O_3$-$CuO$-$Al_2O_3$ catalyst. The effect of catalyst grain size, linear rate of gas flow, temperature, $NO_X$ concentration and contact time was investigated. The influence of oxygen and water vapour on catalytic activity was studied from the point of view of practical catalysis. The investigations of oxygen influence (see Fig. 1) showed that increase of oxygen concentration in a gas from 3 to 10 vol.% strongly reduced degree of decomposition. In so doing oxygen has greater influence on CuO, than on $Fe_2O_3$. But at the same time copper oxides presence in $Fe_2O_3$-$Al_2O_3$ catalytic system increases both catalyst activity and stability of catalyst operation in highly oxidative medium. Inlet of water vapour in reactive gas flow doesn't reduce catalyst activity. Some results of investigations are shown in Table 1.

On the base of kinetic investigations the kinetic equation was deduced, and optimum technological regime of $NO_X$ catalytic decomposition (catalyst grain size - less than 0,25-0,5 mm; linear rate of the flow - more than 74 mm/s; temperature - 350-400 °C; contact time - 0,2-1,5 s) was chosen.

The following reactions routes were used for creation of kinetic model:

$$NO \xrightarrow{K_1} N_2+O_2 \quad (1)$$

$$NO_2 \xrightarrow{K_2} N_2+O_2 \quad (2)$$

$$NO_2 \underset{K_4}{\overset{K_3}{\rightleftarrows}} NO+O \quad (3)$$

## PP-A-17

The calculation of obtained data of kinetic investigations taking into account stoichiometric routes allowed to propose the following model:

$$R_{NO_X} = -K \cdot \frac{C_{NO_X}}{C_{O_2}^2}$$

The obtained model is highly adequate to experimental data.

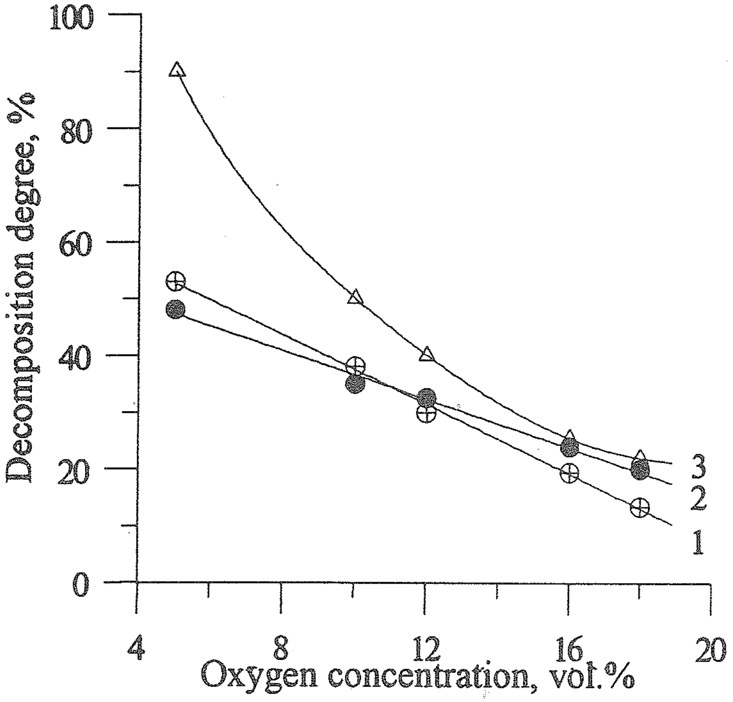


Fig. 1 - $NO_X$ decomposition degree dependency on oxygen concentration on different catalysts: $C_{NO_X}$=1 vol.%, d3=0,25-0,5 mm, 1 - CuO (t=400 °C, $\overline{W}$=1750 $h^{-1}$); 2 - $Fe_2O_3$-$Al_2O_3$ (t=700 °C, $\overline{W}$=1250 $h^{-1}$); 3 - $Fe_2O_3$-CuO-$Al_2O_3$ (t=400 °C, $\overline{W}$=2160 $h^{-1}$).

Table 1 - Laboratory experimental data of kinetics of nitrogen oxides decomposition

| Temperature, K | Initial mixture composition, % | | Contact time, s | Conversion degree, % | | Rate constant, | |
|---|---|---|---|---|---|---|---|
| | $O_2$ | $NO_x$ | | fact. | calk. | k, %/s | $k_{ef}$, 1/c |
| 473 | 5 | 0,993 | 0,63 | 0,697 | 0,803 | 64,9 | 2,59 |
| 473 | 5 | 1,206 | 0,18 | 0,372 | 0,373 | 64,9 | 2,59 |
| 473 | 5 | 2,011 | 0,09 | 0,245 | 0,208 | 64,9 | 2,59 |
| 573 | 5 | 1,120 | 0,18 | 0,440 | 0,403 | 72,3 | 2,89 |
| 573 | 5 | 1,255 | 0,79 | 0,864 | 0,899 | 72,3 | 2,89 |
| 573 | 10 | 1,114 | 0,79 | 0,596 | 0,437 | 72,3 | 0,72 |
| 573 | 12 | 1,147 | 0,79 | 0,343 | 0,329 | 72,3 | 0,50 |
| 653 | 16 | 0,734 | 1,20 | 0,168 | 0,304 | 77,1 | 0,30 |
| 653 | 18 | 1,335 | 1,20 | 0,203 | 0,249 | 77,1 | 0,24 |
| 673 | 5 | 0,403 | 0,68 | 0,859 | 0,879 | 78,1 | 3,12 |
| 723 | 5 | 1,492 | 0,63 | 0,890 | 0,868 | 80,5 | 3,22 |
| 823 | 10 | 1,421 | 1,00 | 0,518 | 0,569 | 84,6 | 0,84 |

# NONSTATIONARY KINETIC MODEL OF DEEP OXIDATION OF ALKYLAROMATIC HYDROCARBONS OVER OXIDE CATALYSTS

**A.N. Zagoruiko**

*Boreskov Institute of Catalysis SB RAS*
*Pr.Lavrentieva, 5, Novosibirsk, 630090, Russia*
*Phone (3832)354591, fax (3832)357678, e-mail: zagor@caty.catalysis.nsk.su*

This study was dedicated to the investigation of nonstationary kinetics of deep oxidation of volatile organic compounds (VOC) on the case study of cumene oxidation at alumina-copper-chromium oxide catalyst IC-12-8. The experimental studies [1] showed that in the area of low and moderate temperatures (below ~$300^0$C) the oxidation of VOC occurs via intermediate steps of adsorption and chemisorption of the oxidised compound, thus giving rise to the significant nonstationarity of the catalyst surface.

Earlier the two-stage scheme was proposed to describe the process [2], including the stage of hydrocarbon chemisorption with formation of surface compound (SC) and the stage of SC oxidation by oxygen with simultaneous reoxidation of the catalyst surface. However, the more detailed analysis of experimental results showed that for more adequate description of the process it is necessary to take into account the surface reoxidation as separate stage.

With account of these factors the kinetic scheme of the reaction may be represented in the following form:

$$C_9H_{12} + n\,[ZO] \Rightarrow [P_n] \qquad (1)$$
$$[P_n] + (24-n)\,[ZO] \Rightarrow 9CO_2 + 6H_2O + 24\,[Z] \qquad (2)$$
$$\underline{24\,[Z] + 12O_2 \Rightarrow 24\,[ZO]} \qquad (3)$$
$$C_9H_{12} + 12O_2 \Rightarrow 9CO_2 + 6H_2O \qquad (4)$$

where $[P_n]$ – irreversibly chemisorbed compound at the catalyst surface, [ZO], [Z] – oxidised and reduced active sites at the surface respectively, n – stoichiometric coefficient. Obviously, the presented scheme does not pretend to represent the detailed reaction mechanism, because every proposed stage really combines the sequence of elementary steps.

The various kinetic models were proposed on the base of the scheme (1)-(3). The optimal description was obtained for the following rate equations:

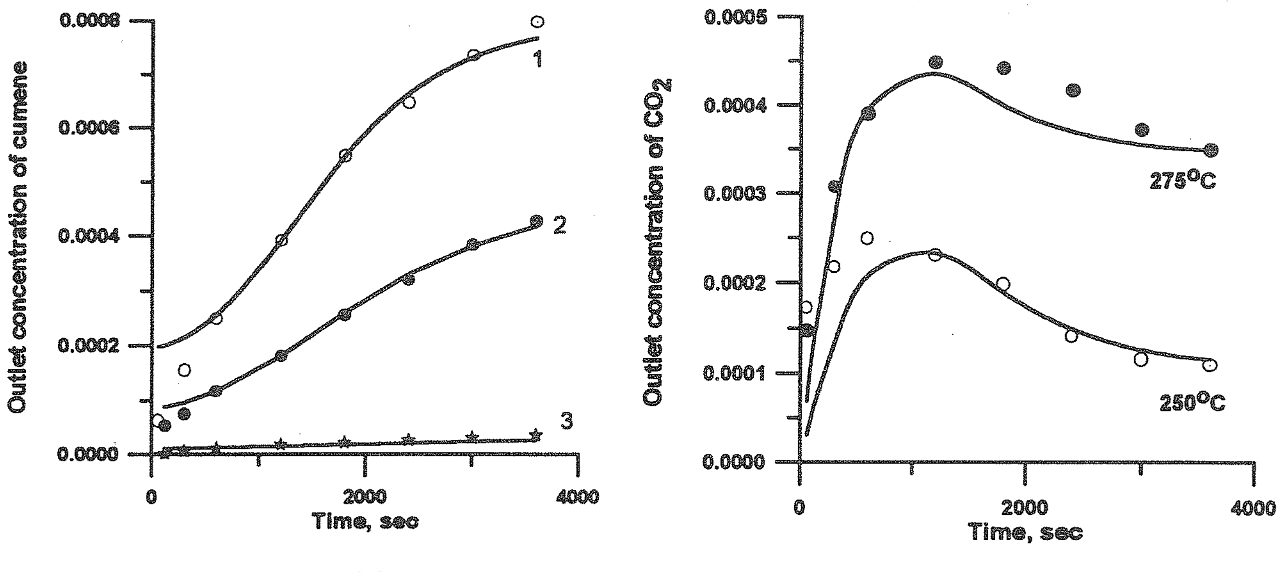
$$W_1 = k_1 C_c^{1/n} \theta_O \qquad (5)$$
$$W_2 = k_2 \theta_P \theta_O \qquad (6)$$
$$W_3 = k_3 (1 - \theta_P - \theta_O) C_{O_2} \qquad (7)$$

where $\theta_O$ and $\theta_P$ – the fractions of catalyst surface, occupied by [ZO] and [P] sites respectively; $k_i$ – rate constants; $W_i$ – rates of stages (1-3) respectively; $C_C$ and $C_{O2}$ – cumene and oxygen concentration in the gas phase.

The model (5-7) is also supplemented by algebraic (for gas concentrations) and differential (for surface variables) mass balance equations and corresponding boundary conditions.

The processing of experimental results was performed numerically by means of the fastest descent algorithm. The best description is obtained for n=2 and activation energies about 5-6, 8-10, 12-14 Kcal/mol for stages (1-3) respectively. Interesting to note, that calculations showed the increase of observed catalyst capacity for oxygen with the rise of temperature, what may be explained with increasing of the oxygen reaction capability at higher temperatures.

Fig.1 shows comparative calculated and experimental data for transient cumene and $CO_2$ concentrations at the reactor outlet under feeding of cumene+air mixture to preliminarily oxidised catalyst.



(a) (b)

Fig.1
Variation of outlet concentrations of cumene (a) and carbon dioxide (b) in time (in molar fractions). Lines – calculations, points – experiments.

It is seen that proposed model provide good coincidence between calculated and experimental results. It is important to note, that description of maximum at the Fig.1b is possible only with account of surface reoxidation as the separate stage.

To prove the adequacy of the model the simulation of other types of experiments was performed on the base of data, obtained from relaxation experiments. In particular, Fig.2 shows the results of reaction modelling, when the catalyst, operating in the steady-state regime, is started to be fed by air instead of reaction mixture.

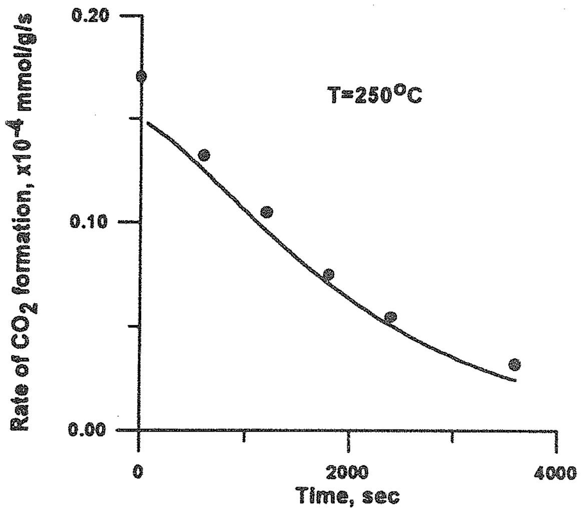


Fig.2
Changing of $CO_2$ formation rate after interruption of cumene feeding into the reaction mixture. Lines – calculations, points – experiments.

It is seen that the good coincidence was observed in this case, as well as in modelling of reaction under programmed temperature rise and steady-state data.

### *References*

1. Yu.A. Kachurovskii. Deep oxidation of aromatic hydrocarbons admixtures in air at alumina-copper-chromium oxide catalyst IC-12-8. PhD Thesis, BIC, Novosibirsk, 1988.
2. A.N. Zagoruiko. Nonstationary kinetic model of deep oxidation of aromatic hydrocarbons on oxide catalysts. - React. Kinet. Catal. Lett., in press.

**PP-A-19**

# KINETICS OF THE HYDROGEN SULFIDE DIRECT OXIDATION INTO SULFUR OVER V-Ti CATALYST IC-27-40

A.N.Zagoruiko, V.V.Mokrinskii

*Boreskov Institute of Catalysis SB RAS*
*Pr.Lavrentieva, 5, Novosibirsk, 630090, Russia*
*Phone (3832)354591, fax (3832)357678, e-mail: zagor@caty.catalysis.nsk.su*

The process of direct $H_2S$ oxidation into sulfur attracts the significant interest of both researchers and engineers as the prospective technology for sulfur removal from sulfur-containing gases. Evidently, the development of hydrogen sulfide oxidation processes is possible only on the base of accurate kinetic data. The current investigation was dedicated to experimental study of direct $H_2S$ oxidation reaction kinetics at the vanadia-titania catalyst IC-27-40, developed in Boreskov Institute of Catalysis [1]. This catalyst is very promising for this technology due to its extremely high activity, stability and crushing strength.

The process of $H_2S$ direct oxidation by oxygen may be described by the set of three reactions:

$$H_2S + 1/2\ O_2 \Rightarrow 1/n\ S_n + H_2O \quad (1)$$

$$H_2S + 3/2\ O_2 \Rightarrow SO_2 + H_2O \quad (2)$$

$$H_2S + 1/2\ SO_2 \Leftrightarrow 1.5/n\ S_n + H_2O \quad (3)$$

Kinetic experiments were performed at the direct flow lab installation. The special experiments gave the way to define the intraparticle diffusion limitations area borders. Because of the very high activity the absence of diffusion limitations was observed only on the catalyst pellets with the size as low as 0.004-0.008 mm. The same reason required to perform the experiments with very small residence time – about 0.001-0.003 sec, providing the $H_2S$ conversion not higher than 50%. The kinetics of more slow Claus reaction (reaction (3)) was studied independently.

To describe the experimental results various kinetic models were proposed. Models discrimination and definition of their parameters were performed by means of algorithm, applying the procedure of the fastest descent. The best description was obtained with the following kinetic model:

$$W_1 = \frac{k_1 C_{H_2S} C_{O_2}}{(C_{H_2S} + k_4 C_{O_2} + k_5 C_{O_2}^2)(1 + k_{H_2O} C_{H_2O})} \quad (4)$$

$$W_1 = \frac{k_2 C_{H_2S} C_{O_2}}{(C_{H_2S} + k_6 C_{O_2})(1 + k_{H_2O} C_{H_2O})} \quad (5)$$

$$W_1 = \frac{k_3 C_{H_2S} C_{SO_2}}{(C_{H_2S} + k_7 C_{SO_2})(1 + k_{H_2O} C_{H_2O})} \left(1 - \frac{\Pi}{K_P}\right) \quad (6)$$

where $W_i$ – rates of reactions (1)-(3) respectively, $C_i$ – reagents concentrations, $k_i$ – rate constants, $K_P$ – Claus reaction equilibrium constant, $\Pi$ – the product of concentrations in Claus reaction:

$$\Pi = \frac{C_{H_2O} C_{S_6}^{1/6}}{C_{H_2S} C_{SO_2}^{1/2}} \quad (7)$$

Figures 1a-1d show the comparison of calculated and experimental data.

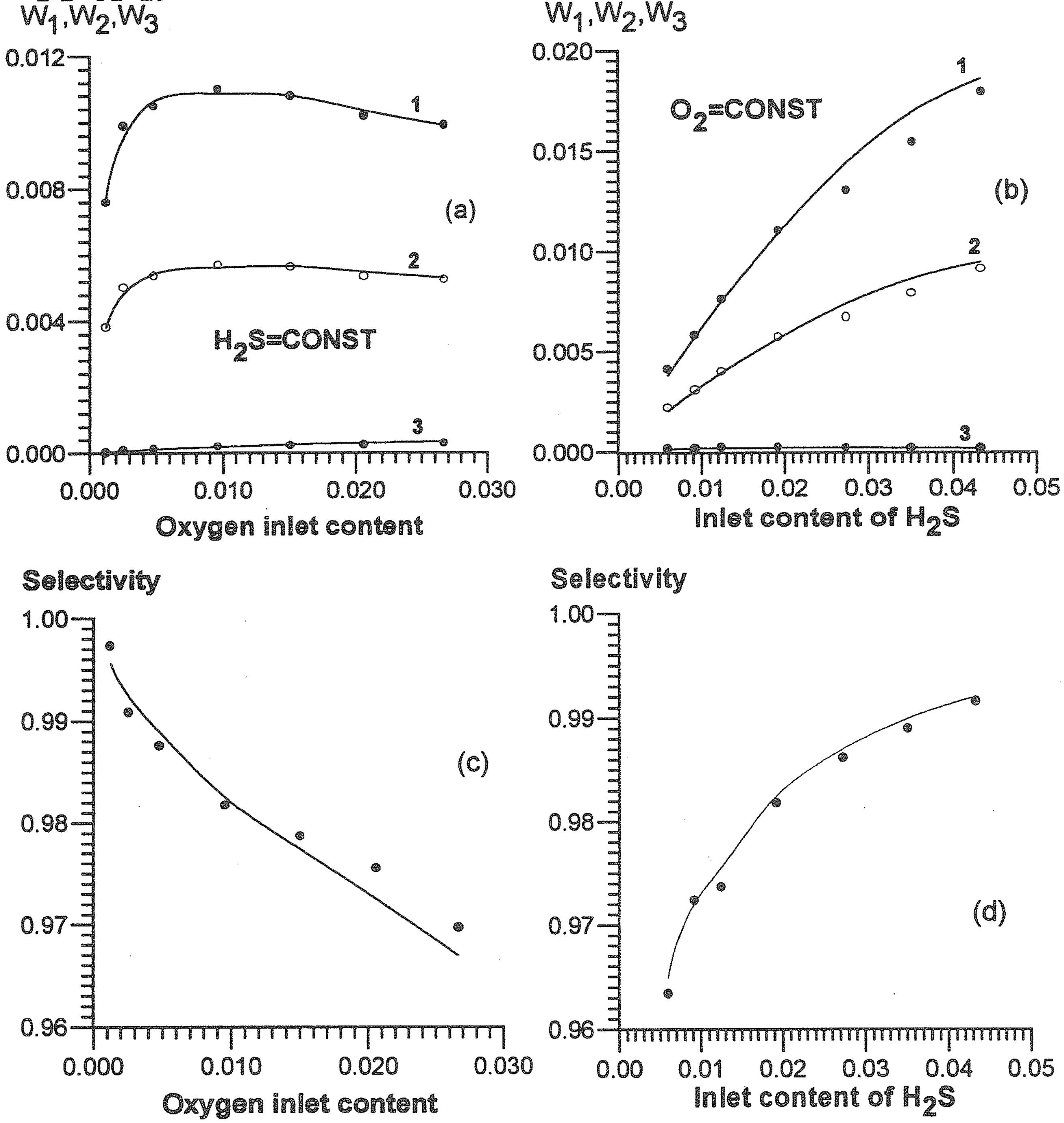


**Fig.1 Comparison of calculated and experimental data.**
Rates of reactions (1)-(3) (in sec$^{-1}$, plots (a) and (b)) and selectivity (plots (c) and (d)) *versus* inlet concentrations of oxygen ((a) and (c), in molar fraction at constant inlet $H_2S$ content) and hydrogen sulfide ((b) and (d), in molar fraction at constant inlet $O_2$ content). Lines – calculation, points – experiment. T=230$^{0}$C.

It is seen that the model (4)-(7) provides good quality of experimental data desciption both in qualitative and quantitative terms and may be applied for development of different processes of $H_2S$ oxidation. The treatment of the experimental data, obtained within the temperature range from 230 to 300$^{0}$C, gave the way to evaluate the activation energies of reaction stages.

**References**

1. V.I.Marshneva, V.V.Mokrinskii, K.A.Dubkov et al. USSR patent #1398304, 1986.

### PP-A-20

# ETHYLENE DIMERIZATION ON Pd AND Ni ORGANOMETALLIC COMPLEXES ENCAPSULATED IN Na(H)Y ZEOLITES

R. Zavoianu*, E. Angelescu*, C. Nenu**
** University of Bucharest, Dept. of Chemical Technology and Catalysis, bd. Carol I no. 13, Bucharest, Romania*
*** ZECASIN S.A., Spl. Independentei, No 202A,Sect. 6, Bucharest, Romania*

The study of zeolite encapsulated metal - complexes is of great and current interest [1-5]. This paper presents the results concerning Pd(bipy)$Cl_2$ , Ni (2,2' bipy)$Cl_2$, $NiCl_2$-$AlCl(C_2H_5)_2$, $NiCl_2$ -$P(C_6H_5)_3$, $NiCl_2$-$P(C_6H_5)_3$ -$AlCl(C_2H_5)_2$ , $NiCl_2$-$P(nC_4H_9)_3$ -$AlCl(C_2H_5)_2$ and $NiCl_2$-2,2' bipy-$AlCl(C_2H_5)_2$ complexes encapsulated in Na(H)Y zeolite and their application in ethylene dimerization.

The catalysts were prepared using the " ship in bottle " technique reported for Ni (salen) encapsulation in zeolite [6].

The catalysts were characterised by diffuse-reflectance UV-VIS spectroscopy, IR spectroscopy, and TGA analysis. Their spectra presented the maxims characteristic of complexes. The TGA analysis revealed the instability of Ni complexes at the increase of temperature.

The dimerization of ethylene to n-butenes was carried out in continuous reactant flow at normal pressure in the range of temperature 20 – 150°C and WHSV = 2 $h^{-1}$ in the case of Pd encapsulated complex catalysts and in he range of temperature 20 - 60°C and same conditions in the case of Ni encapsulated complexes. The best results on Pd complex catalysts were obtained at 80°C and in the case of Ni complex catalysts at 20°C. The activity of Ni binary complexes was lower than that of Ni ternary complexes.

$NiCl_2$-2,2' bipy-$AlCl(C_2H_5)_2$ presented the highest activity among ternary complexes. In Table No. 1 and Table No. 2 we present the performances of the studied catalysts.

Table No. 1

The results for ethylene dimerization on Pd encapsulated complex catalysts

| Catalyst Pd (wt. %) | T (°C) | $C_2H_4$ conversion (%) | Selectivity to $C_4H_8$ (%) | Molar ratio 2-$C_4H_8$/1-$C_4H_8$ | Molar ratio 2-t-$C_4H_8$/2-c-$C_4H_8$ |
|---|---|---|---|---|---|
| 0.8 | 20 | 24.82 | 78.80 | 1.55 | 0.69 |
| 0.8 | 80 | 60.68 | 72.45 | 3.92 | 1.08 |
| 0.8 | 150 | 65.70 | 67.20 | 4.28 | 1.36 |
| 1.8 | 20 | 12.76 | 94.21 | 1.20 | 0.46 |
| 1.8 | 80 | 41.01 | 88.76 | 0.71 | 0.63 |
| 1.8 | 150 | 47.71 | 81.12 | 0.63 | 0.71 |

Table No. 2

The results for ethylene dimerization on Ni encapsulated complex catalysts

| Catalyst | T (°C) | $C_2H_4$ conversion (%) | Selectivity to $C_4H_8$ (%) | Butenes concentration in the reaction product | | |
|---|---|---|---|---|---|---|
| | | | | 1-$C_4H_8$ (%) | 2-t-$C_4H_8$ (%) | 2-c-$C_4H_8$ (%) |
| Ni (2,2' bipy)$Cl_2$ - Y | 60 | 12.31 | 7.35 | 1.48 | 0 | 0 |
| $NiCl_2$-$AlCl(C_2H_5)_2$ - Y | 60 | 59.71 | 15.47 | 4.99 | 3.84 | 0.97 |
| $NiCl_2$ -$P(C_6H_5)_3$ - Y | 60 | 19.83 | 9.09 | 1.43 | 0.54 | 0.36 |
| $NiCl_2$-$P(C_6H_5)_3$ -$AlCl(C_2H_5)_2$ - Y | 60 | 21.41 | 10.19 | 1.57 | 0.72 | 0.60 |
| $NiCl_2$-$P(nC_4H_9)_3$ -$AlCl(C_2H_5)_2$ - Y | 60 | 19.51 | 14.77 | 1.07 | 2.15 | 1.08 |
| $NiCl_2$-2,2' bipy-$AlCl(C_2H_5)_2$ - Y | 60 | 49.20 | 35.53 | 9.56 | 6.00 | 3.41 |
| $NiCl_2$-2,2' bipy-$AlCl(C_2H_5)_2$ - Y | 20 | 69.27 | 77.22 | 18.00 | 5.40 | 4.73 |

In this work, ethylene conversion and selectivity to 1- and 2-$C_4H_8$ (cis and trans) as a function of reaction temperature is analysed. Correlation between the nature of encapsulated complex species and the catalytic activity and the selectivity to ethylene dimerization are established.

## REFERENCES

[1] E . Derouane, J. Catal., 72 (1981), p.177

[2] T. N. Huang, J. Schwartz, J. Am. Chem. Soc., 104 (1982), p. 5445

[3] N. Herron, Inorg. Chem., 25 (1986), p. 4714

[4] T. N. Huang, J. Schwartz, N. Kitajima, J. Mol. Catal., 22 (1984), p. 389

[5] D. E. DeVos, F. Thibault-Starzyk, P. P. Knops-Gerritis, R. F. Parton, P. A. Jacobs, Macromol. Symp., 80 (1984), p. 157- 184

[6] D. Chatterjee, H. C. Bajaj, A. Das, K. Bhatt, J. Mol. Catal., 92 (1994), L 235

# SECTION B

## PHYSICO-CHEMICAL AND MATHEMATICAL FUNDAMENTALS OF PROCESSES IN CHEMICAL REACTORS

# ON INCREASING THE PRODUCTIVITY OF CATALYTIC FIXED-BED REACTORS UNDER UNSTEADY-STATE CONDITIONS

**V.V. Andreev**
*Chuvash State University, Cheboksary, Russia*

In papers [1,2] for separate porous catalyst granules relations were established, at fulfillment of which the average for period productivity of desirable product at realization of the catalytic reaction under unsteady-state conditions is higher in comparison with a steady-state condition.

The purpose of the given work is the research of an opportunity to increase desirable product production under unsteady-state conditions at flow of a reactionary mixture through a stationary layer of porous catalyst granules. For simplification of the analysis, as well as in papers [1,2] it is supposed, that the quasi-stationary conditions are fulfilled. In this case the processes in the porous catalyst granules can be described on the basis of steady-state quasi-homogeneous model [3]. Modeling of a reactionary mixture through stationary layer of the catalyst granules is also made on the basis of steady-state quasi-homogeneous model.

Peculiarities of process realization under unsteady-state condition on a basis of described model are analysed. Simple for application relations are obtained at fulfillment of which the average for period production of desirable product under unsteady-state reaction performance is higher in comparison with a steady-state conditions.

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.

## PP-B-2

# MULTICOMPONENT NONISOTHERMIC DIFFUSION IN HETEROGENEOUS PROCESS OF DECOMPOSITION CONDENSED SUBSTANCE

V.S. Beskov, M.G. Davidkhanova

*Mendeleev University, Moscow, Russia*

The heterogeneous interactions of condensed and gas phase substances are accompanied by the phenomena of a heat and mass transfer between phases. Chemical reaction causes additive flows of heat and mass - stephan's flow, thermal diffusion, diffusion heat transfer [1]. Earlier the general approaches to such description of process [1] were considered which were derived in work [2] for catalytic processes. When a solid or liquid substance is composed the gas phase is made only by products of reaction. Therefore the model of decomposition can be constructed, using other system of readout, than at the description of catalytic process:

$$j_l = -\frac{PD_l}{RT}\,grad\,x_l - \frac{P}{RT}D_l k_{Tl}\frac{grad\,T}{T} + v_l x_l \qquad (1)$$

$$q = -\lambda gradT + \sum_i j_i H_i - \frac{P}{\sum \nu}\sum_{ii}\left[v_i\frac{\mathrm{grad}\,x_i}{x_i}\sum_l \overline{D}_l k_{Tl}\right], \qquad (2)$$

where $j_i$, $q$ - flows of substances and heat; $D_i = 1\Big/\sum_k \frac{x_k}{D_{ik}}$;

$$k_{Ti} = \sum_k x_i x_k \frac{M_i - M_k}{\sum_l x_l M_l}(2 - m_{ik}); \quad v_i = j_i\frac{D_i}{\nu_i}\sum\frac{\nu_k}{D_{ik}}; \quad \overline{D}_i = D_i\Big/\left(1 - \frac{D_i x_i}{\nu_i}\sum_k\frac{\nu_k}{D_{ik}}\right).$$

Products of reaction are removed from a surface of the condensed reagent basically at the expense of a hydrodynamic flow.

The heat of reaction is not only removed from a surface in volume of gas, but also goes on by warming up decomposed substance. In this case the equation (2) will be transformed as:

$$V_{y\partial}c_{pi}\frac{\partial T_{\Pi}}{\partial\ t} + \alpha\frac{\partial T}{\partial\xi} = \left[Q_p(T^*) + \bar{c}_p(T - T^*)\right]r(T^*) \qquad (3)$$

where $T$, $T_{\Pi}$ - temperature of gas and surface: $\bar{c}_p$- heat capacity of products of reaction; $r(T^*)$, $Q(T^*)$ - velocity and thermal effect of reaction; $V_{уд}$ - the attitude of volume to a surface of condensed substance; $\xi$ - non-dimensional thickness of a boundary layer.

During decomposition initial substance is spent, and if it was as a drop, changes of his size can be described by the following equation:

$$\frac{\partial d_c}{\partial t}=2\frac{M}{\gamma}r(T_{\Pi}), \tag{4}$$

where $M$, $\gamma$- molecular weight and density of a drop.

Accepting, that by warming up a drop which is more inertial process, than change of temperature in a gas phase, the equation (3) can be integrated in terms of thickness of a boundary layer:

$$ln\frac{Q_P(T^*)+\bar{c}_P(T_0-T^*)}{Q_P(T^*)+\bar{c}_P(T_{\Pi}-T^*)}=\frac{\bar{c}_P}{\alpha}c_c r(T_{\Pi}) \tag{5}$$

The obtained model of decomposition of condensed substance was used for calculation of process and design of the reactionary apparatus for industrial process of production of medical nitrogen oxide by a thermal decomposition of ammonia nitrate:

$$NH_4NO_3 = N_2O + 2\ H_2O \tag{6}$$

Reaction is carried out at 270°C. For prevention of formation of by-products the reaction should proceed in a rather narrow interval of temperatures, that requires a detailed substantiation of mathematical model for more exact calculation of process.

## References

1. D.A. Frank-Kamenetskii, “Diffusion and Heat Transfer in Chemical Kinetics”, M: Nauka, 1987.
2. V.S Beskov, Yu.L. Vyatkin, L.S. Zelenyak. “Controlled Systems”. В сб. Управляемые системы. IM., Institute of Catalysis, 1970, n4-5, p. 108-122.

## PP-B-3

# STUDY OF HETEROGENEOUS-HOMOGENEOUS PROCESSES IN METHANE OXIDATION ON Al-Mn CATALYST IC-12-40

L.L. Gogin, I.A. Zolotarskii, Yu.V. Malozemov, P.G. Tsyrulnikov, V.S. Sal'nikov

*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

Use of reverse-flow operation for heat production from coal mines' gases containing the methane is one of possible applications of this operation [1]. The aluminum-manganese catalyst IC-12-40 is used at this process owing to its high thermostability. Maximal temperature in catalytic bed is equal to 700 -1000°C during methane oxidation at the regime of gas flow reverse. It is possible not only heterogeneous but also homogeneous process of oxidation at these temperatures. It is known [2] that catalyst can initiate formation of free radicals that lead to homogeneous prolongation of heterogeneous process. If there is gas phase reaction it is necessary to take into account mathematical modeling of reverse-flow operation of methane oxidation.

The aim of present work was detection of reaction not only on the catalyst surface but also in gas phase during methane-air mixtures' oxidation on the catalyst IC-12-40 at high temperature (500-850 °C). Besides the separate determination was supposed for contribution of homogeneous reaction for account of initiating by catalyst surface, and properly the gas phase reaction as well. Method of Gorohovatskii [2] (it consist in the alteration of free volume of reactor with the help both catalyst grain sizes' alteration and use of additional inert packing) was used. The contribution of properly heterogeneous catalytic reaction was estimated with extrapolation of kinetics data to higher temperatures' range. The kinetics data was obtained at 450-570 °C with catalyst fraction sizes 0.4-0.8 mm. Also reaction in empty reactor was studied (600-850 °C).

The experimental conditions were: a) up to 600 °C - non-gradient furnace with blow, recycle reactor, rate of circulation was 800 l/h, rate of gas flow was 4-50 l/h, inlet methane concentration was 0.2-2.5%vol.; inner diameter of reactor from molybdenum glass was 16 mm.; the catalyst was fraction 0.4-0.8 mm and cylinders 4-5 mm; б) at 600-850°C - non-gradient furnace with inner circulation; diameter of quartz reactor (it had the coiled pipes for preliminary heating of gas) was 15 mm; rate of circulation was 300-1300 l/h, rate of gas flow was 4-65 l/h, inlet methane concentration was 0.4-4.5%vol.; the catalyst was cylinders

4-5 mm, inert packing was microspheric (250 mc) $Al_2O_3$ and fraction of quartz 1.6-2.5 мм. Temperature was measured with thermocouple that was located directly in catalytic bed; analysis of gas mixture was made with gas chromatography.

The experiments have resulted, that:

1) methane oxidation reaction on catalyst IC-12-40 at temperatures up to 600 °C has the first order on methane (activation energy for fraction 0.4-0.8 mm is about 25 kcal/mol);

2)methane oxidation in empty reactor starts with 700 °C; strong dependence of methane conversion X on the rate of circulation take place; also original dependence X (provided that rate of gas flow is constant) on concentration C is observed - at first increase of value X occurs, then decrease of value X does (provided that value C is increased); another reaction product is observed in addition to carbon dioxide and water (probably, ethylene or CO);

3) methane oxidation on the catalyst at the temperature more than 600 °C occurs with formation of carbon dioxide and water only, dependence of conversion on the rate of circulation is absent; monotonous dependence X on C is observed. The signs of homogeneous reaction may be observed at temperature more then 700°C only at very strong decrease of the catalyst weight (from 4.6 g to 0.3 g, catalyst occupies small part of reactor volume). Addition of inert packing influences the reaction in the presence of catalyst weakly.

So our experiments allow to conclude that gas phase reaction of methane oxidation do not occurs in the presence of catalyst IC-12-40 at temperature up to 850 °C .

## References:

1. A.S. Noskov, L.L. Gogin, O.P. Klenov, V.S. Lakhmostov. In: Coalbed methane: forecasting, monitoring, utilization. Preprint of Russian Coalbed Methane Center.-1995.-N1-3-p.21.
2. Ya.B. Gorohovatskii. Kinet.Kat., 1969, vol.10, N 3, p.552.

## PP-B-4

# INVESTIGATION OF THE STEADY-STATE MULTIPLICITY A SOLID-CIRCULATION MODEL BY HOMOTOPIC METHOD

E.A.Ivanov, A.V.Kazhichov, S.I.Fadeev

*Boreskov Institute of Catalysis, Novosibirsk, Russia*
*Lavrentiev Institute of Hydrodynamics, Novosibirsk, Russia*
*Sobolev Institute of Mathematics, Novosibirsk, Russia*

A two phase solid-circulation model is used to investigate the steady-state multiplicity features of a fluidized bed reactor in which a single, first order, exothermic reaction occurs. A more accurate prediction of the dynamic response can be attained from the solid-circulation model which accounts for the upwards flow of particles in the bubble phase and the corresponding downwards flow of particles in the dense phase [1]. The purpose of this study is to examine the steady-state multiplicity and stability features of fluidized bed reactors and to determine the key factors which affect the behaviour of the system. We consider a reactor cooled by an internal heat exchanger with an area A per unit volume of the reactor. We define as $\beta_g$ and $\beta_s$ the volumetric rate of exchange of gas and solids between the two phases per unit volume of the reactor. This solid-circulation model is initial-boundary value problem for hyperbolic system of partial differential equations.

A new procedure for the calculation of solutions for process described by boundary problem of hyperbolic equations is presented. We have used the revised homotopic method (i.e., continuation algorithm) [2] in order to consider the solid circulation model under steady-state conditions. Homotopic method has been applied previously for the non-linear numerical analysis. The Newton method applied to the continuation algorithm involves a residual control on iterations, and a mechanism of a step adjustment for the parameters. Numerical simulation included a bifurcation analysis of solutions and a simultaneous analysis of their stability.

ACKNOWLEDGEMENT. This work is supported in part by grants from the Siberian Branch of RAS Fund.

REFERENCES

1. Sheplev V.S., Luss D. Chem. Engng Sci. 1979. V.34, ¹ 3, p.515-520.

2. Dyatlov V.L., Konyashkin V.V., Potapov V.S., Fadeev S.I. Film Electromechanics, , Novosibirsk: Nauka, Sib. Div., 1991.- 248 p. (in Russia)

PP-B-5

# INTELLECTUAL EXPERT SYSTEM FOR INDUSTRIAL METHANOL PRODUCTION

A.A. Novikov, P.I. Koval, S.V. Navoenko

*Tomsk Polytechnic University, Tomsk, Russia*

Methanol production is one of the largest in modern chemical industry. Need in methanol constantly grows, therefore the problem of perfection and increase of efficiency of working manufactures is very urgent.

For the successful decision of problems of modeling, designing, forecasting and management of technological processes the most perspective direction is use of intellectual expert systems (IES).

Given IES is realized on an example of working installation M-750 of Tomsk Petrochemical Combine. The scientific work was carried out in frameworks of chemical-technological system (CTS):

- Conversion of natural gas
- Synthesis of methanol

The basic modules of developed IES are:

- database (DB)
- base of knowledge (BK)
- bloc of the applied programs (BAP)

The structure of BAP consists of the programs, simulating processes of natural gas conversion and methanol syntheses and allowing balance and optimization calculations, and preliminary statistical data processing as well.

For an effective utilization of earlier developed BAP an environment and the managing program BD is realized on the programming language Borland Pascal with the use of the module Turbo-Vision. The basis of BD consists of technological parameters of M-750 manufacture:

- pressure
- temperature
- mass and volumetric speeds
- concentration of components,

which are fixed on Central Board of Management (CBM) and local sources. For the best presentation and convenience of input/output of the information in the static text BD, number of technological flows and position of devices for the control and automation are included. Generated BD is dynamic,. so updating, correcting, expansion of its elements are possible.

In systems of an intelligent type knowledge about subject area are submitted as descriptive model, which is stored in BK irrespective of procedures of its processing. The presence of BK is necessary for operative realization of diagnostics of deviations in work of plants, choice of optimum variant of the technological circuit and optimum parameters. The structure of BK functionally is coordinated with particular problems, soluble by the technologists of methanol production. Ordering expert knowledge (EK), are used accumulated in the result of research work and experience of operation of plants.

Thus, the intellectual expert system developed by us allows to put process of perfection and increase of efficiency of industrial methanol production on a qualitatively new level.

# MODELLING AND ANALYSIS OF METHODS OF STEADY STATES MULTIPLICITY ORGANIZATION OF ADIABATIC REACTORS

Pisarenko V.N., Pisarenko E.V.
*D. Mendeleyev University of Chemical Technology of Russia*
*Moscow, Russia*

One of the most efficient methods to intensify catalytic processes is to organize them in the way when appearence of steady states multiplicity in catalytic reactors becomes possible. These bindings open new opportunities for investigators because there is a choice of different technological regimes. The technological regime which can provide the highest productivity and selectivity is realized. There are two alternatives in organization of chemical technological process: one is to determine the region of steady states multiplicity occuring in catalytic reactor, the other is purposeful creation of the region of steady states multiplicity of exploiting regimes of catalytic reactor (by changing physicochemical properties of reaction medium and catalyst beds).

The aim of the report is to consider new efficient methods of analysis and purposeful organization of the establishment of steady states multiplicity of reactors' exploiting when single or multi-routes catalytic reactions occur. Methods of catalytic processes modelling are stated, which provide such realization of exploiting regimes of reactors when steady states totality which is characterised by high economic efficiency takes place. New methods of a catalytic processes modelling on the catalyst's grain have been considered in assumption that quasi-homogeneous grain model with Dirichlet and Neumann boundary conditions adequately reflects the chemical conversion in the grain of catalyst. It's often turned out that every steady point in kinetic region can correspond to several steady points in diffusion region (that is on the catalyst's grain or on the phase surface). The latter can promote an increase of the quantity of steady states in catalytic or chemical reactor. The diffusion stoichiometry equations for single or multi- routes of chemical reactions were derived. On the basis of these equations the numerical methods for the calculation of exploiting regimes of grain and determination the region of steady states multiplicity were developed. Their total number is established in dependence of physicochemical properties of the catalyst's grain and reaction medium. Possibility of the influence of grain's geometry and its physico-chemical chacracteristics on the variables characterizing the steady state are shown. Deliberate changing of these physico-chemical chacracteristics of grain results in shift of every steady point (steady state) on the phase space The efficiency of the given catalytic process is demonstrated. New methods of catalytic processes modelling in adiabatic reactors are considered. The reactor stoichiometry equations for single or multi- routes reactions, occuring in catalytic reactors were derived. Numerical methods for calculation of exploiting regimes of industrial apparatus were developed. It seems that both calculation of every steady state and determination of the region of steady states multiplicity are simplified. Their total number is established in dependence of the reactor's design, catalyst's physico-chemical properties and reaction medium. Possibility to regulate the quantity of steady states and the variables which characterize every steady state, in particular, by regulating physico-chemical properties of catalyst bed in reactor are shown. Thus possibility to shift steady points of a catalytic process on phase space has been proved. These circumstanses open principally new opportunities in the field of catalytic processes intensification.

The results of this work are illustrated by the examples of such industrial processes as methanol synthesis, butanol and higher alcohols synthesis.

# NEW APPROACH TO ANALYSIS OF OZONATION KINETICS OF CHEMICAL SOLUTIONS IN A BABBLE REACTOR

A.N. Pryakhin, K.V. Kasterin, E.M. Ben'ko, N.A. Mamleeva, A.N. Mitrofanova, V.V. Lunin

*Lomonosov Moscow State University, Moscow, Russia*

The theory and methods of solving the reverse kinetics tasks for the reactions in barbotage reactor are suggested. The mathematical model of barbotage reactor was analysed for the case when chemical reaction is a rate determining process. This model contains the system of non-linear differential equations which have not analytical solution in an explicit form. The most of ozonation reactions could be described by this kind of model.

A new theoretical approach for solving the system of differential equations was developed. It permits to find the solution of the system in implicit form. It allows to test kinetic model of barbotage reactor and discriminate kinetics mechanisms and to define corresponding rate constants.

The different kinetic schemes of chemical compounds solutions ozonolysis were considered. The process of chemical compounds ozonation could be performed as a combination of *n*- parallel bimolecular reactions:

$$A_i + O_3 = P_i, \qquad i=1,2,...n$$

where $A_i$ - *i*-functional group of A compound, or $A_i$ - an individual compound in the mixture of *n* - components.

Ozone-air mixture flows through the barbotage reactor with initial ozone concentration $C_0$, feed rate of the gas mixture into the reactor *W*, ($W = \omega/V$, where ω-volume feed rate of gas mixture into the reactor , *V*- reactor volume). The equilibrium distribution of $O_3$ between liquid and gas phases with equilibrium constant *K* is reached in the reactor.

$$O_{3\,(g)} \Leftrightarrow O_{3\,(s)}$$

The ozonation process of $A_i$ could be performed by the reaction equation

$$A_{i\,(s)} + O_{3\,(s)} \xrightarrow{k_i} P_i, \quad i=1...n,$$

with the rate constant $k_i$

The full kinetic curve is described by the system of differential equations:

$$\frac{dC}{dt} = U(\varphi - C) - \sum_{i=1}^{n} k_i C A_i \,, \tag{1}$$

$$\frac{dA_i}{dt} = -KCk_iA_i \;, \qquad i=1,2...n, \qquad (2)$$

where $U=W/K$; $\varphi$, $C$-ozone concentration in the moment of time-$t$ in the outlet of the reactor filled with solvent and solution, accordingly. The solution of this system of equations (1), (2) is:

$$y = y_\infty\left(1-\sum_{i=1}^{n}\frac{A_{i0}}{y_\infty}e^{-k_iKx}\right), \qquad (3),$$

where $$y \equiv W\int_0^t(\varphi - C)dt - KC(t)\,, \qquad (4),$$

$$x \equiv \int_0^t Cdt\,, \qquad (5)$$

$y_{\propto}$- maximum ozone consumption.

The analogues approach was used for analysis of kinetic scheme including several sequential reactions. For example, for the simplest scheme:

$$A+O_{3\,(s)} \xrightarrow{k_1} P_1$$

$$P_1+O_{3\,(s)} \xrightarrow{k_2} P_2,$$

when the initial compound A reacts with the dissolved ozone and forms intermediate compound $P_1$, which, in turn, is oxidized into the final product $P_2$. The solution to the corresponding system of differential equations is:

$$x=y_{\propto}\left[1-\frac{1}{2}\frac{2k_2-k_1}{k_2-k_1}\exp(-k_1Kx) - \frac{1}{2}\frac{k_1}{k_1-k_2}\exp(-k_2Kx)\right] \qquad (6)$$

The suggested approach was used for investigation of kinetics and mechanism of lignin ozonation reactions, lignin model compounds (phenol, veratrole, guaicol and others), as well as transition metal ions ($Fe^{+2}$, $Mn^{+2}$). The corresponding kinetic parameters were determined and the data on the process mechanism were obtained.

**PP-B-8**

# MODELLING OF CATALYTIC CONVERSION OF METHANOL TO FORMALDEHYDE ON SILVER

A.I. Rusinov, A.N. Butenko, A.S. Savenkov

*Kharkiv State Polytechnic University, Kharkiv, Ukraine*

Silver on pumice catalyst with silver content ca. 40 wt. % is used for formalin production. It is necessary to have information about kinetics of the process for elaboration of effective catalyst with less silver content.

There are known papers in which authors determined observed kinetic parameters without taking into consideration mass transfer of reagents or noted the fact of diffusion braking, but didn't evaluate one quantitatively. Generally accepted fact is that this process can be described with following reactions:

$$CH_3OH + 0{,}5O_2 \xrightarrow{K1} CH_2O + H_2O \tag{1}$$

$$CH_3OH \xrightarrow{K2} CH_2O + H_2 \tag{2}$$

$$CH_2O \xrightarrow{K3} CO + H_2 \tag{3}$$

$$CH_2O + O_2 \xrightarrow{K4} CO_2 + H_2O \tag{4}$$

We marked current concentrations in the flow bulk of each substances: C1 - $CH_3OH$, C2 - $O_2$, C3 - $CH_2O$, C4 - $CO_2$, C5 - CO, C6 - $H_2$, C7 - $H_2O$. The equation system of each substance changing taking into account the changing of system volume has the following view:

$$\frac{dC1}{dt} = -K1 \cdot C1_s \cdot C2_s^{0,5} - K2 \cdot C1_s - 0{,}082 \cdot T \cdot C1 \times \\ \times (K1 \cdot C1_s \cdot C2_s^{0,5} + K2 \cdot C1_s + K3 \cdot C3), \tag{5}$$

$$\frac{dC2}{dt} = 0{,}5 \cdot K1 \cdot C1_s \cdot C2_s^{0,5} - K4 \cdot C2 \cdot C3 - 0{,}082 \cdot T \cdot C2 \times \\ \times (K1 \cdot C1_s \cdot C2_s^{0,5} + K2 \cdot C1_s + K3 \cdot C3), \tag{6}$$

$$\frac{dC3}{dt} = K1 \cdot C1_s \cdot C2_s^{0,5} + K2 \cdot C1_s - K3 \cdot C3 - K4 \cdot C2 \cdot C3 - 0{,}082 \cdot T \cdot C3 \times \\ \times (K1 \cdot C1_s \cdot C2_s^{0,5} + K2 \cdot C1_s + K3 \cdot C3), \tag{7}$$

$$\frac{dC4}{dt} = K4 \cdot C2 \cdot C3 - 0{,}082 \cdot T \cdot C4 \cdot (K1 \cdot C1_s \cdot C2_s^{0,5} + K2 \cdot C1_s + K3 \cdot C3), \tag{8}$$

$$\frac{dC5}{dt} = K3 \cdot C3 - 0{,}082 \cdot T \cdot C5 \cdot (K1 \cdot C1_s \cdot C2_s^{0,5} + K2 \cdot C1_s + K3 \cdot C3), \tag{9}$$

$$\frac{dC6}{dt} = K2 \cdot C1_s + K3 \cdot C3 - 0{,}082 \cdot T \cdot C6 \times \\ \times (K1 \cdot C1_s \cdot C2_s^{0,5} + K2 \cdot C1_s + K3 \cdot C3), \tag{10}$$

$$\frac{dC7}{dt} = K1 \cdot C1_s \cdot C2_s^{0,5} + K4 \cdot C2 \cdot C3 - 0{,}082 \cdot T \cdot C7 \times$$
$$\times (K1 \cdot C1_s \cdot C2_s^{0,5} + K2 \cdot C1_s + K3 \cdot C3), \qquad (11)$$

where $C1_s$, $C2_s$ - presurface concentrations of methanol and oxygen respectively. $C1_s$, $C2_s$ were calculated with knowns formula:

$$1 - \frac{C_{is}}{C_i} = \frac{2{,}32 \cdot W_s \cdot d_0}{D \cdot C_i \cdot Re^{0,7} \cdot Sc^{0,33}} \qquad (12)$$

Observed rate of the conversion $W_s$ was determined on oxygen conversion rate in flowing reactor on silver on pumice catalyst with diameter - 0,13; catalyst volume - 2 ml; air expenditure - 1,4 l/min; $O_2/CH_3OH$ =0,3 mol/mol; area reactor section - 1,72 $cm^2$; and calculated with 1st order kinetic equation on oxygen. Results of kinetic experiment are shown in Table 1.

Table 1 - Indices of the process at kinetic tests

| Temperature, K | Methanol conversion, mol % | Selectivity to formaldehyde, mol % | Conversion degree of oxygen, mol % | $W_s \cdot 10^5$ mol/(s·cm²) |
|---|---|---|---|---|
| 753 | 53,0 | 93,7 | 88,4 | 1,107 |
| 773 | 54,8 | 93,7 | 89,5 | 1,158 |
| 803 | 57,0 | 93,6 | 90,8 | 1,226 |
| 833 | 58,8 | 93,5 | 92,0 | 1,298 |
| 863 | 60,0 | 93,4 | 92,8 | 1,352 |

Necessary data for identification D, Re, Sc were taken from reference literature.

The solution of equation system (5)-(11) with Runge-Cutt method with taking into consideration found $C1_s$ and $C2_s$ allows to determine the real rate constants (see Table 2). Table 2 data in lnK and 1/T coordinates are grouped along right lines with tangents of energy of reactions (1), (2) and (4) equal to 30,3; 50,0 and 21,4 kJ/mol respectively. The calculation of methanol conversion rate on real rate constants and activation energies showed that mass transfer phenomenon put on the brakes process rate in 5 times. I.e. 20% of operating surface of the catalyst is sufficient for processing all feed methanol. It is useful fact for elaboration of catalyst with low silver content.

Table 2 - Real rate constants of the reactions on argentum on pumice catalyst

| Temperature, K | K1 | K2 | K3 | K4 |
|---|---|---|---|---|
| 753 | 6015 | 18,0 | - | 17960 |
| 773 | 6700 | 22,4 | - | 19540 |
| 803 | 8225 | 29,2 | - | 22580 |
| 833 | 9670 | 38,4 | 0,36 | 24830 |
| 863 | 11150 | 49,9 | 0,60 | 27800 |

On obtained data base the catalyst with 20-15 mas % of silver content with high activity and selectivity was worked out by us.

PP-B-9

# FLOW STRUCTURE IN MONOLITH CHANNELS

F.P.L. Magne and J.J. Witton*

Combustor Heat Transfer Technology Group
Department of Propulsion, Power, Energy and Automotive Engineering
School of Mechanical Engineering
Cranfield University  Cranfield  Bedford  MK43 0AL  England
Tel. No. +44-(0)-1234-754636, Fax No. +44-(0)-1234-750728
Email: j.j.witton@cranfield.ac.uk

## Introduction

The use of monoliths in catalytic reactors is well-established in numerous areas, notably in exhaust gas clean-up for power and process plant and automobiles. The flow rates and reactor sizing are often such as to make the hydrodynamic flow regime laminar, where numerical and analytical solutions exist to predict the flow and transport characteristics. In other cases, designs may require a higher reactant throughput and the flow regime becomes nominally turbulent, with Reynolds numbers greater than 3000.

Channel surfaces have high relative roughness and are often unsymmetrical in cross section. Reynolds Numbers may be between 7-1500. Flow characteristics in these circumstances are not covered in the general database, where Reynolds Numbers above about 40000 have been examined but little work exists below this to guide design.

## Experimental Study

The work arose from a study of catalytic combustion for gas turbines. In many gas turbine catalytic combustion systems the flow is transitional in Reynolds number and, with a restriction on channel aspect ratio set by the installation, the flow is not fully developed over most of the monolith length. The simulation was of a typical 400 cells per square inch cordierite extrudate that had been wash coated with catalyst in a conventional manner. The study was conducted using two component laser doppler anemometry on a superscale (x 15) metal channel, assuming Reynolds similarity. The walls of the channel were roughened randomly using electro discharge machining and optical access provided through the wall at intervals along the channel. The corners of the channel were radiussed to produce typical extrusion/coating dimensions. Nominal dimensions were:

## PP-B-9

| | |
|---|---|
| channel side wall width | 15 mm |
| corner radius | 3 mm |
| hydraulic diameter | 15.85 mm |
| aspect ratio (length/hydraulic diameter | 70 |
| nominal roughness height, (specified as peak to valley difference | 40 µm |

relative roughness (experiment) $2.53 \times 10^{-3}$

maximum relative roughness (monolith) $5 \times 10^{-3}$

The channel could be heated electrically to simulate the thermal boundary layer produced during heterogeneous catalytic reaction. Experiments were performed cold and hot but only the cold results are reported in the poster.

Two component laser doppler anemometry was used with beam expansion and a 120mm focal length lens. This gave sufficient spatial resolution and an optical probe volume of 560 µm x 50 µm dia. In order to obtain measurements close to the wall the channel could be rotated about its lengthwise axis so that one beam could be at grazing incidents to the wall. High seeding rates were necessary to produce adequate data rates and signal/noise ratios in the near wall region. Wall pressure taps were fitted along the channel length.

Air flow into the channel was fed from a metered system into a bell mouth and tripped at the channel leading edge, to simulate a plug flow approach velocity profile to the monolith.

### Results

Data on the development of axial velocity profile, centreline maximum velocities and flow structure will be shown. Alterations in structure between flow cross sections with radiussed and sharp corners will be illustrated.

**PP-B-10**

# LIQUID PHASE HYDROGENATION PROCESS OF ANESTHESYNE PRODUCTION ON Pd/C CATALYST IN A SLURRY STIRRED REACTOR

O.P. Zhukova, E.F. Stefoglo

*Institute of Coal SB RAS, Kemerovo, Russia*

A new reactor module with two batch connected reactors was used. The first works as saturator of the catalyst suspension by hydrogen in the isopropanol solvent. In the second one the substrate solution in the same solvent is presaturated by hydrogen under the same condition (temperature and pressure). Then after pumping the suspension from the first to the second reactor, switching on a stirrer and opening hydrogen flow input the reaction begins. A special mode of procedure to study kinetics of para-nitrobenzoic acid (EEpNBA) hydrogenation in a batch reactor was proposed. To do this, one should maintain (create) such conditions in the reactor at which the initial catalytic rate is determined by gas concentration close to equilibrial. This allows to determine the values of the equation parameters from the initial rate values in a real kinetic regime. The temperatures and catalyst concentrations also have very strong influence on the suspension saturated by the gas especially for active catalyst and a high reaction rate.

We studied the gas-liquid reaction on a suspended catalyst in a batch stirred vessel. Hydrogenation of EEpNBA to anesthesyne was carried out in isopropyl alcohol medium on 5% Pd/C powder catalyst ($d_P$=10 μm). The temperature effect on hydrogen solubility in isopropanol and EEpNBA and anesthesyne solution in this solvent was studied. Dissolved hydrogen concentrations were measured with chromatography T=40-120° C and p=1-6 bar. Accounting for the reduction mechanism of nitroaromatic compounds and reagents adsorption of both components the following rate is proposed:

$$R_{cat}=\frac{kK_H C_{HL}}{1+K_H C_{HL}}\cdot\frac{K_L C_L}{1+K_L C_L+K_P C_P},\quad \frac{kmol}{kg_{pd}\cdot s} \tag{1}$$

The temperature constants dependencies are defined:

$$K_H=5.38\cdot 10^{-9}\exp(66.58/RT),\ K_L=8.186\cdot 10^{-4}\exp(25.23/RT),$$
$$K_P=0.025\exp(19.7/RT),\ k=1.544\cdot 10^{11}\exp(-81.7/RT).$$

Henry's constant for the initial nitroether solution in isopropyl alcohol with $C_{NE_0}=0.73\ kmol/m^3$, $He_{NE}=1.708\cdot 10^6\exp(7.15/RT)\ Pa\cdot m^3/kmol$;

# PP-B-10

for anesthesyne (reaction product) solution with

$$C_{AN_0} = 0.64\ kmol/m^3, He_{AN} = 1.681 \cdot 10^6 \exp(6.85/RT)\ Pa \cdot m^3/kmol.$$

We presaturated the solution with hydrogen (without the catalyst) and at the very beginning of the reaction it starts with the gas concentration in the suspension equal to $C_H^*$. A special methods for obtaining results treatment allowed step by step graphically to calculate rate equation parameters. The plot of $1/R_0$ from $1/C_H^*$ and $1/C_L$ for different temperatures and pressures makes possible to evaluate from intercepts and reciprocal of obtained linear dependencies the constant of eq.(1).

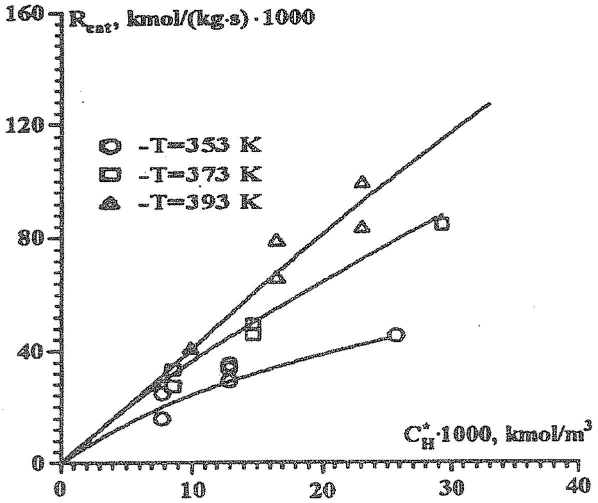


Fig.1. Dependencies of $R_{cat}$ on equilibrium hydrogen concentration (experimental and calculated data from equation (1)) $C_{cat}$= 0.02 $kg_{Pd}/m^3$ , $C_{Lo}$= 0.73 kmol/ $m^3$.

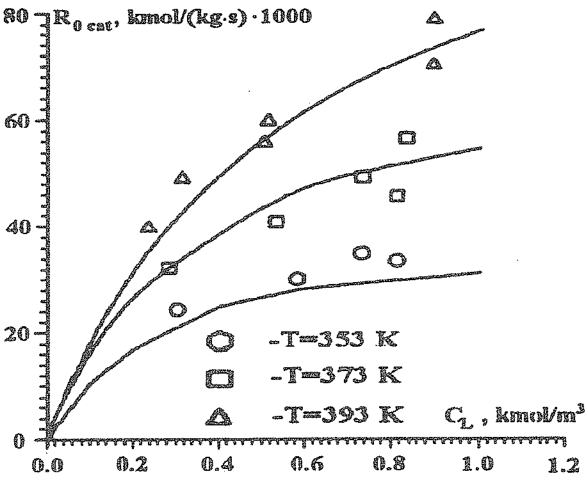


Fig.2. Experimental values of reaction rate and those calculated from equation (1) for different temperatures ($P_{H_2}$=2.5 bar, $C_{cat}$=0.02 $kg_{pd}/m^3$).

Dependencies of catalytic rate on hydrogen equilibrium concentration and liquid component concentrations were obtained experimentally at different temperatures (Fig.1,2) and calculated from the rate equation (1) using the resulted constants (Fig.3).

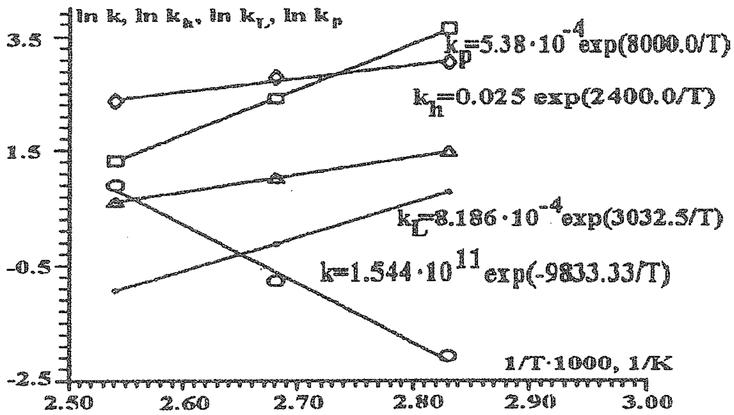


Fig.3. Temperature dependencies of the kinetic reaction rate equation (1) parameters.

# SECTION C

## NEW TYPES OF CHEMICAL PROCESSES AND REACTORS

# EARTH CRUST AS A GIANT CATALYTIC REACTOR

## (on a new catalytic approach to mechanisms of geochemical processes in earth fluid phases)

V.V. Barelko, V.A. Zharikov, I.V. Zakirov, U.I. Goldshleger

*Institute of Chemical Physics RAS, Chernogolovka, Russia*
*Institute of Experimental Mineralogy RAS, Chernogolovka, Russia*

In the present paper a principally new approach for modern geochemistry is developed for an analysis of the substance chemical evolution mechanisms in the fluidic phases of Earth's crust. The approach assigns a special role to the heterogenous-catalytic factor in the transformation chain leading to the formation of the fluidic cavities components. On the base of the classical representations of theoretical and applied catalysis it is shown that a fluidic cavity can be considered as a high-effective natural catalytic reactor. It is caused by the next circumstances: first, the fluidic cavities are surrounded and filled by the porous earth rocks being very catalytically active ( the rocks as alumina and silica modified by the various metal ions are the analogues of the traditional man-made catalytic systems created under the Earth conditions); second, the mode parameters into the fluidic cavities are very favourable for the known catalytic processes (the temperatures up to 1000 °C and higher, the pressure of the hundreds atmospheres); third, the many reactive components of the geological "fluid" composition (such as water steam, mono- and dioxides of carbon, hydrogen, nitrogen, hydrocarbons) are possible to form the widest spectrum of the various transformation products. Thermodynamic and kinetic analysis of the possible catalytic reactions routes in such fluidic cavities have shown that some processes among the possible transformations must have an essential importance with respect to the earth rocks evolution. Such processes are the hydrocarbons (and their oxygen-derivatives) synthesis on the base of $H_2O$, CO, $CO_2$ and $H_2$ (these reactions by their mechanism are near to the known Fisher-Tropsch reactions), the pyrolysis of the petroleum heavy components (it is an analogue of the hand-operated processes of the catalytic cracking, platforming and reforming reactions class), the catalytic retreatment of the petroleum light fractions (similary to the well-known process of nitrogen-hydrogen mixture formation in the ammonia synthesis technology using the reaction of the water gas conversion), the Haber ammonia synthesis, the hydrocarbons transformations with the production of a carbon solid phase. The developed notions form a base for the formation of a new independent trend in the geochemistry which can be named the "catalytic geochemistry". The formulated approach allows to consider from the new positions such important geochemical questions as the problems of the chemical composition of the earth crust fluidic phases, the kinetics and the dynamic characteristics of their formation, the fluidic processes role in the geological rocks formation. The authors are modelling the "catalytic geochemistry" processes in the laboratory conditions.

# CATALYTIC INCINERATION OF GASEOUS WASTE

Freiria Candara, M.J. and Freiria Candara, M.C.

Faculty of Sciences
University of Vigo. Vigo, Pontevedra, Spain

Many gaseous wastes are characterized by odor or color. Often these characteristics result from the presence of organic compounds which, when properly incinerated, will destruct.

Catalytic incinerators normally destruct gaseous waste at low concentrations. Heated gas passes through a perforated plate to straighten the flow and then passes through a catalytic material prior to discharge. The catalyst has the property of increasing the rate of oxidation at lower temperatures (i.e., use of a catalyst promotes destruction of gaseous waste at lower temperatures).

The actual steps in the catalytic reaction are as follows:

- Diffusion of the reactants within the gas stream, plus the gas stream, through the stagnant fluid surrounding the surface of the catalyst.
- Adsorption of the reactants on the catalyst surface.
- Reaction of the reactants to form products (usually oxides).
- Desorption of the products from the catalytic surface.
- Diffusion of the products from the catalyst pores and surface film to the vapor or gaseous phase outside (downstream) of the catalyst.

Catalyst materials normally used are the noble metals, i.e., platinum, palladium, rhodium, etc. Other materials which function as catalyst are copper chromite and oxides of copper, chromium, manganese, nickel and cobalt.

Catalytic incineration systems must effect intimate mixing of the combustibles within the system. The gas must be brought to the required ignition temperature for the combustible to be burned, and good temperature control throughout the catalyst bed is essential. Sufficient oxygen must be present in the gas stream or must be added to it to ensure oxidation of the contaminants.

The gas stream must be free of particulate matter to protect the catalyst from fouling. If particulate matter is present, pretreatment of the gas, such as cyclonic separation or electrostatic precipitators, may be necessary upstream of the catalyst.

## PP-C-2

The catalytic incinerator chamber is constructed of steel or refractory, depending on the temperature developed. From 750 to 1100 °F heat-resistant steel can be used, stainless steel from 1100 to 1300 °F, and refractory materials above 1300 °F. Steel is normally protected with 4 to 6 in of insulation.

### PP-C-3

# A FLUIDIZED CATALYST BED INSTALLATION FOR TREATMENT OF BIOLOGICAL WASTES

Z.R. Ismagilov, M.A. Kerzhentsev, B.I. Lunyushkin*, Yu.V. Ostrovskii*,
J.B.M. Wouters**
*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*
**Novosibirsk State Design and Research Institute VNIPIET, Novosibirsk, Russia*
***WEET B.V., Eersel, The Netherlands*

In collaboration with a Dutch firm WEET B.V. a project for development of a process for treatment of biological wastes, in particular pig manure, in a catalytic fluidized bed was started. This problem is of great importance for Western Europe because such wastes spread bad odor and cause pollution of air, soil and water with toxic substances. The process proposed provides total oxidation of the organic part of the wastes at low temperatures: 600-750°C with the separation of the mineral part. The process is autothermal at organics content 15-20%, i.e., it does not require the supply of fuel. The original off-gas treatment system allows efficient purification of the exhaust gas from dust and gaseous pollutants. For the study of the process a special pilot installation with a capacity of 10 kg/h was designed and fabricated. The installation was assembled, its initial start-up and operation were carried out, and its tests have been started at Research Institute for Pig Husbandry in Sterksel, The Netherlands.

The installation (Fig. 1) consists of a fluidized bed catalytic reactor (1) with a water cooled heat exchanger (2) installed in its upper part, electric heater (10) for initial heating of the catalyst to the light-off temperature (300-400°C), cyclone (3) for removal of dust from the gas stream, jet scrubber (4) for removal of low-sized dust particles and acidic pollutants from the gas, absorber-condenser (5) and aerosol filter (6).

The installation operates as follows. The compressed air is supplied by the blower (11) to the lower part of the catalytic reactor in the amount required for catalyst fluidization and oxidation of organic compounds; biological wastes are fed to the reactor by the pump (7) from the tank (9). In the catalytic reactor total oxidation of organic compounds takes place with the temperature of the gas and catalyst rising to 700-760°C. The water cooled heat exchanger in the upper part of the apparatus provides the decrease of the exhaust gas temperature to 350-370°C.

# PP-C-3

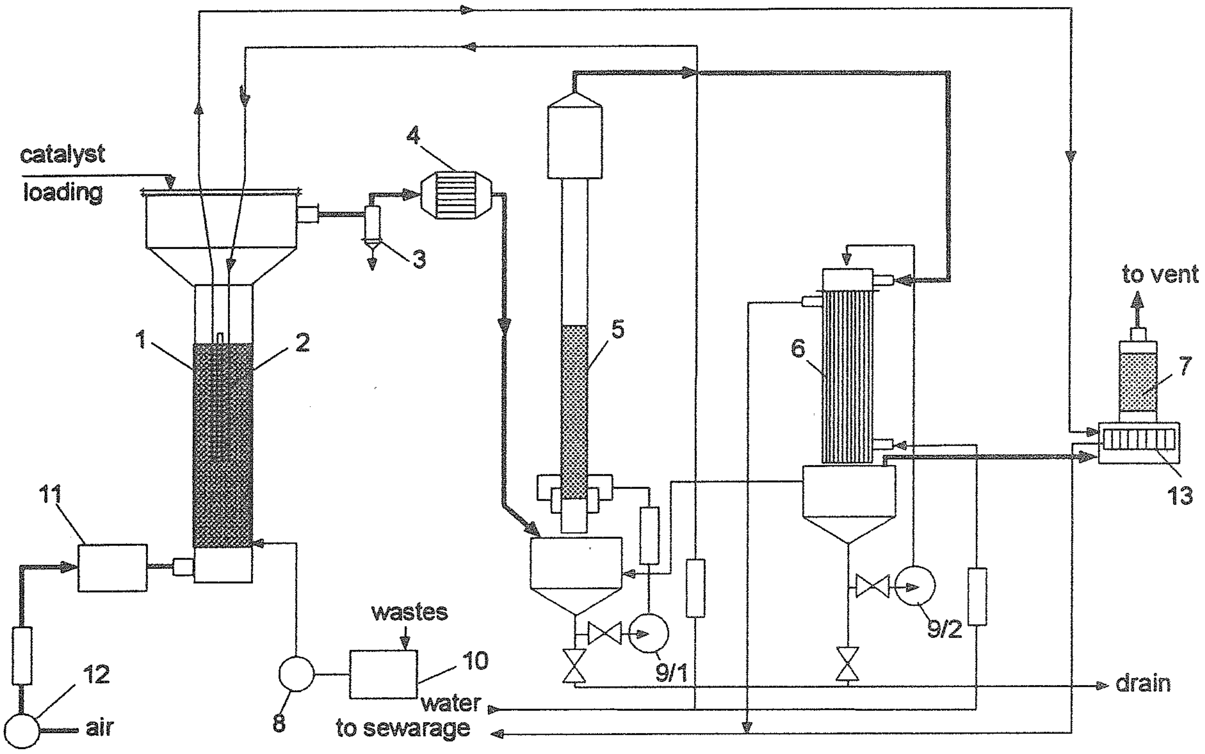


Fig. 1. Flow diagram of the pilot plant for catalytic treatment of biological wastes:
1 - catalytic reactor; 2 - heat exchanger; 3 - cyclone; 4 - jet scrubber; 5- absorber-condenser;
6- filter; 7 - waste pump; 8/1, 8/2 - circulation pumps; 9 - tank with wastes,
10 - electric heater; 11 - blower; 12 - heat exchanger, 13- non-isothermal grid

The exhaust gas leaving the catalytic reactor (1) contains dust, consisting mainly of the mineral residue resulting from waste catalytic combustion. For the removal of larger fraction of the dust the cyclone (3) is used. The temperature of the gas after the cyclone before it is fed into the jet scrubber lowers to 300°C. In the jet scrubber dust particles with a size over 3 μm and acidic pollutants, such as sulfur and phosphorous oxides, are almost totally removed from the gas stream, with the gas temperature decreasing to 60°C. The supply of water (or scrubbing solutions) for the formation of the jet grid is provided by the pump (8/1).

The absorber-condenser (5) is intended for the removal of the smaller dust particles with a size below 3 μm and the final gas purification from acidic admixtures. The gas temperature decreases in this apparatus from 60 to 20-25°C. The scrubbing solution is fed to the nozzles by the pump 8/2. The final purification of the exhaust gas from low sized dust articles is carried out by the fibrous filter (6).

PP-C-4

# CATALYTIC ACTIVATORS OF BURNING FUEL FOR DECREASE OF HARMFUL SUBSTANCES IN WASTE PRODUCTS OF DEVICES OF BOILER-HOUSE AND TECHNOLOGICAL FURNACES

A.J. Karengin, I.A. Tikhomirov, R.A. Arefieva*,
T.A. Gubaidulina, A.V. Merkulov, S.A. Sosnovsky

*The Tomsk Polytechnic University 30 Lenin avenue,*
*Tomsk 634004 Tel.(382.2) 419-143, Russia*
**Join-stock company "Sibkabel",Ltd. 46 Pushkin st.,*
*Tomsk 634003 Tel.(382.2) 904-498 Fax (382.2) 774-518, Russia*

Burn device of technological boiler-house and furnaces, burning gas, liquid and firm fuel are one of the basic sources of pollution of air pool of cities of Russia. Their waste gas are characterized by large volumes, strong dust content, low temperatures, contents of soot, oxides of carbon, nitrogen, sulfur, vanadium and other compounds. The installation of catalytic filters in these cases is technically and economically inefficient and other approach is necessary. It is, that in burn device directly with fuel is entered catalytic activator of fuel burning (CABF) on a basis of ultradispersive catalytic materials (UDCM), preliminary specially processed. UDCM, due to the very small sizes of particles (less 0.01mkm), large specific surface (50-500 $m^2/g$) and special phase condition have suitable catalytic and chemical properties /1/. Introduction of CABF in burn device together with fuel will allow constantly to have in each point of burn device catalytically and chemically active UDCM particles. It enables from the very beginning to operate mechanisms of burning of fuel, the training and liquidations of harmful substances and will be provide more complete combustion of fuel /2/.

In the table results of tests of CABF on technological boiler - house of

## PP-C-4

JSC "Sibkabel", Ltd, working on liquid fuel (boiler - ДЕ-10, pressure of black oil – 5ati, pressure of vapour on sprayer - 1,0-1,2 ati, consumption of air - 3,87 $m^3/s$) are given.

| Mark | Proportion mazut:CABF kg/kg | Temperature C | Concentration of waste products | | | |
|---|---|---|---|---|---|---|
| | | | CO,g/s | NOx,g/s | $SO_2$,g/s | Smoke ,% |
| M-100 | 1000:0 | 160 | 0,15 | 0,48 | 1,76 | 16 |
| | 1000:2 | 160 | 0,2 | 0,48 | 1,26 | 10 |
| | 1000:2 | 160 | 0,22 | 0,5 | 1,26 | 9 |
| M-40 | 1000:0 | 180 | 7,06 | 0,243 | 0,244 | 8 |
| | 1300:1 | 160 | 0,296 | 0,255 | | 3 |
| M-40 | 1000:0 | 190 | 10,837 | 0,239 | 0,24 | 11 |
| | 1300:0,25 | 180 | 5,656 | | | 9 |

Thus, the results of fulfilled technological tests show high efficiency and basic opportunity of use of CABF for decrease and liquidation of harmful substances in gas waste of a various sort of burn devices.

The literature:

1. Karengin A.J., Gubaidulina T.A., Arefieva R.A., Savin B.P. " A Way of reception of the catalyst for clearing departing gases of technological processes and exhaust gases of a vehicle ". The patent of Russian Federation № 2017524, BI № 15 from 15.08.94г.

2. Karengin A.J, Tikhomirov I.A., Gubaidulina T.A., Merkulov A.V., Arefieva R.A Ultradispersive catalytic materials for decrease of harmful substances in waste products of burner devices, boiler-house of installations and technological furnaces. Materials 2-nd international scientific - practical conferences " Safety of ability to live in Siberia and on extreme North ". Tuimen 1997. C.97-98.

# ENERGETIC ANALYSIS OF CALCIUM CARBIDE PRODUCTION FROM VARIOUS RAW MATERIALS

V.V. Kolesnik, V.N. Orlik, V.G. Kulbachny, V.N. Proskudin*

*Institute of Gas, Ukraine NAS, Kiev, Ukraine*
**Electric Art Welding Institute, Ukraine NAS, Kiev, Ukraine*

The carbide calcium production relates to power-intensive processes owing to significant endothermicity and high temperature level of chemical conversion. Therefore the energy saving problem for this process is especially urgent and it is important to compare energy expenditures at reception of carbide calcium from different kinds of initial raw material: oxide calcium, limestone, calcium hydroxide.

The energetic efficiency of process was characterised by two criteria: specific charge of electric power per 1kg of produced technical calcium carbide and specific charge of electric power per litre acetylene, which can be received from produced carbide calcium. The varied parameters were the oxide calcium concentration in produced calcium carbide and preheating degree of initial mixture of raw materials.

The calculations were made on base of the elaborated mathematical model of calcium carbide production process, with regard of presence in initial raw material various impurities which essentially influence on the energetical and ecological parameters of process.

For carbide calcium production on the base calcium oxide it take place the extreme dependence of specific energy consumption per litre of acetylene versus oxide calcium concentration in produced technical calcium carbide. The reason is that increasing of CaO concentration from 0 to 29 % (eutectic point) leads to such decreasing of the melting temperature, that the joint reduction of energy consumption on raw materials preheating and chemical conversion surpass the loss from decreasing of acetylene yield. A raw materials preheating reduces the total energy expenditures in carbide calcium production, however does not influence on the nature of extreme dependence of energy consumption versus calcium oxide concentration in produced calcium carbide.

The efficiency of any process depends on opportunities for output flows energy utilization, and it is desirable the immediate energy recuperation for needs of the main technological process. In calcium carbide production the energy is carried away by two high-temperature flows - melt of carbide calcium and gases exhaust, consisting, basically, from carbon oxide. The utilization of a melt warmth, releasing in crystallization and cooling processes, remains still difficult and insufficiently studied technical problem and in present work is not considered. At the same time the utilization of the heat and chemical energy of the exhausting oxide carbon is not a very complex problem. The estimations show, that production of 1 kg of technical calcium carbide containing 20% calcium oxide yields 0.35 kg of oxide carbon, heated to temperature 1820 °C. Its stoichiometric combustion with air permits to heat raw materials to 1500 °C and thus to save 2362 MJ of electric energy. The warmth of formed high-temperature combustion products (1500 °C) can not be directly utilize in frameworks of considered technology only, and the additional consumer of this energy is required.

For calcium carbide production process based on limestone the specific energy consumption approximately two times surpass the consumption for analogous process based on calcium oxide (it is to mention that maximal raw materials preheating temperature is limited by limestone decomposition temperature - 1000 °C). It is explained not only by expenditure on limestone thermal decomposition, but also by expenditure on producing of additional carbon oxide, the chemical energy of which can not be used in frameworks of considered process only. Besides the carbon charge increasing takes place. As well as in previous case, preheating of raw materials provides the reduction of specific electric power expenditure (up to 2754 MJ/kg). The restriction on maximal temperature of a raw materials preheating reduces the opportunities for exhaust gases energy utilization for internal needs of the process.

On energy consumption the process of calcium carbide production based on the calcium hydroxide lies between the two processes mentioned above. The initial mixture preheating to 500 °C (temperature of boiling and beginning of decomposition - 580 °C) enables to lower the electric power expenditure on 1195 MJ/kg for calcium carbide containing 20 % oxide calcium. As in previous case physical properties of raw materials limit the opportunities of direct uses of exhaust gases energy for internal needs of the process.

It is necessary to note that in difference from the case of calcium carbide production from calcium oxide, in last two cases (with using limestone or calcium hydroxide) there is not observed the extreme dependence of specific energy consumption per litre of acetylene versus calcium oxide concentration in produced of calcium carbide. It is explained by total growing of energy charge and, as the consequence, decreasing of specific weigh of energy expenditures for preheating of initial mixture, which depend on the melting temperature. The last is a function of calcium oxide concentration in a produced calcium carbide.

I spite of considerable distinction in specific electric power and raw material consumption per unit of produced production (calcium carbide, acetylene) final choice between considered variants can be made only with regard of additional technological parameters: the distance from raw materials base and consumer of ready products; the correlation of prices on initial raw material, electric power and ready product; the capital and operational costs etc.

# RESEARCH OF PLASMA - CHEMICAL PROCESSES, INITIATED BY HIGH POWER ELECTRON BEAMS

N.A. Kondratyev[1], V.A. Krasilnikov[2], Yu.A. Medvedev[3], B.I. Sokolov[4],
A.N. Prilepin[5], G.E. Remnev[5], V.I. Smetanin[5]

[1]*East Petroleum Company, Tomsk, Russia;*
[2]*Tomsk Polytechnic University, Tomsk, Russia;*
[3]*Siberian Physical Technical Institute, Tomsk, Russia;*
[4]*Tomskgas, Tomsk, Russia;*
[5]*Nuclear Physics Institute of Tomsk Polytechnic University, Tomsk, Russia.*

High power electron beams possess high-energy storage capacity. They can be used for initiation of excitation of plasma-chemical reactor, as well as for carrying out gas-phase chemical processes. Application of high current electron beams, propagated in working volume of the reactor, allows to increase considerably the reactor working volume and pressure in this volume, as well as to reach a high level of non-equilibrium state of the excited medium.

The Engineering Physical Center of the Nuclear Physics Institute carries out investigations on plasma-chemical processes initiated by electron beams. These investigations are based on high current accelerators of the Center.

The report presents result of study of the process of metal reduction. The action of high power electron beams using beam-plasma discharge leads to transformation of hexafluorides to the relative metal. The processes of Re and W reduction from their gaseous halogenides were carried out on the "Tonus" accelerator operating in the electron regime. These metals were deposited on the reactor walls as ultra-thin powders with grain size up to $10^{-7}$m. The grain size is found to depend on the number of pulses. The efficiency of metal reduction is about 30%.

The possibility of production of petroleum paraffin by using of high current relativistic electron beams is studied. The results can be estimated as optimistic.

The report analyses possibilities and problems of practical application of high power electron beams for discribed applications.

## PP-C-7

# AN ELECTROCHEMICAL REACTOR FOR CATALYSTS SYNTHESIZING AND MODIFYING

A.A. Lamberov, R.G. Romanova, S.R. Egorova, A.G. Liakumovich

*Kazan State Technological University*
*68 K. Marx St, Kazan 420015, tel. 36 58 92*

Currently great attention has been given to the production of highly efficient carriers and catalysts for petroleum and petroleum products processing. Technologies, ecologically safe and economically effective, have been very promising.

We have designed an elecrtochemical reactor making it possible to conduct the processes of aluminium hydroxide synthesis and zeolite modification.

It is common knowledge that the properties of the active aluminium oxide used as a carrier and catalysts for chemical and petrochemical synthesis depend completely on its preqursor - aluminium hydroxide. The most widespread technology of its synthesis is the aluminium trihydrate (aluminia) reprecipitation. Despite the fact that this method is of most common use in industry, it has considerable drawbacks implying that it is impossible to produce aluminium hydroxide with reproducible properties in view of the precipitation regime instability. The sediment obtained is a mixture of different composition products. Besides, a high metal- and power-consumption and the production of a vast sewage tonnage (up to 240 t/t $Al_2O_3$) characterize such technology.

The essence of producing aluminium hydroxide in the electrochemical reactor lies in precipitation of hydroxide in the anode or the cathode chamber of a membrane electrolyzer through the utilization of electrochemically generated hydroxyl- and hydroxonium ions. The advantage of the aluminium hydroxide electrochemical precipitation is that this method makes it possible to automate and regulate the precipitating agent feed providing a way for obtaining a product with preset qualitative characteristics.

The dependence of the morphology, porous structure, particle sizes, admixture ion content of aluminium hydroxide upon the electrochemical precipitation conditions has been studied. It has been found that the main parameters forming the aluminium hydroxide structure are pH and the precipitation temperature. Careful investigations have established optimal regimes of aluminium hydroxide electrochemical precipitation leading to the production of a competitive item.

One of the advantages of the electrochemical way of producing aluminium hydroxide is the sediment simultaneous purification of admixture ions, which are concentrated in the cathode chamber as a consequence of elctromigration. The processes of sodium ion migration from the anode chamber to the cathode one during hydroxide precipitation have been investigated. The sodium residual content may be substantially reduced without resorting to labor-intensive and expensive washing operations if the finishing electrochemical processing of aluminium hydroxide will be conducted just in the precipitation chamber. The essence of the finish treatment is that after finishing the aluminium dose, the electrochemical process does not stop, and the current parameters, are kept in such a regime as to achieve the most effective distribution of charge carriers in the electrolyzer chambers owing to their electromigration. As a result of the aluminium hydroxide finish processing, $Na_2O$ content decreases to 0.08 %.

Precipitation conditions optimization made it possible to obtain a hydroxide consisting of pseudoboehmite to the extent of 99.8 % and having a specific up to 400 $cm^2/g$. In this case energy consumption was 8000 kWt Hr/t, and the wash water volume was not more than 25 t/t $Al_2O_3$.

We have carried out the modification of zeolites in the electrochemical reactor consisting in the processing of zeolite water suspension in the electrolyzer anode chamber. Interaction of $H_3O^+$ ion generated on the anode with zeolite leads to its decationation and acid-base properties transformation. As a result of electrodialysis sodium ions diffuse to the electrolyzer cathode camber and are concentrated with sodium hydroxide formation. When zeolite is treated in the anode chamber, its decationation to the $Na_2O$ residual content of less than 0.1 % of the mass takes place. The decationation procedure optimization has been conducted according to the following parameters: electrolyte nature and concentration, hydromodulus, processing period, interchamber membrane material. The present method is ecologically safe, makes it possible to reduce considerably the quantity of the reagents used, and shortens the process duration. For high-silicon and low-silicon zeolites the decationation degree made up 0.05 % and 1.1-2.0 % of $Na_2O$, respectively.

**PP-C-8**

# PHYSICAL-CHEMICAL AND MATHEMATICAL BACKGROUNDS OF THE CONTINUOUS PROCESS OF MANUFACTURING Ga AND Li COMPOUNDS

ORLOV A.A.

*Tomsk Polytechnic University, Tomsk, Russia*

The construction of reactor for implementation of process of continuous receiving of compound of gallium and lithium and mathematical model describing present process were examined.

The receiving of compound of gallium and lithium in reactor occur in process of diffusion of lithium in gallium at continuous passing of the drops of liquid gallium, under influence of gravity, through layer of fusion lithium.

In basis of mathematical model of process of continuous receiving of compound of gallium and lithium by direct solution of lithium in gallium in fusions of metals were laid the well-known notion [1-4] about the processes of forming and tearing off the drop of liquid at passing it through aperture, the falls of the drop of liquid under influence of gravity in gas atmosphere, motion of the drop of liquid under influence of gravity in other liquid, diffusion in liquid metals. The process of continuous receiving of compound of gallium and lithium was considered as consistentment of aforesaid physical processes, occur with separately taken drop.

At elaboration of mathematical model of process of continuous receiving of compound of gallium and lithium by mentioned method were made the following admissions:

1. The drop of gallium (compound of gallium and lithium) has globular form and doesn't change it at co-accent with the surface of fusion lithium, and also at further motion in layer of lithium (doesn't deforms).
2. The trajectory of motion of the drop of gallium (compound of gallium and lithium) in atmosphere of argon and in layer of fusion lithium is rectilineal.
3. At diffusion of lithium in gallium changes only the radius (volume) of the drop of receiving compound of gallium and lithium proportionally to quantity (volume) of inculcated in compound of gallium and lithium.
4. The reverse diffusion (gallium in lithium) is left out of account.
5. The lithium inculcating into the drop of gallium forms at first solid layer on the border of partition of the received drop of compound of gallium and lithium and liquid lithium, and then redistributes on the whole volume of drop of compound of gallium and lithium.

Taking into account this admissions was made up the algorithm of calculation of parameters of physical processes, running with drop of gallium from the moment of its beginning to receiving of compound of gallium and lithium of set concentration.

The algorithm of calculation included the consistent determination of the following characteristics of the process:

1. Determination of radius of the drop of gallium.
2. Finding of the speed of the drop of gallium in the moment of its entering in lithium, at various values of height of fall of the drop (distances between perforated plate and layer of lithium).
3. The accurate definition of speed significance of the drop of gallium at its entering in the layer of lithium.
4. Determination of coefficient of lithium in gallium diffusion.
5. Determination of the time of motion of the drop of gallium in layer of lithium, necessary for saturation of the drop of gallium up to set concentration of lithium.
6. Finding the thickness of lithium layer.

Accordingly with present algorithm was written the program "DROP" for calculation of the basic parameters of the process of uninterrupted receiving of compound of gallium and lithium by computer.

The mathematical model and the program of calculating can be used for other liquid-metallic systems.

## REFERENCES

1. Kutateladze S.S., Styrikovith M.A. Hydrodynamics of gas-liquid systems. - M., Energy, 1976. p. -296.
2. Frenkel IA.I. Kinetic theory of liquids. L., Science, 1975. p. -592.
3. Iavorski B.M., Detlaf A.A. Reference book on physics.- M., Science, 1964. p. 848.
4. Sivukhin D.V. Thermodynamics and molecular physics: Training appliance for institutes of higher education. 3-rd Issue, corrected and added.- M.: Science. Basic redaction of phys.-math. Lit., 1990. p.-592.

# PP-C-9

# APPARATUS “KART” FOR UNSTEADY STATE CATALYTIC PROCESSES

Yu.V. Ostrovskii, G.M. Zabortsev, A.A. Shpak

*Novosibirsk State Design and Research Institute VNIPIET, Novosibirsk, Russia*

Phone: (3832) 76-96-35, E-mail: ost@ pri.sib.ru

Steady state catalytic incinerators, in spite of the fact that their efficiency is close to 100 %, have one essential drawback. At the small content of oxidized substances either additional input of heat to the reactor for heating the gas mixture to the temperature of catalytic reaction is required, or the excessively large surface of the regenerator of heat of exhaust gases is needed, resulting in the high cost of gas purification. The autothermal process in these incinerators is possible at rather large contents (5-7 g/m$^3$) of organic substances in the gases treated. The other mandatory condition - relative constancy in time of the contents of these impurities also limits the applicability of this method.

The alternative method is unsteady state catalytic process, based on cyclic change of the direction of the gas flow through the catalyst bed, located between two heat exchangers [1]. Owing to a high specific geometric area of the regenerative heat exchanger the gas is heated at a rather small part of the bed to temperatures at which chemical reactions proceed with significant speed and heat release. In the catalyst bed a moving heat front is formed. To keep this front inside the bed the switching of directions of the gas flow is carried out. Because of a high heat accumulating ability of these apparatuses it is possible to maintain auto thermal operational modes at the concentrations considerably lower than those for steady state reactors.

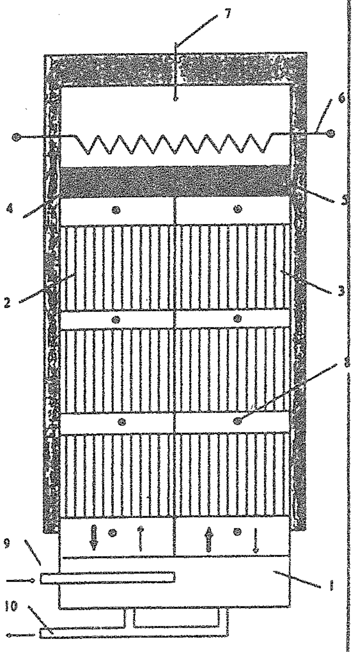


Fig. Scheme of the catalytic apparatus .

Our Institute together with the employees of Laboratory of Mathematical Modeling of Boreskov Institute of Catalysis developed and designed a catalytic apparatus KART-720 with a gas capacity of 720 m$^3$/h (see Fig.). The apparatus contains the chamber of switching the gas flow direction (1), regenerative heat exchangers (2, 3), catalyst beds (4, 5); electric heater (6); an inlet pipe for fuel supply (7); thermocouples (8), branch pipes for inlet and outlet gases (9, 10) and thermal insulation (11).

KART-720 is the horizontal catalytic apparatus with an area of regenerative heat exchangers 1500 m$^2$, power of electric heaters 15 kW and overall dimensions 640*640*4200 mm. The regenerative heat exchanger is manufactured from plates of corrugated stainless steel assembled in sections, with empty spaces between them. The degree of gas purification from organic compounds was in the range of 92-94 % at the initial concentration of vapors of solvents of paint and varnish materials 0,6-0,8 g/m$^3$.

The apparatus KART-720 passed two rounds of testing in cleaning ventilation gases at the Painting Shop in the Production Corporation "SEVER" (Novosibirsk) and on the whole showed a satisfactory operation. However the tests revealed that in comparison with steady state incinerators its operation control is more difficult because of moving parts in the gas fittings, and the degree of organic compounds removal is lower because of the basic impossibility of achievement of 100% degree of purification. Table 1 shows the calculated highest degrees of gas purification in the apparatus KART, depending on the catalyst activity and the period of switching of the gas flow direction.

Table 1

Calculated degrees of gas purification in the apparatus KART-720 at various activities of the catalyst.

| Time of switching Flows, (sec) | Activity of catalyst, %. | | | |
|---|---|---|---|---|
| | 100 | 90 | 80 | 70 |
| | Degree of cleaning, % | | | |
| 3 | 27,3 | 24,6 | 23,1 | 20,2 |
| 5 | 56,4 | 50,8 | 45,8 | 40,1 |
| 10 | 78,0 | 70,2 | 62,9 | 55,0 |
| 20 | 89,1 | 80,2 | 71,5 | 62,5 |
| 30 | 92,7 | 83,5 | 74,3 | 65,0 |
| 50 | 95,6 | 86,1 | 76,6 | 67,0 |
| 100 | 97,8 | 88,0 | 78,3 | 68,5 |
| 500 | 99,5 | 89,6 | 79,6 | 69,7 |

For gas purification from low concentrated vapors of organic compounds with the minimum costs of the consumed electric power the introduction of liquid or gaseous organic fuel (e.g. industrial wastes) in the catalyst bed is stipulated [2]. This technique prevents the slip of untreated air with the increased content of vapors of organic compounds from the undercontact space, and on the whole increases the degree of gas purification by 2-3 %.

The apparatus showed a stable operation in an autothermal mode at concentrations of vapors of organic compounds 1,0-1,5 g/m$^3$.

The alumina supported copper chromate catalyst ICT-12-8 produced in Special Catalyst Technological and Designing Bureau with Experimental Catalyst Production Plant (Novosibirsk) displayed high activity in reactions of deep oxidation of hydrocarbons, which was practically unchanged during catalyst testing. However in the mode of periodic change of the direction of movement of thermal front the mechanical properties of catalyst underwent some changes (Table 2), i.e. the catalyst strength increased.

Table 2

Change of mechanical strength of catalyst ICT-12-8 during tests in the apparatus KART-720.

| Sample | No | Crushing strength (P), kg/cm$^2$ | | | Specific surface area, (S), m$^2$/g |
|---|---|---|---|---|---|
| | | P min. | P max. | P average. | |
| Fresh | - | 13 | 30 | 21 | 198 |
| Spent | 1 | 16 | 53 | 31 | 170 |
| On height of basket of catalyst | 2 | 11 | 42 | 24 | 200 |
| | 3 | 12 | 39 | 21 | 172 |
| | 4 | 13 | 44 | 25 | 197 |

The results obtained formed the basis for the design of the catalytic apparatus KART with a capacity of 3000 m$^3$/h [3], intended for purification of gases with concentration of organic compounds from 150 up to 1500 mg/m$^3$.

This work was carried out in 1986-1987.

# PP-C-9

## References

1. Matros Yu.Sh., Chumachenko V.À. Unsteady state method of catalytic cleaning of industrial off-gases // Chemical technology, Kiev: Naukova Dumka- 1986.- N 4 - p.66-73.
2.USSR Inventor's certificate No 1418957 USSR, B01D53/36. A method of purification of oxygen contaning gases from the admixture of organic substances /Zabortsev G.M, Ostrovski Yu.V., Shpak A.A./- No 4118204/23-26; date of application 15.09.86
3. Govor V.V., Ostrovski Yu.V., Shpak A.A. The catalytic`apparatus with regenerative heat exchangers (KART) // Information leaflet about technological achievement No 91-2053.-VIMI.-1991.

### PP-C-10

# INCINERATOR "KROT" FOR STEADY STATE CATALYTIC PROCESSES

Yu.V. Ostrovskii, G.M. Zabortsev

*Novosibirsk State Design and Research Institute VNIPIET, Novosibirsk, Russia*
Phone: (3832) 76-96-35, E-mail: ost@ pri.sib.ru

For cleaning ventilation gases of the drying equipment at Lithography Shop of the Plant of Household Chemicals in Novosibirsk from vapors of volatile organic compounds (VOC) a steady state catalytic incinerator "KROT" with a capacity of 2500 $m^3/h$ was designed, manufactured and installed. The appearance of the reactor is shown in Fig.1.

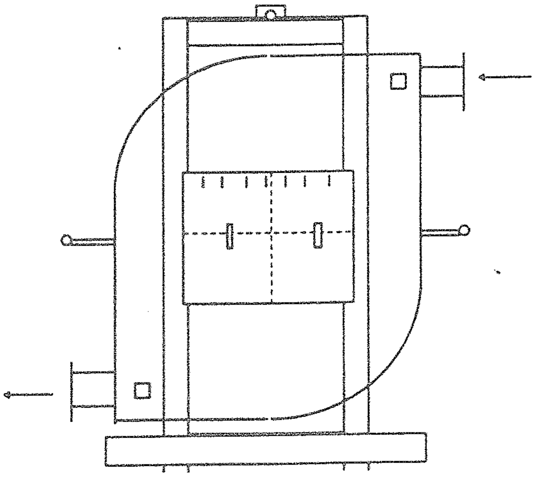


Fig 1. Appearance of the incinerator

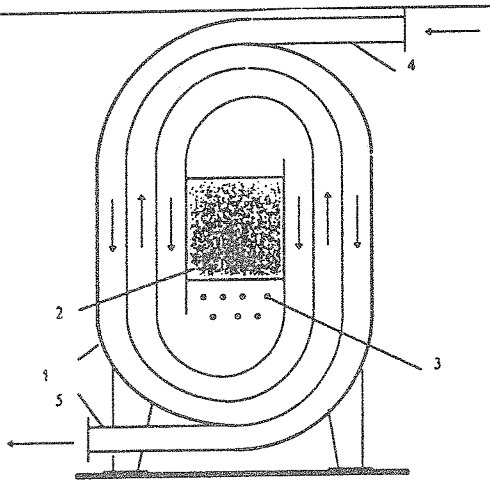


Fig 2. Scheme of catalytic incinerator

The reactor (Fig. 2) is a module of a vertical design [1] with connecting pipes for inlet and outlet gases (4, 5) and two-channel spiral heat recuperator (1), inside which a catalytic section (2) and electric heater 3 are placed. In comparison with the analogues the reactor "KROT" has lower loss of heat and higher heat recuperation: 80-85 %. The area of heat exchange surface reaches 180 $m^2$. The calculation of the incinerator was made with the use of an improved technique [2].

An alumina supported copper chromate catalyst ICT-12-8, manufactured at Special Catalyst Technological and Designing Bureau with Experimental Catalyst Production Plant (Novosibirsk), was used in the incinerator "KROT" for oxidation of vapors of organic compounds.

The kinetics of deep catalytic oxidation of main components of paint and varnish materials of the Lithography Shop: toluene, xylene, acetone, ethylcellosolve, cyclohexanone and white spirit was studied. The experiments were carried out with small catalyst granules of 1,0-1,6 mm in the integral laboratory reactor in a temperature range 370-600$^0$C. The process can be satisfactorily described by a kinetic equation of the first order with respect to the substance oxidized (Table 1).

Table 1.In addition, an experimental study of the oxidation of a hydrocarbon mixture, simulating actual industrial gas stream, on commercial catalyst grains ( 3 × 8 mmtemperature of 430 $^0$C and a space velocity of $V=10000\ h^{-1}$ was carried out. Under these conditions the practically complete oxidation of hydrocarbons takes place (Table 2).

# PP-C-10

Table 1.

Activation energies and pre-exponential factors for reactions of hydrocarbon oxidation.

| Compound | Temperature range, $T^0C$ | Activation energy E, кJ/mole | Pre-exponential factor, $k_0$ |
|---|---|---|---|
| Toluene | 563-603 | 79,4 ± 3,5 | $1{,}787 * 10^8$ |
| Xylene | 512-578 | 100,6 ±12,0 | $2{,}420 * 10^{10}$ |
| Acetone | 480-580 | 62,8 ± 4,6 | $8{,}920 * 10^6$ |
| Ethylcellosolve | 373-473 | 58,8 ± 2,5 | $1{,}086 * 10^8$ |
| Cyclohexanone | 453-528 | 45,1 ±3,2 | $5{,}390 * 10^5$ |
| White spirit | 490-563 | 48,2 ±6,5 | $2{,}838 * 10^5$ |

Table 2

Results of oxidation of a mixture of VOC (over commercial catalyst grains) at $T = 430^0C$ and $V = 10000\ hour^{-1}$.

| Compound | Concentration, $mg/m^3$ | | Destruction degree, %. |
|---|---|---|---|
| | Inlet | Outlet | |
| Toluene | 821 | 0.8 | 99.9 |
| Xylene | 562 | 1.1 | 99.8 |
| Acetone | 293 | 0.3 | 99.9 |
| Ethylcellosolve | 452 | 0.9 | 99.8 |
| Cyclohexanone | 152 | 0.0 | 100,0 |
| White spirit | 128 | 0.4 | 99.7 |

The algorithm of calculations of reactor parameters was developed, and a program for a personal computer was composed. The following initial data are entered: the initial gas temperature and the temperature of the gas leaving the catalyst bed, volumetric gas flow rate, initial width of the apparatus, initial area of heat exchange surface, thermal capacity of a constructional material and catalyst, equivalent diameter of the latter, catalyst mass and porosity, maximum pressure in the incinerator. For the calculation of the duration of the start-up of the incinerator installed power of the electric heater is entered.

During the program operation a criterion Re is initially calculated and at its small size, when the version is economically unsatisfactory, the program returns to the initial data. Then verifying calculation of the parameters of the heat exchanger is executed and at its discrepancy the return to the beginning of the calculation also takes place. Afterwards the calculation of the pressure drop through the catalyst bed and its comparison with the maximum allowable value are made. In the case when the calculated pressure is too high the parameters of the catalyst basket are changed and the calculations are repeated. An example of calculations performed for the incinerator of 1000 $m^3/h$ capacity with a heat exchange surface of 75 $m^2$ at various inlet gas temperatures is given in Table 3.

Table 3.

Results of calculation of the catalytic incinerator KROT-1000.

| Process parameters | Inlet gas temperature , $^0$C | | | | | |
|---|---|---|---|---|---|---|
| | 10 | 50 | 100 | 150 | 200 | 250 |
| Temperature of process, $^0$C | 400 | 400 | 400 | 400 | 400 | 400 |
| Temperature of outlet gas, $^0$C | 90,3 | 118 | 154 | 192 | 232 | 272 |
| Degree of heat recuperation | 0,794 | 0,805 | 0,818 | 0,829 | 0,839 | 0,847 |
| Power of electric heater, kW | 22890 | 17880 | 13230 | 9730 | 6990 | 4770 |
| Time for reactor starting , hour | 0,675 | 0,542 | 0,429 | 0,340 | 0,263 | 0,193 |

The calculated hydraulic resistance of the reactor is less than 800 Pa.

The design documentation for a series of incinerators of this type with capacity 150, 200, 800, 1000, 1800 and 2500 nm$^3$/h [3] has been elaborated.

This work was carried out in 1990 year.

## References.

1. USSR Inventor's Certificate No 1762459, B01J8/02. The catalytic incinerator / V.V.Govor, G.M. Zabortsev, Yu.V.Ostrovski. No 4833073/26; application date 12.04.90

2. Gubaidullin R.Z., Treskova A.C., Limanski G.M. Engineering calculation of incinerators for catalytic purification of industrial off-gases. Review information. Industrial and sanitary gas treatment. - Series HM-14-1987.

3. Govor V.V., Zabortsev G.M., Ostrovski Yu.,V. The catalytic incinerator with recuperative heat exchanger (KROT) // Information leaflet of technological achievement. No 92-1499-VIMI-1992.

## PP-C-11

# THE MATHEMATICAL MODELLING OF THE BITUMINOUS COAL GASIFICATION IN A PILOT PLANT REACTOR-GASOGENERATOR SYSTEM WITH CIRCULATED FLUIDISED BED AT ELECTED PRESSURE

VADIM P. PATSKOV
*Coal Energy Technical Centre of Ukraine NAS and*
*Ministry of Energtetic of Ukraine, Kiev, Ukraine.*

This paper is a continuation of researches [1,2] for developing of methodic of mathematical modelling, calculation and optimisation of complicated technological schemes for thermochemical conversion (pyrolysis, combustion and gasification) of low grade energetical coals in circulated fluidized bed under pressure. The mathematical model, algorithm, program and some results of calculation of process of air gasification of high ash bituminous coal type GSH under pressure in reactor-gasogenerator of pilot demonstration plant for two-stage gasification of coal in PCFBC [3] are examined here.

The reactor-gasogenerator of this plants [3] is a long cylyndrical apparatus ($H \approx 17m$). In the bottom in the developed psewdofluidization regime (zone of fluidized bed) and in the top in phnewmotransport regime (zone of freobard space) the process of air gasification of polyfractional cokes of coal type GSH are passing. The process includes heterogeneous chemical reaction of coke combustion and gasification with $CO_2$ and also homogeneuos chemical reaction of CO oxidation.

The one-dimensional and unstationary mathematical model of the process in the zone of fluifized bed is build on the base of two-phase theory of pseudo-fluidization and takes into account a longitudinal effective diffusion and heat conductivity, the gas component filtration, circulation of particles, phase-to-phase heat/mass transfer between the bubbles and density phase, convective and radiation heat transfer between the gas flow, fuel and inert ash particles, near wall heat transfer, heat conductivity in walls of reactor, the surface heterogeneous reaction of combustion/gasification of cocke residue, homogeneous reaction for CO oxidation [4].

The one-dimensional unstationary mathematical model in zone of the freobard space bases on a theory of multi-rate penetrating phases. The surface heterogeneous combustion and gasification of coke residue, homogeneous reaction of CO oxidation, convective mass transfer between phases, gravitation forces, pressure drop, phase-to-phase friction, friction of wall, convective and radiation heat transfer between phases and up of reactor walls, conductivity on walls of reactor are taken into account.

The contact between the phases in reactor is realise with the help of empirical correlations, which repel the taken of solid particles in the zone of freobard space.

An algorithm of the process calculation in reactor bases on sure-differential methods. The method of automatic choise of time step is provided by Rychardson extrapolation. This algorithm is like Zeidel method.

The program of the process parameters calculation for the facility is made using FORTRAN-90 (version 1.0 Microsoft for Windows). This program is realised on IBM PC AT 386/387.

By numerical calculation it is shown, that worked up mathematical model, algorithm and program are effective and stable. They allow to receive the information in the form of profiles of basic parameters of process through the height of reactor in different moments of time. This information can be used in engineering technological practice for working out testing regimes and planing the experiments in the plant, for prediction of optimal regimes of it's functionation.

## REFERENCES

1. Korchevoy Yu.P., Maystrenko A.Yu., Patskov V.P. et al//Khim. Prom.-1995.-№1.-p.23-29.
2. Patskov V.P.//XIII Int. Conf. on Chem. React.: Abstr, Novosibirsk (RUSSIA), Boreskov Institute of Catalysis SB RAS, 1996.-P.1.-p.251-257.
3. Maystrenko A.Yu., Dudnik A.N., Yatsckevitch S.V. Coal gasification technologies for combined cycle power plants.-Kyjv: Znannya,1993.-68pp.
4. Patskov V.P., Korchevoy Yu.P., Maystrenko A.Yu. //Chem. Phys. for Comb. and Expl.:XI Int. Symp. for Comb. and Expl.: Abstr. Chernoglovka, Inst. Chem. Phys. RAS (Chernogolovka), 1996.-p.1.-p.138-140.

## PP-C-12

# INTENSIFICATION OF CATALYTIC OXIDATIVE REMOVAL OF $H_2S$ FROM SOLUTIONS IN THE PRESENCE OF TETRASULFONATE OF COBALT PHTHALOCYANINE IN A BUBBLE-CENTRIFUGAL REACTOR

S.G. Zavarukhin, G.G. Kuvshinov, L.V. Gogina and N.N. Kundo
*Boreskov Institute of Catalysis, Pr. Akademika Lavrentieva, 5,*
*Novosibirsk 630090, Russia*

Hydrogen sulfide is found in sewage waters of different productions of electric-power, wood-pulp-and-paper, petrochemical, and leather industries [1]. Large volumes of sewages and low sulfur concentrations in solutions call for the development of new technologies providing efficient purification of such solutions. We have developed the catalytic oxidative purification method, using tetrasulfonate of cobalt phthalocyanine $CoPc(SO_3Na)_4$ as the catalyst [2-4] and a bubble-centrifugal reactor (BCR) [5,6], which is one of the modern small-sized heat-mass exchanging devices, providing a high efficiency operation.

To study the process, we have developed the BCR and installed it into a flow circulating system (with respect to air and mixture, respectively). The system permits a simultaneous heating of solution and air. The experimental parameters are as follows:

| | |
|---|---|
| - solution consumption | 40 L/h |
| - solution volume | 3-5 L |
| - solution composition: | |
| $H_2S$ ($Na_2S$) | 0.05 mol/L |
| $NaHCO_3 + Na_2CO_3$ | 30 g/L (refered to $NaHCO_3$) |
| $Na_2S_2O_3$ | 0; 106 g/L |
| $CoPc(SO_3Na)_4$ | 1-10 mg/L |
| - pH of solution | 9.4 - 9.5 |
| - temperature of solution | 15; 25°C |
| - air flow rate | 50 $m^3$/h |

Sodium sulfide solution was used to model $H_2S$-containing solutions. In the course of runs, the solution was analyzed a few minutes apart until its complete oxidation.

As found, parameter variations within the given ranges do not markedly affect the rate of solution oxidation.

Using the experimental data, we have determined that a space velocity of hydrogen sulfide oxidation was 20 mol/L h in the BCR at the initial stage, with $H_2S$ concentration being 0.05 mol/L.

For comparison, similar solutions were oxidized with pure oxygen and air in a laboratory-scale reactor with intensive shaking.

We have also compared the BCR, laboratory-scale reactor with intensive shaking and slurry reactor (tested at the Novokuibyshev oil refinery) with respect to reaction space velocity and found that the BCR parameter is significantly higher. Thus, bubble-centrifugal reactors have strong potentials for the liquid-phase oxidative purification of various solutions.

The technology in concern can be used in the liquid-phase catalytic oxidative purification of gases from hydrogen sulfide at the stage of circulation solution regeneration.

**References**

1. Ponomarev V.G., Iokimis E.G., Mongait I.L., Purification of Sewage Waters of Oil Refineries, //Khimiya, Moscow 1985 (in Russian).
2. Author Certificate No 246487 (USSR), Discoveries, Inventions, No 21, 1969.
3. Kundo N.N., Keiker N.P., //Kinet. Katal., 11 (1) 1970, 91.
4. Kundo N.N., //Ross. Khim. Zh., 37 (4) 1993, 97.
5. Burdukov A.P., Goldshtik M.A., Dorokhov A.R., Kazakov V.I., Li T.V., //Zh. Prikl. Mekh. Tekhn. Fiz., No 6, 1981, 129.
6. Burdukov A.P., Dorokhov A.R., Kazakov V.I., Kuvshinov G.G., Petin Yu.M., //Izv. Sib. Otd. Akad. Nauk SSSR, ser. Tekhn. Nauk, No 4, 1985, 99.

**PP-D-1**

# GETTING MAGNET ALLOYS ON THE Nd-Fe-B BASE BY METALLOTHERMAL REDUCTION OF METAL FLUORIDES WITHOUT STOVE WITH POURING METAL INTO A CRYSTALLIZER

A. S. Buinovsky, P. A. Buinovsky, A. N. Kachurovsky,
V. V. Skripnikov, V. L. Sofronov, Yu. P. Shtefan
*Seversk Technological Institute*
*of the Tomsk Polytechnic University, Seversk*

Fluoride metallurgy for getting metals and alloys is perspective. So along with common processes of getting metal uranium, plutonium and reduction of their fluorides, fluoride metallurgy is used for getting individual REM, zirkonium, titanium and other metals, and alloys on their base. Expansion of using fluorides is explained by their small tendency to hydrolysis and large thermal effects during metallothermal reduction in comparison with other halogenides, which allows to make reduction in selfspread-hightemperature synthesis (SHS).

We developed the method to get magnet alloys on Nd-Fe-B base by calcicthermal reduction of metal fluorides without stove, which is used at the Siberian Group of Chemical Enterprises (SGCE). The reduction is made in the hermetic reactors. The charge, consisting of metal fluorides, alloying additions, iron boron and other components, is charged into a metal crucible lined by free calcium fluoride charging. Initiation of the reduction process is made with the help of electric spiral. The products of metal fluorides reduction are heated, melted and overheated at the expense of the reaction heat and alloys ingots are formed. However this method has some disadvantages, e. g. different cooling rate of different parts of an alloy on its radius and height. The latter leads to unevenness of components distribution in the ingot and accordingly to nonstability of chemical and phase composition in different points of an ingot, though the total concentration of REM in an ingot can satisfy the required composition for making Nd-Fe-B type magnets. Ingots formation under reduction melting (RM) occurs on the surface of calcium fluoride which was charged onto the crucible bottom, so the lower ingots surfaces have cavities roughness covered by a layer of melted calcium fluoride which makes the articles appearance worse. From the literature it is known, that to get alloys with even phase and chemical composition it is necessary to get metal ingots by pouring metal melt into metal moulds which gives quick and rather even from all sides cooling of alloys and reduces the thermal effect of slag.

Because of this to improve the quality of ingots surface we offered and developed the method for getting magnet alloys combining RM and pouring metal into a mould. For this purpose we used a melting blocking (membrane). To realize this process the following conditions must be observed:

- metal or alloy melting must be formed first in the upper crucible, i.e. practically "to be separated" from slag;
- the material composition of a melting membrane must not differ from the metal or alloy composition or correspond to one of two alloy components;
- crystallizer material must quickly absorb the heat liberating while cooling by metal and alloy;
- melted slag getting into a crystallizer is not desirable as it makes metal dirty and increases thermal contents of the system metal - slag;
- the slag is better to be collected into a separate capacity situated above the crystallizer or to be left in the crucible after metal melting pouring.

While pouring the melting into a metal mould the slag does not get into it so the ingots surfaces are clean and the ingots have good appearance and only the place of metal “adding” differs from the rest surface of the ingot. In this case there is almost no necessity to clean the ingots surfaces with sand and so there is no one category of wastes.

We investigated the processes of getting the next types of alloys in the new type of reduction reactors:

1) alloy with the Nd contents of (60-70) % (max) and the rest - Fe;
2) alloys with the Nd contents of (35-38) % (max), (1,2-1,3) % of boron and the rest - Fe;
3) alloys with the Nd contents of (12,5-13) % (max), (4,2-4,3) % of boron and the rest - Fe;
4) alloys of 2 and 3 compositions, synthesized by RM with adding into charge of Nd-Fe alloy.

While investigating we defined the optimal conditions of making RM process in the combined reactors, different sizes and materials of membranes are tested, and also the order and method of blending, thermal conditions of RM process and a number of other factors. The methods of thermal and design calculation of these reactors are also developed.

# SECTION D

## CHEMICAL REACTORS FOR SOLVING THE FUEL AND ENERGY PRODUCTION PROBLEMS. OIL AND GAS PRODUCTION AND PROCESSING

**PP-D-2**

# DEVELOPMENT OF THE TECHNOLOGY AND REACTORS FOR MAGNET PRODUCTION WASTES PROCESSING

A.S. Buinovsky, A.Y. Makaseev, Y.N. Makaseev, V.L. Sofronov,
S.G. Sulima, V.V. Khlebenkov, J.P. Shtefan
Seversk Technological Institute
of the Tomsk Polytechnic University, Seversk

Under modern conditions the necessity of different industries in Nd-Fe-B type magnets is constantly growing.

Usage of these magnets in d. c. engines, generators, separators and many other articles allows to reduce considerably their mass gabarit and improve their energetic characteristics.

However the production of these magnets according to the method of powder metallurgy is connected with the formation of a considerable amount of wastes (10-40 % from the mass of ready products), containing valuable REM. The most part of these wastes is formed while grinding magnets slabs into the size - 15-30 % from the mass of ready product, so-called grinding wastes.

Besides main metal phase which is mostly magnet material $Nd_2Fe_{14}B$, grinding wastes contain 5-14 % мass. oxygen, 5-7 % of carbon (in the form of oils forming oiling-cooling liquid-OCL), 10-30 % - moisture and up to 1.5 % of Si and Al impurities, the letter get into wastes from the grinding instrument. The typical chemical composition of dry grinding wastes, got at the Siberian Group of Chemical Enterprises (SGCE) is the following: Nd 19-24; Fe 45-50; B < 1.0; C 5-7; Ni 0.4; Ca 0.09; Cu 0.09; Pr 0.50; Co 3.03; Al 0.6; Si 0.3; About 12-14 % мass.

Nowadays in Russia grinding wastes from magnet production on REM base are not processed because REM production is stopped.

The leading among the producers of rare earth production French firm Ron-Pulenk has a possibility to process grinding wastes as well as rare earth raw by using the technology of extraction elements separation and getting of pure metals. At this cost of REM, got after grinding wastes processing, can be compared with the cost of initial REM.

Seversk technological institute (STI) together with the SGCE made complex investigations of different wastes processing from constant magnet production. On the base of received results there has been developed principally new anhydrous fluoride technology for processing of Nd-Fe-B type magnets production. The suggested technology allows to process grinding wastes practically without changing the metal phase. Only organic components of OCL in the form of $CO_2$ as well as $SiF_4$, and $BF_3$ are removed. The most part of OCL is removed from grinding wastes by decantation and purified OCL may be used again while grinding magnets. Drying and oxidation are necessary to remove excess amount of water and thermal decarbonizing of grinding wastes. The selection of the thermal regimes allowed to combine two processes in one without external heating. After oxidation the complex oxide, containing $Fe_2O_3$, $REM_2O_3$, Fe $(REM)O_3$ and α-Fe, is subjected to magnet separation to remove Si, AL and other non-magnetic impurities on a drum separator where Nd-Fe-B magnets are used.

The magnet fraction of oxidized grinding wastes is then subjected to fluoriding with element fluorine. The low degree of wastes oxidation allows to make this operation at lower temperatures in comparison with fluoriding of pure REM and iron oxides, which allows to reduce power consumption for heating fluoriding reactor. As it was mentioned above, B and Si are removed from the wastes during fluoriding process in the form of volatile $BF_3$, $SiF_4$.

The received fluorides are subjected to calcic thermal reduction without stoves in hermetic reactors. If necessary, besides FeB some alloying additions are added into the charge.

The received secondary magnet alloy can be used either immediately for getting Nd-Fe-B type magnets or melted in the induction stove to purify from volatile impurities and get more uniform crystal structure and then can be used for getting magnets.

According to this developed theory of processing grinding wastes while producing Nd-Fe-B type magnets at the SGCE there has been processed experimental-industrial batch of grinding wastes and magnet alloys have been received.

The received materials according to the main impurities met the requirements of the SGCE technical conditions. From the experimental batch of received secondary magnet alloys (without induction melting) with Nd-34 % contents there have been made constant magnets according to the powder industry method. The magnet samples had the following characteristics: remain induction $B_r$ - 1.0-1.1 T; coercive force $M_{c\mu}$- 15-18 кOe, which correspond to the characteristics of common magnets produced by the SCP.

We developed, calculated and designed some types of reactors for drying, oxidation, fluoriding and reduction of magnet production wastes.

**PP-D-3**

# ELECTRIC EXPLOSION OF CONDUCTORS AS A METHOD OF CHEMICAL SYNTHESIS

Ilyin A.P., Nazarenko O.B., Ushakov V.Ya.

*High Voltages Research Institute, Tomsk, Russia*

Design of the chemical technologies to prepare new materials puts the question of investigation of highly nonequilibrium processes under extreme conditions of pressure, temperature, chemical reaction rates and other physical parametres. One of these processes is wires electric explosion (WEE). Wires electric explosion is a drastic change in the physical state of metal upon passing pulse current of high density ($j > 10^6$ A/cm$^2$) and followed by intense heat release. One of the applications of WEE is its use as chemical reactor. At sufficient energy input, WEE products are ultrafine powders (UFP). The powders have a number of unique properties which define the area of UFP application - as catalysts, sorbents, ceramics component, etc.

Investigations on the preparation of UFP were started in the 70th in High Voltages Research Institute by Yu.A. Kotov, G.V. Ivanov, M.A. Melnikov, N.A. Yavorovskiy. The investigations were directed to the study of WEE in gases and mainly on the preparation of metal powders. The investigations on WEE in liquids were connected essentially with use of resulting powerfull hydrodynamic pulses in the production process. The interaction of dispersed metal with environment during WEE in condensed media can be used for the preparation of the chemical compounds in the UFP form.

The present work is devoted to the experimental investigation of WEE as chemical synthetic technique, to study the effect of WEE parametres, composition of environment and some technological factors on the process characteristics. Destilled water and saturated hydrocarbon decane differing considerably in chemical and physical properties have been chosen as liquid media. Aluminium, tungsten, titanium, iron, copper wires were taken for explosion. To study the pecularities of the water as reduction-oxidation system the metal with various oxidation states have been chosen: titanium, iron, copper. X-ray data show the WEE of iron in water resulting in FeO, titanium - $Ti_2O_3$, $\gamma$-$Ti_2O_3$, $Ti_4O_7$, copper - $Cu_2O$, contrary to WEE in oxygen containing gases giving $Fe_2O_3$, $TiO_2$, CuO respectively. Interaction of metal particles and protons yields hydrogen, an active reductant, shifting the chemical equilibrium to the initial substances. WEE of aluminium in water in dependence of energy input, water state and measure of chamber gives a stable suspensions of $Al(OH)_3$, low and high temperature crystal forms of $\gamma$-$Al_2O_3$ and $\alpha$-$Al_2O_3$. Particles formed are of spherical shape and average surface diametre 0,02-0,04 mcm.

WEE in liquid hydrocarbons was studied previously by I.I. Vishnevetskiy. X-ray analysis of solid products of hydrocarbon-metal reaction has showed the presence of metal carbides. The relation between composition and properties of powders formed with WEE parametres has not been established. At rising of energy input in the wire the yield of carbides increases, size of powder particles decreases. This is general tendency for WEE in any medium. Thermodynamic analysis of chemical compounds formation at the various steps of WEE has been made. Relative content of carbides depends considerably on the upper bound of their thermal stability. The higher stabilisation temperature explains the higher content of tungsten and titanium carbides in comparison with aluminium carbide providing at equal energy input values. WEE in condensed media makes possible to obtain some compounds when the upper bounds of thermal stability are close, and enviroment is multicomponent. WEE of aluminium in the hexametilenetetramine - decane suspension yields aluminium carbide and nitride.

## PP-D-4

# OIL SLUDGE DESTRUCTION IN A CATALYTIC FLUIDIZED BED REACTOR

Z.R.Ismagilov, M.A.Kerzhentsev,
B.I.Lunyushkin*, Yu.V.Ostrovski*, G.M.Zabortsev*
Boreskov Institute of Catalysis, Novosibirsk; *NGPII VNIPIET, Novosibirsk

One of important problems of environmental protection is development of an environmentally safe technology for treatment of oil sludge accumulated in tanks. Storage of the residue extracted from tanks requires large area and may cause soil contamination with hydrocarbons. Both in Russia and abroad the most widespread method of oil sludge treatment is flame incineration. This method leads to pollution of the atmosphere with nitrogen and sulfur oxides, carbon monoxide and soot [1].

We propose a novel environmentally safe technology for oil sludge treatment, based on sludge destruction in a fluidized catalyst bed. The installation consists of a catalytic reactor and off-gas treatment system. The catalyst provides full sludge oxidation at relatively low temperatures (600-750°C), which suppresses formation of nitrogen oxides [2]. The process was studied in an experimental installation of catalytic combustion with samples of oil sludge from Torgili Reservoir Yard (Tyumen Region).

The installation (Fig.1.) consists of a fluidized bed catalytic reactor (1) with a water cooled heat exchanger (2) installed in its upper part, electric heater (11) for initial heating of the catalyst to the light-off temperature (300-400°C), cyclone (3) for removal of larger dust particles from the gas stream, catalytic after-burner (4) with honeycomb catalyst for oxidation of trace amounts of CO and organic compounds in the exhaust gas; jet scrubber (5) and adsorber-condensers for removal of low-sized dust particles and acidic pollutants from the gas, and filter (7).

The installation works as follows. The compressed air is supplied by the blower (12) to the lower part of the catalytic reactor in the amount required for catalyst fluidization and oxidation of organic compounds; oil sludge is fed to the reactor by the pump (8) from the heated tank (10). In the catalytic reactor total oxidation of organic compounds takes place with the temperature of the gas and catalyst rising to 700-760°C. The water cooled heat exchanger in the upper part of the apparatus provides heat utilization and the decrease of the exhaust gas temperature to 300-350°C.

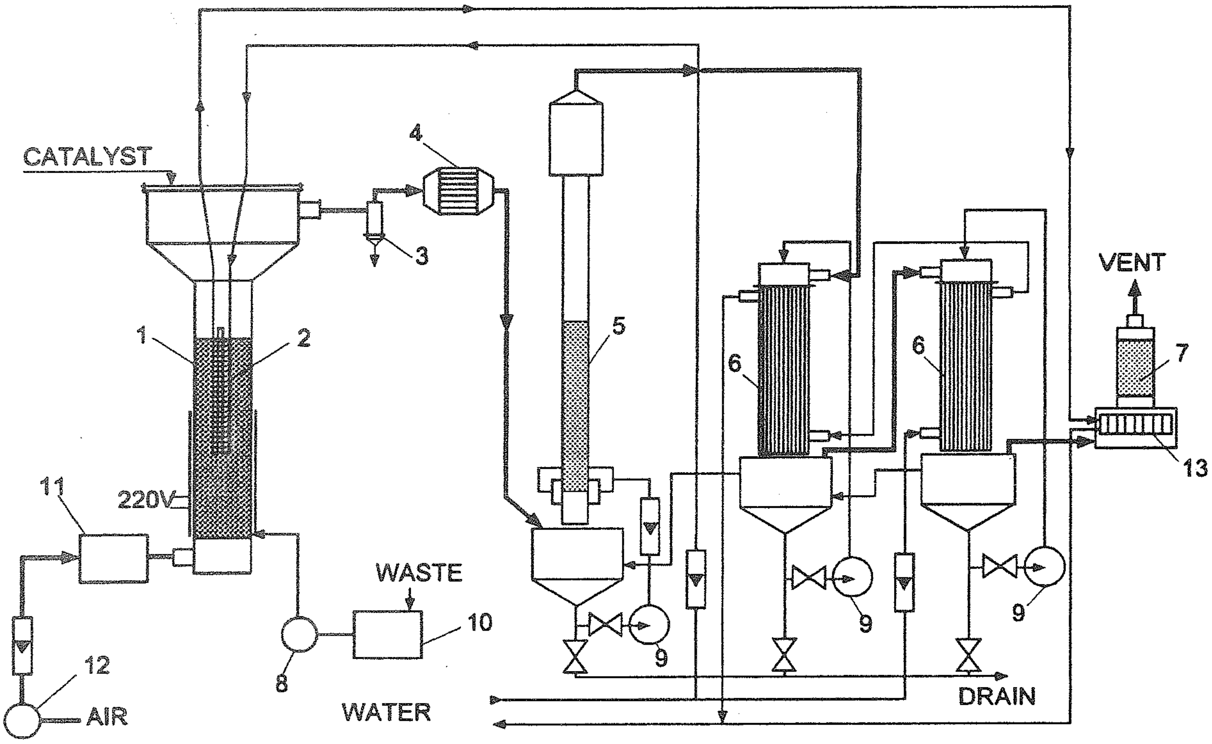


Fig. 1. Schematic diagram of experimental setup for study of organic waste catalytic combustion and off-gas treatment: 1 - fluidized bed reactor, 2 - heat exchanger, 3-cyclone, 4 - CO catalytic converter, 5 - jet scrubber, 6 - absorber-condensers, 7 - filter, 8 - pump for sludge, 9 - water pumps, 10 - heated tank with sludge, 11 - electric heater, 12 - compressor, 13 - heat exchanger.

Various regimes of the processes of waste catalytic destruction and off-gas treatment were studied. In optimum operational regimes the concentrations of pollutants in the exhaust gas do not exceed (mg/m$^3$): ÑÎ - 1; nitrogen oxides - 20, sulfur dioxide 1; dust -1. Basing on these studies design documentation of a prototype industrial plant for oil sludge catalytic destruction was elaborated.

References

1. Fryazinov V.V., Bonz B.I. Kuptsov A.V., Rassvetlov, B.A. Incineration of slurries and activated sludge.- Topical Review - Environmental Protection Series. Moscow. - 1985.
2. Z.R.Ismagilov, M.A.Kerzhentsev. Catal. Rev. - Sci. Eng. , 1990, **32**, 51.

## PP-D-5

# PHYSICO-CHEMICAL REGULARITIES OF CHANGE IN Pt-CATALYSTS ACTIVITY IN NAPHTHA REFORMING PROCESS

E.D. Ivanchina, O.G. Asadchy, A.V. Kornienko

*Tomsk Polytechnic University, Tomsk, Russia*
*E-mail: TPU@TPU.EDU.RU. Fax 22-39-95.*

The fuel and energy needs of Tomsk area create necessity to obtain high-octane motor fuels in northern industrial centers (Strezhevoy, Kedroviy and etc.). From practice of an oil refining industry it is known, that the cost price is reduced, and profitability grows at increase of volumes of manufacture. At construction ORF of low power (less than 1 million t.y.) there is the number of complications:

1. The high cost price of production.
2. Small depth of processing of petroleum raw material and narrow assortment of developed products.

It results in irrational use of raw material.

In connection with stated, modular ORF, despite objective necessity of their construction for manufacture of high-octane fuels in remote regions with the undeveloped transport circuit, the question arises about estimation of efficiency of an again created industrial complex. In 1998 year input in operation of mini-ORF (Strezhevoy) on technology of «PETROFAC » is planned.

For an estimation of efficiency of the technology of high-octane petrol production the approach is offered which was used earlier for the large tonnage ORF.

The approach is based on the physico-chemical non-stationary model, taking into account deactivation of the catalyst.

As a level of activity of the catalyst an output of a product (aromatic hydrocarbons) is accepted, which defines both efficiency of technology, and modes of operation of catalysts. We have carried out calculations of a level of activity of the catalyst of reforming process on «PETROFAC» installation (Factory of Condensate Stabilization, SurgutGasProm division) at hydrocarbon raw material, fraction 85-170 $^0$C, processing on platinum-rhenium catalyst (gas condensate with the high naphthen content - 40 % and more). The catalyst, sensitive to sulfur, is used, and flow to the reactor of reforming should contain no more than 1 mg/kg. With this purpose the reactor R-204 for removal sulfur compounds is stipulated, in which catalyst for desulfurization HRD-264 is loaded.

An active component of the catalyst of sulfurpurification is manganese oxide MnO. This catalyst combines catalytic and adsorptive properties. It decomposes sulfurorganic compounds and simultaneously absorbs sulfur.

$$RSH + H_2 \xrightarrow{\text{catalyst}} RH + H_2S \xrightarrow{\text{MnO}} MnS + H_2O \qquad (1)$$

In the first case HRD-264 acts as the catalyst, in second as adsorbent. The reaction (1) is reversible. The constant of balance of this reaction $K_1$ is expressed by the equation:

$K_1 = [H_2O]/[H_2S]$ $MnS + 2HCl \leftrightarrow MnCl_2 + H_2S$ (2)

Constant of balance $K_2$ of reaction (2.) is expressed by the equation:

$K_2 = [H_2S] / [HCl]^2$,

At the expense of increase of temperature in reactor of desulfurization and at decrease of the chlorides content the equilibrium content of hydrogen sulfide can be decreased.

$$MnO + 2HCl \leftrightarrow MnCl_2 + H_2O \qquad (3)$$

The reaction (3) is of big importance, as it is connected with content of a moisture and chlorine in reforming system, necessary for maintenance of a given level of the contents of chlorine on platinum catalyst.

Estimation of platinum-rhenium catalyst activity at «PETROFAC» installation has been carried out. The catalyst has a low level of activity during the period between regenerations. It is a consequence of the fact that the given catalyst was developed for raw material with high humidity of environment (100 ppm) and low contents of sulfur in raw material (under the project not more than 20 mg/kgs).

On deactivation of the catalyst the big influence renders also basic adjustable parameter of the process - temperature. The operative change of temperature is necessary at variation of productivity of installation for maintenance of a constant level of octane number. The reforming process on installation «PETROFAC » proceeds at high temperatures 508-530 $^0$C, and for increase of octane number on one item temperature should be raised on 2-4 $^0$C.

In addition model calculations on comparison of efficiency of operation of catalysts in «PETROFAC » installation and catalysts KR-110 in Kirishi ORF have been made.

Under condition of processing of raw material of a condensate from Urengoy deposit on installation LG-35-8/300B (Kirishi) it is possible to obtain product with the contents of aromatic hydrocarbons only 51 %. While the processing of west-Siberian oils in conditions of «PETROFAC » installation provides an output of aromatic hydrocarbons -34 %, processing of the same raw material over the catalyst E-601 -23 %.

Thus the calculations have shown low activity of work of the catalyst E-601. Hence it is possible to recommend replacement of the catalyst E-601 by the catalyst KR-110.

# PP-D-6

# CONTROL OF PRODUCTIVITY OF THE CATALYST FOR REASONABLE PROCESSING OF PETROLEUM FEED-STOCKS

E.D. Ivanchina, V.N. Reshetnikov, A.V. Sgibnev
*Tomsk Polytechnic University, Tomsk, Russia*
*E-mail: TPU@TPU.EDU.RU. Fax 22-39-95*

The catalysts used in oil processing, are obtained, as a rule, on the basis of precious metals and have a high price. Their cost in the majority of cases is comparable with the cost of the equipment of installations, on which they are applied.

Only the optimum operation of the catalyst allows to use it with higher efficiency, extending between regeneration run, increasing "rigidity" of process running and etc..

With reference to installation for catalytic reforming of petrols, a problem of process intensification, from the point of view of use of catalysts, it is possible conditionally to divide into two directions:

1. Development of highly effective catalysts;
2. Increasing of efficiency of working catalysts at the expense of maintenance of optimum modes of their operation and regeneration.

Effective way of maintenance of optimum work of aluminum-platinum catalysts for reforming is regulation of the content of chlorine by addition of chloroorganic compounds to raw material, that directly influences efficiency of process. At the same time it results in decrease of sulfur adsorption on the catalyst, and reduction of quantity of formed coke.

Despite gravity of a considered problem, a reliable technique of catalytic process management on working installation is not offered till now. The offered approach is based on physical-chemical and technological regularities of hydrocarbon transformation on Pt-catalysts. The basic stages of the management of catalyst productivity consists of normalization of the mechanism of hydrocarbon transformation, construction of kinetic model of the process with an estimation of parameters according to experimental data and, at last in representation of the complete mathematical description of technology of processing with the account of nonstationarity.

The earlier offered ways of management of productivity of the catalyst are inefficient, as in change of activity of the catalyst and structure of initial raw material are not taken into account. So, the management of reactor block of installation for catalytic reforming is carried out based on humidity of the system and content of hydrogen chloride. Such management does not allow to provide a high output of a target product during all time of operation of the catalyst, as far as a degree of coking, aging and poisoning of the catalyst are not taken into account. The management of process by criterion $C_{H2}/C_{Ap}$ does not provide the necessary information because of constantly varying structure of raw material. For the same reason increase of concentration of aromatic hydrocarbon does not provide an estimation of a level of activity of the catalyst in view of the temporary factor. At a rough estimation and at identical humidity chlorine is submitted on account of an optimum parity $H_2O$: HCl.

It has beem shown, that the content of chlorine on monometal and polymetal catalysts differs and makes 0,7 and 0,9 % weights, accordingly. However, surplus or lack of chlorine is diagnosed under the analysis of a number of the facts, which can be a consequence of absolutely other phenomena.

In turn the change of concentration of hydrogen in the system can be the result of incomplete dehydrogenation of naphtens, however, it can also be a consequence of intensive proceeding of reactions on acidic centers, that can be the result of excessive drying of the raw materials.

Lightening of raw material and reduction of concentration of naphtens results in decrease of concentration of hydrogen in the system, and also rechlorination of the catalyst and its coking.

The computer express-estimation of a level of acidic and metal activity allows under the daily analysis of gases, in view of structure of initial raw material and technological parameters, to expect current activity of the catalyst. The technique is introduced on a number ORF of Russia.

Literature

1. Kravtsov A.V., Ivanchina E.D. .Intellectual systems in chemical technology and engineering formation. - Novosibirsk: Nauka. - 1996.-200 p.

**PP-D-7**

# THE COMPUTER ANALYSIS OF PETROLS PRODUCTION

E.D.Ivanchina, K.A.Molotov, S.S.Kovirshin

*Tomsk Polytechnic University, Tomsk, Russia*
*E-mail: TPU@TPU.EDU.RU. Fax 22-39-95*

To the end of 1990-th oil refining industry will further test pressure from the part of the defence counsels of an environment and petrols consumers.

The basic problems of petrols production on an extent 10 - 20 years follow from specifity of all technologies existing in world practice:

1. Octane number and volume of manufacture;
2. Octane number and ecology of environment;
3. Octane number and cost price of a product.

High-octane petrols consumption grows in accordance with perfection of automobile park.

The general tendency to change of structure of petrol and decrease of concentration of aromatics hydrocarbons, benzene, residual sulfur, percentage of the oxygen containing additives, and also vapor tension was planned. In this connection the technology of petrols production is improved by the way of development and introduction of new processes on ORF, and also by means of use of the more effective additives.

Growing demand for petrol in a combination with higher octane number have resulted in replacement of a fraction $C_5$ - $C_6$ by isomerisat or alkylat in a combination with oxygen containing additives, more often by MTBE and its derivatives. The tendency to decrease the content of reformat in high-octane petrol was planned at simultaneous increase of capacities of catalytical cracking in fluidized layer. Each part of the world independently decides a problem of compaund commodity petrols. Comparing commodity petrols, produced in the different countries, it is possible to note, that the content of products of catalytic cracking, alkylation, polymerisation and isomerisation in total petrol is much higher, than in Russia. And in petrol, made in Japan and Western Europe the contents of reformat is the highest.

Basis of development and the introductions on ORF of new processes is physical-chemical and technological regularities of carbon transformation in many stages commodity petrols manufacture:

1. Catalytic reforming
2. Catalytic cracking
3. Hydrocracking
4. Alkiyation
5. Isomerisation.

On a modern level of development of a science and engineering the account of the complex "know-how" motor fuel is impossible without use of methods of computer modeling and artificial intellecte. As the manufacture of motor fuel technologically occurs in a number of interconnected stages, the computer analysis should be carried out stage by stage, namely:

1. Consideration of a problem of manufacture motor fuel;
2. The analysis of existing standards on production of petrols and other fuels;
3. The possible technology of manufacture of fuels (within the framework of given ORF and in the plan of necessary reconstruction);
4. Choice and substantiation of the most effective variant of technologies.

Therefore the purpose of the given work is choice and technological forecasting of a chosen direction of manufacture of high-octane petrols, that is possible only by use of methods of mathematical modeling and physical-chemical models of processes.

The basic source of obtaining of high-octane petrols on Achinsk ORF is section 200, including process reforming and selective hydrocracking (accordingly reactors R-202, R-203, R-204 and R-205).

The today working circuit of section 200 is unsufficiently effective from the point of view of use of the catalyst of selective hydrocracking in reactor R-205, as well as polymetal catalysts for reforming of a series KR.

The working technological circuit is nonoptimal, since the additional charge the system for cooling of R-205 is required and optimum parity the hydrocarbon /hydrogen is broken.

The advantages of the circuit offered consist in an opportunity of additional processing of fraction $C_5$-$C_6$ and partial optimization of structure of raw material R-205. The carried out computer calculations have shown, that efficiency of cooling of fraction $C_5$-$C_6$ depends on it hydrocarbons of structure.

The greatest effect of a gain of octane number is reached by use dual-reactor installation of average temperature isomerisation.

The system developed by us has allowed to count third variant of reconstruction with allocation of R - 205 in separate installation with inclusion in its structure of the additional furnace heating.

It is obvious, that the final choice of technology of isomerisation should be certained by results of technological accounts and comparison of competitive conditions of the market at realization petrols in region.

Being based on a most extensive literary material, and also using our experience on researches of the given processes during work, variants of modernization of working installation are offered.

## PP-D-8

# PURIFICATION OF ENAMEL FURNACES GAS EFFLUENTS OVER THE ULTRADISPERSED CATALYSTS BASED ON TRANSITION AND RARE-EARTH METALS

**A.J. Karengin, I.A.Tikhomirov, R.A. Arefieva*, T.A. Gubaidulina, A.V. Merkulov**

Tomsk Polytechnic University, Tomsk, Russia
*JSC “Sibkabel", Tomsk, Russia
*Tomsk 634003 Tel.(382.2) 904-498 Fax (382.2) 774-518, Russia*

In modern conditions enterprises are compelled to reduce waste products of harmful substances to atmosphere and to search for reserves to decrease the cost price of letting out production. Such reserve, on our sight, is manufacturing of new and restoration of second-hand catalysts with application of cheaper and effective ultradispersive catalytically active materials on the basis of complex oxides of transition and rare-earth metals (UDCM). In Join-stock company "Sibkabel", Ltd since 1990 works on regeneration SHC by cheap and effective materials are conducted and positive experience on their application /1/ is saved.

Earlier laboratory and stand test of catalysts on a basis of UDCM allowed to define their optimum structure with reference to conditions of work of enamel unit /1-3/.

In tables 1 and 2 results of operational tests of blocks of catalysts (600 x 300 x 80mm) and (500 x 500 x 144mm), respectively, on enamel unit as PGZ 15/40 and HE-1000/8 are submitted, in which on the new carrier, high – porous shave the material (ВПСМ), UDCM is supported.

Table 1

| Time, days | Factor Efficiency | Concentration Krezol, mg/m$^3$ | | Diameter wire, | The mark Varnish | Amount of courses |
|---|---|---|---|---|---|---|
| | Catalytic Clearing, % | Before | After | mm | | |
| 0 | 98,5 | 2240 | 32,1 | 0,335 | terebec | 18 |
| 32 | 99,3 | 5783 | 36,4 | 0,335 | monester | 15 |
| 40 | 99 | 8194,4 | 30,1 | 0,335 | monester | 8 |
| 46 | 99 | 9938,2 | 34,7 | 0,38 | monester | 12 |
| 86 | 99,7 | 2277,7 | 28 | 0,4 | terebec | 8 |
| 127 | 99,3 | 1727,7 | 27,8 | 0,335 | terebec | 8 |
| 196 | 99,5 | 8200 | 34,7 | 0,4 | F-35 | 18 |
| 224 | 99,2 | 4355,5 | 33,6 | 0,315 | PETV-2 | 7 |

Table 2

| Time, days | Factor Efficiency Catalytic Clearing, % | Concentration Krezol, mg/m$^3$ | | Diameter wire, mm | The mark Varnish | Amount of courses |
|---|---|---|---|---|---|---|
| | | Before | After | | | |
| 0 | 94.9 | 763.3 | 38.8 | 0.335 | Terebec | 4 |
| 1 | 98 | 608.8 | 11.4 | 0.335 | Terebec | 3 |
| 2 | 98 | 402 | 10.2 | 0.6 | Terebec | 4 |
| 7 | 98.5 | 763.3 | 11 | 0.6 | Terebec | 4 |
| 8 | 98.6 | 763.3 | 10.1 | 0.6 | Terebec | 4 |
| 114 | 97.4 | 859.9 | 22 | 0.45 | MT-533 | 6 |
| 133 | 95..5 | 327.8 | 14.7 | 0.3 | MT-533 | 2 |
| 157 | 96.6 | 812 | 27.1 | 0.6 | MT-533 | 4 |
| 188 | 94.5 | 593.7 | 32.4 | 0.5 | PETV-2 | 2 |

Thus, long operational tests have shown, that efficiency of catalytic purification on a basis of UDCM does not concede to catalysts on a basis of platinum and palladium and lays in limits 94-99 %, poorly depends on a diameter wire, mark of a varnish and amount of courses. Thus cost of catalysts on a basis of UDCM has appeared much below than cost of catalysts on a basis of platinum and palladium (in 5-7 times). It confirms perspective and economic feasibility of use of catalysts on a basis of UDCM for effective clearing of departing gases enamel unit from harmful organic connections.

## THE LITERATURE

1. Karengin A.J., Jubaidulina T.A., Arefieva R.A., Catalysts consume of departing gases enamel unit on the basis of complex oxides of base metals. Cable engineering, № 6,1995, c.41-42.

2. Tikhomirov I.A., Karengin A.J., Gubaidulina T.A., Arefieva R.A. Clearing of departing gases of furnaces enamel unit by ultradispersive catalysts. Materials of a Conference "Ultradispersive powders, materials and nanostructure. Reception, properties and application. " Krasnoyarsk, 1996, 209-211.

3. Tikhomirov I.A., Karengin A.J., Gubaidulina T.A., Arefieva R.A.Catalytics covering on a basis of ultradispersive powders based on complex oxides of transition and rare - earth metals. Materials of a Conference " Ultradispersive powders, materials and nanostructure. Reception, properties and application." Krasnoyarsk, 1996, c.143-145.

**PP-D-9**

# CATALYTIC TRANSFORMATION OF NATURAL GAS INTO $C_2$ - HYDROCARBONS

Kurzina I.A., Galanov S.I., Belousova V.N., Pastuhova N.V.
*Russia, Tomsk, Tomsk State University, Russia*

The lack of petroleum stocks puts forward a problem for searching of alternative raw materials for chemical industry. It is possible to use natural gas to solve such kind of problem. The basic component of natural gas is methane. The problem of development of methane transformation process to produce liquid fuel and variable chemical products is actual. The process of oxidative coupling of methane into ethane and ethylene is the most perspective way of natural gas transformation. However, the role of the structure and the surface properties of complex oxide systems is not established finally. In the present work the influence of methods of Sn - Pb - O oxide catalysts preparation, its structure and surface properties on the catalytic activity in course of oxidative coupling of methane are investigated.

Catalysts were prepared by the calcination of hydroxides mixture at 800°C in air. The catalytic activity was investigated in a flow catalytic device under the following condition: temperature 800°C, contact time 0.5 sec. and atmospheric pressure. The quantity of benzoic acid adsorbed on the unit of a contact surface from benzol solution was chosen as a measure of surface basicity of catalysts.

The increasing of PbO content in the catalysts leads to the growth of $C_2$ - hydrocarbon yield. The composition with the ratio $PbO:SnO_2$ = 80:20 (% mass.) was the most selective ($S_{total}$ = 51,4 %). Probably, significant selectivity of Sn-Pb-O samples may be explained by formation of multiphase system.

It was noticed, that under influence of high temperature loss of catalytic activity occurs during the time, possibly because of conglomeration processes. The system during the ratio $PbO:SnO_2$ = 80:20 (% mass.) was supported on a number of carriers for the increase of thermal stability. It was noticed, that the catalytic properties of obtained samples depend on a nature of carrier. The methane conversion increased with the reduction of the $SiO_2$ content in carrier. Probably, it is connected with the formation of silicate structures, which decrease the catalysts activity. The greatest yield of ethane and ethylene was obtained on the catalysts prepared by supporting of the damp mixture of $Pb(OH)_2$ and $Sn(OH)_2$ on $\alpha$-$Al_2O_3$. This catalyst was stable and did not lose the activity for a long time.

For Sn-Pb-O catalysts the increase of the Pb- content led to the growth of concentration of the basic centres. Probably, nucleophilic ions $O^{2-}$ are basic centres in this case. The composition with the ratio of Pb:Sn = 80:20 (% mass.) is the most selective catalyst of oxidative dimerization of methane and is characterized by the greatest content of the basic centres on a surface. The observed dependence for Sn-Pb-O oxide catalysts can be a proof for the heterolytic mechanism of the methane activation by means of nucleophilic ions of $O^{2-}$.

Results obtained allow to carry out search of active and selective systems for this process.

## PP-D-10

# FILAMENTARY CARBON AS A CATALYST FOR HYDROGEN SULFIDE OXIDATION TO SULFUR

G.G. Kuvshinov, Yu.I. Mogilnykh and M.Yu. Lebedev
Boreskov Institute of Catalysis, Pr. Akademika Lavrentieva, 5,
Novosibirsk 630090, Russia

The process of catalytic direct oxidation of hydrogen sulfide to sulfur as a way to purify gases with large oxygen excess attracts considerable interest at present. A demand for this process can arise, for instance, on the purification of combustion gases produced by bitumen deposits. The process usually goes in the presence of activated carbon or oxide metal catalysts. The main drawbacks of these catalysts are as follows: high cost, expensive transportation, low activity or low selectivity in gases with large oxygen excess. This paper discusses the possibility to use catalytic filamentary carbons (CFC) as alternatives to these catalysts [1].

The process of CFC generation has been the objective of many researches. The fact that CFC can be manufactured as granules [2] is very important for their application as catalysts. In [3] we reported on the CFC production during the natural gas utilization in a pilot plant.

To elucidate the ability of CFC to catalyze the direct oxidation of hydrogen sulfide to sulfur, we have studied the CFC granules, obtained on the natural gas decomposition ($CH_4$ , 95 wt.%, $C_3H_6$, 5 wt.%) in a quartz flow vibrofluidized bed catalyst microreactor of ideal mixing. Following the reduction of catalyst particles (NiO, 87 wt.%, $Al_2O_3$, 10 wt.%, and CuO, 3 wt.%) at 500°C, the CFC was produced at 550°C, with natural gas flow rate being 120 $(L/h)/g_{cat}$.

The resulting samples were tested in the direct oxidation of hydrogen sulfide to sulfur in a vibrofluidized bed microreactor of ideal mixing at 160-220°C. Initial concentrations of $H_2S$ and oxygen were 1-2%, and 5-15% respectively.

Comparing the CFC test results obtained at 175°C with that of Hydrodargo activated coal (similar testing conditions) /4/, we come to the conclusion that they exhibit close activities, whereas CFC shows considerably higher selectivity. Moreover, the specific surface of CFC (200 $m^2/g$) is much lower than that of the activated coal (~ 500 $m^2/g$). As for oxide metal catalysts (IC-27-40, ICT-12-8, and CU-16), CFC exhibits much higher activity and selectivity at 200°C, gaseous mixture rate being 36 $(L/h)/g_{cat}$.

In order to determine whether Ni, comprising the initial catalyst, is the active phase of CFC, the samples were washed with nitric and hydrochloric acid ( Ni concentration decreased from 0.6 to 0.25 wt.%). The CFC activity was found to be independent on Ni concentration. The activity appeared to depend on the value of mesopore surface. Moreover, the surface of small pores (several nanometers in diameter) does not act in the direct oxidation of hydrogen sulfide.

As we have established the regime of CFC efficient regeneration, the process of hydrogen sulfide oxidation to sulfur can be performed even under conditions of sulfur condensation. After some hours operation as the catalyst, the CFC sample was tested under the "sulfur production - CFC regeneration" cycle regime. As found, the CFC catalyst properties do not change after several cycles.

Thus, we come to the conclusion that CFC is competitive in process efficiency with the best oxide metal catalysts and activated carbon.

Moreover, the cost of CFC production is almost an order of magnitude lower than that of the latter catalysts, since the technology does not use such expensive operations as activation and anchoring of the active component. The main advantage of CFC is that it can be produced from those hydrogen-sulfide containing gases that are purified from it. Thus, CFC can be produced from combustion gases of bitumen deposits and immediately used to purify these gases from hydrogen sulfide. This process scheme will permit one to reduce the cost of catalyst transportation.

The experimental data indicate that CFC is one of the most efficient and lower cost catalysts for the direct oxidation of hydrogen sulfide to sulfur in oxygen excess.

## References

1. Kuvshinov G.G., Mogilnykh Yu.I., Lebedev M.Yu., Kuvshinov D.G., Zavarukhin S.G., Positive Response to Application No 97103804 of 29.09.97.
2. Kuvshinov, G.G., Avdeeva, L.B., Goncharova, O.V. and Mogilnykh, Yu.I., *Extended Abstracts of International Meeting on Chemical Engineering and Biotechnology, Thermal Process Engineering, ACHEMA '94*, Frankfurt on Main, 1994, 9.6.
3. Avdeeva, L.B., Kuvshinov, G.G., Goncharova, O.V., Mogilnykh Yu.I. and Likholobov, V.A. *Proceedings of the 1st World Congress Environmental Catalysis*, Pisa (Italy), 1995, pp. 459 - 462 .
4. Chowdhury A.I., Tollerson E.L., *The Canadian Journal of Chemical Engineering*, 1990, 68, pp. 449-454

PP-D-11

# ADIABATIC AND TUBULAR REACTORS APPLIED TO THE PROCESS "ZEOFORMING"

**Y.V. Malozemov**, V.G. Stepanov, K.G. Ione

Construction Technology Institute "ZEOSIT", Siberian Branch of the Russian Academy of sciences. Russia, 630090, Novosibirsk, Pr. Ak. Lavrentieva 5. (Tel/fax: (007)-3832-355-763. E-mail: zeosit@batman.ict.nsc.ru)

Nowadays when the ethylized autobenzines are being refused the interest has grown for the processes permitting to obtain high-octane benzines at one stage and without any additive and compounding. One of such processes permitting to process the boiling out to 200–220°C carbohydrate raw material without any previous S- and hydro-refining is the process of Zeoforming based on the application of the new zeolite-containing catalyst [1-2]. This process makes it possible to obtain non-ethylized benzines with any octane numbers (ON) up to the Eurosuper-95 benzine (ON – 85 MON and 95 RON) and have passed the stage of industrial approbation at the experimental-industrial installation (5000 t/year) at the Nijnevartovsk GF and at the industrial installation (40 000 t/year) at the PF " Glimar" (Gorliche, Poland). The process of Zeoforming is actively developing at present both in the sphere of creation of the new types of catalysts and in the sphere of design of the new equipment with the capacity from 5 to 300 (thousand t/year).The last one requires optimization of the technological implementation of the process including the optimization of the reactors construction and of the apparature representation of the reactor unit on the whole.

This paper contains comparative analysis of the functioning of adiabatic and tubular reactors in the process of Zeoforming. At the example of model and industrial raw material conversion the modeling of the process is fulfilled with the calculation of the summary heat effect of the chemical process and of the reactor temperature profile on the catalyst layer for the industrial tubular and adiabatic reactors.

This work results in setting of the linear dependence between adiabatic heating of reaction and aromatic carbohydrates generation selectivity (Fig. 1), the lines being practically parallel. The reason of parallelity may possibly be that in all cases regardless of the raw material nature the arenas are generated by similar reactions ways. Temperature profile on the catalyst layer both in laboratory (Fig. 2) and industrial (Fig. 3) reactors has one and the same character. It is shown that the

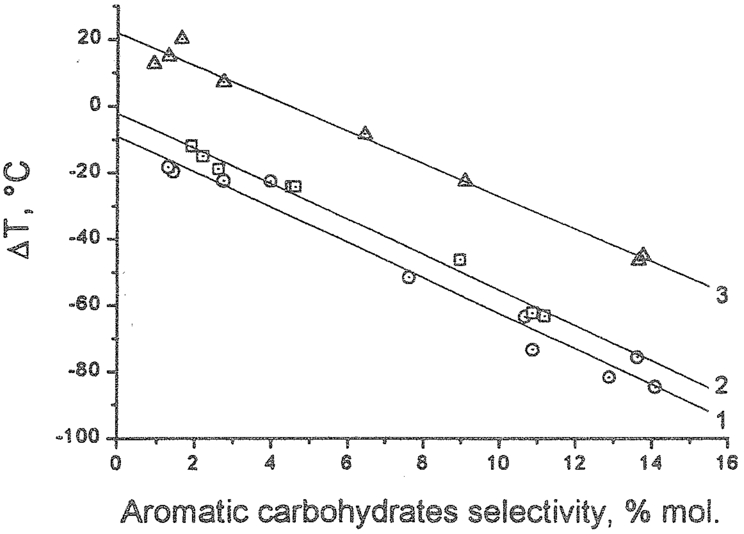


Fig. 1. ΔT of carbohydrate conversion reaction versus arenas selectivity for c-hexane (1), n-heptane (2), the mixture of n-heptane and c-hexene-1 (90+10%mass) (3) with T = 380°C; P = 10 atm.

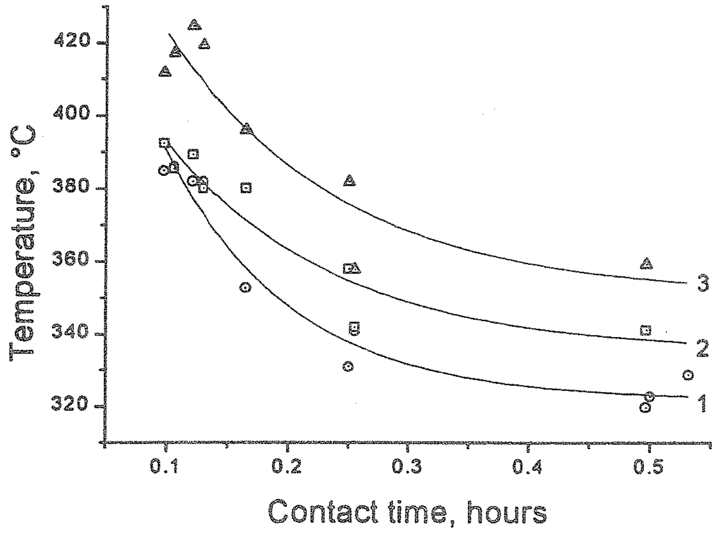


Fig.2. Temperature profile on the catalyst layer for the adiabatic reactor upon the data of isothermic laboratory reactor for c-hexane (1), n-heptane (2), the mixture of n-heptane and c-hexene-1 (90 + 10%mass) (3) with T = 3800C; P = 10 atm.

application of the basic reaction and the catalyst deactivation reaction formal kinetics makes it possible to optimize and calculate in detail the process on the catalyst layer. In the boundaries of the received knowledge of the process regularities a good correspondence of the laboratory and industrial data is shown.Recommendations on the optimal using of adiabatic and tubular reactors in the process of Zeoforming taking account of the catalyst regeneration stage are made.

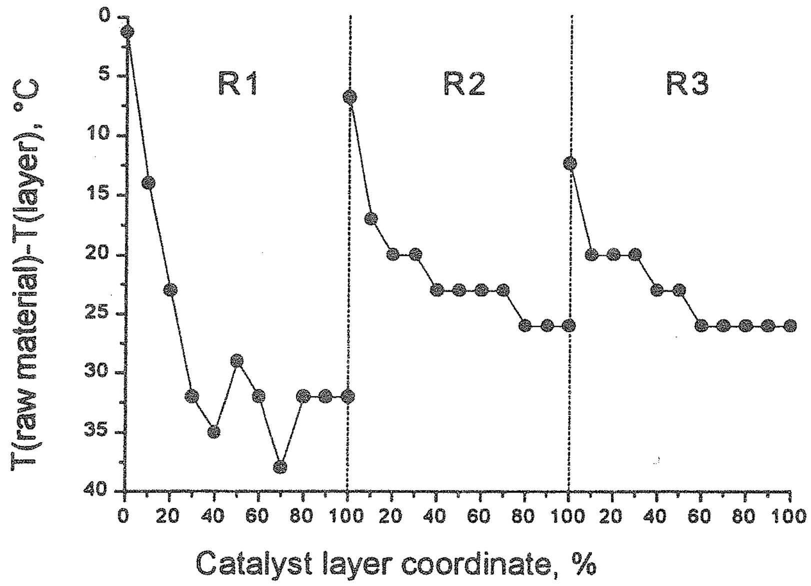


Fig.3 Temperature profile on the layer of 3 subsequent adiabatic industrial reactors

## Literature:

1. Stepanov V.G., Ione K.G. Chemical Technology 196, N3, p.59-70.
2. Stepanov V.G., Ione K.G., Snytnikova G.P. Catalyst in petroleum refining and petrochemical industries. Amsterdam: Elsevier Science. 1996. v. 100. p. 477-482.
3. Stepanov V.G., Ione K.G. The materials of the 3-rd International Conference on petroleum chemistry , December 2-5, 1997, Tomsk, Russia, v. 2, p. 123-126.

# THERMOCHEMICAL DESTRUCTION OF ASPHALT-TAR AND PARAFFIN-HYDRATE DEPOSITIONS

Nizov V.A., Anshits A.G.[*]

*Institute of Chemistry and Chemical Engineering, Siberian Branch of Russian Academy of Sciences, Krasnoyarsk, Russia*

*Section "Chemical Processes", Siberian Branch of Russian Engineering Academy, Krasnoyarsk, Russia*

Oils being produced in Russia contain high-molecular compounds which, as thermobaric conditions change, are deposited as asphalt-tar and paraffin-hydrate formations (ATPH) in a reservoir critical zone, at borehole walls and other oil-extracting equipment.

The novel process to remove ATPH depositions is based on interaction of alkaline metals with water. The peculiarities of alkaline metal behaviour in alkaline metal-water system allow to conclude that realization of such process with use of lithium and sodium is possible only at a balanced heat removal. The probability of uncontrolled explosive processes is very high using potassium, rubidium, cesium and low-melting mixtures of alkaline metals.

The pilot thermochemical cartridges (TCC) were made from tube skelps of size 500x32x1 mm (alloy AD31N) filled with an active mass of sodium. Two sorts of sodium were used including "Thecnical-grade metal sodium" (GOST 3273-75) and "Crude metal sodium" (TU 6-01-20-69-91).

The main advantage of the novel process is localization of heat action directly in a reaction zone without transport communications and intermediate working agents. It allows to avoid the considerable heat losses, rapid heads and energy of generated vibrations. The sub- and supercritical conditions are formed in a reaction zone where the solubility of hydrocarbons in aqueous mediums sharply increases.

The testing of the process in situ showed that method of thermochemical destruction of ATPH formations is more promising for oil deposits with the intensive deposition of wax for which the traditional methods of purification are low effective.

Upon field testing the main attention was paid to working through modes for unloading of wax slams, reglamentation of technological methods depending on the borehole condition and elucidation of the process drawbacks. The technology for thermochemical destruction of ATPH depositions was recommended for industrial implementation in "Tuimazaneft". The results of treatment of some boreholes in "Tuimazaneft" were presented in a table as an example.

Table

The results of industrial implementation of the process in "Tuimazaneft"

| Borehole № | Technological mode | | Output, $m^3$/day | | Increase $Q_{oil}$, ton/day | Date of treatment |
|---|---|---|---|---|---|---|
| | $Q_{oil}$, ton/day | $Q_{liquid}$, $m^3$/day | before treatment | after treatment | | |
| 2490 | 8 | 25 | 23 | 25 | 0,6 | 29.11.96 |
| 2330 | 4 | 110 | 98 | 111 | 0,5 | 18.02.97 |
| 1872 | 2,5 | 30 | 21 | 30 | 0,3 | 19.03.97 |
| 329 | 3,2 | 38 | 32 | 40 | 0,6 | 30.06.97 |
| 1228 | 10 | 71 | 64 | 60 | 0,6 | 05.08.97 |

The presented data show that one-time treatment of boreholes with TCC rehabilitates the technological mode of a borehole operation and causes the increase of a day output of oil by 10-30 %.

The practical experience of new process realization showed that the following actual tasks can be solved on its basis:

- destruction of ATPH depositions in boreholes where other methods are low effective;
- treatment of critical zones to renew their permeability at underground reparation of boreholes;
- treatment of boreholes for termination of water affluent in washed zones and inclusion into working of stagnant reservoir zones.

## PP-D-13

# MINI-REFINERIES OIL PROCESSING OPTIONS: AN EXAMPLE OF NOVOSIBIRSK REGION OIL-FIELDS

B.S. Krasnov, O.S. Krasnov*, N.M. Ostrovskii**

*IEiOPP SB RAS, Krasnoyarsk, Russia*
***SNIIGTiMS, Novosibirsk, Russia*
*** Boreskov Institute of Catalysis SB RAS, Omsk Department, Omsk, Russia*

In conditions of recession in a petroleum and oil refining industry the aspiration of the subjects of Federation to maintenance the own resources of raw materials and refinery products is natural. Thus, the role of mini-refineries grows which have both advantage and lacks. In the report, they will be considered on an example of analysis of Verkh-Tarskoe oil-field of Novosibirsk region. Novosibirsk region is rather large consumer of petroleum. A maximum level of consumption (3.6 million tons) is achieved in 1990. In the long term until 2000, the general demands consist of 3.8-4.0 million tons, including 63 % of light products, 32 % of fuel oil, and 2 % of oil bitumen.

Some variants of development of Novosibirsk region oil-fields have been analyzed. Optimum production is a level of 1.5 million tons per year. Three directions of its development are possible:

1. Submission the oil in a trans-siberian oil pipeline to Omsk or Achinsk refineries.
2. Construction the mini-refineries (MR) near to places of recovery.
3. Construction the small refinery (SR), ca. 1-3 million tons/years.

The combined decision consists in consecutive transition from 1-st to 3-d of variants. Thus, the means from sale of petroleum will be one of sources of investment for construction.

***Submission the Novosibirsk oil to Omsk or Achinsk refineries*** is easily sold problem, since the quality of oil is high, and there are free capacities in each refinery. Besides, the expenses of Novosibirsk oil transportation are lower, than of Tomsk oil. Moreover, the basic profit will thus be accumulated in refinery.

***Construction the mini-refineries (MR)*** has some advantages. It will allow supplying the area of oil production with the main oil products and will promote fast development of oil-field and territory. For MR the flexibility of the technology and a modular construction are characteristic. At last, MR is attractive to the investors owing to low cost and fast repaying.

## PP-D-13

With processing of Verkh-Tarskaya oil using MR with capacity of 100 thousand tons/year, the following production is possible:

| *Product* | *Issue, thousand tons/year* |
|---|---|
| Gasoline A-76 | 28-30 |
| Diesel fuel (summer) | 15-18 |
| Diesel fuel (winter) | 16-19 |
| Black oil 40 | 20-25 |
| Black oil 100 | 15-20 |

Thus, the expenses will make 65-70 million rubles/year, cost of products - about 700 rubles/ton, and annual profit - about 40 million rubles. The repaying period for MR (for example, "Omsk project") does not exceed 1 year.

Nevertheless, MR will not become alternative for the complex refinery and gas processing plant, and can replace them neither now nor in future. First, they do not provide the necessary assortment of products (lubricating oils, electrode coke, solvents), have the high cost and low depth of refining.

***Construction of the small refinery (SR)*** is reasonable only at total capacity close to 3 million tons/years. The production of fuels is the optimum variant for Verkh-Tarskaya oil refining. The production of bitumen oils from this petroleum is impossible, and production of lubricating oils, and coke on SR is unprofitable. In SR, the depth of refining can be low initially, with subsequent increasing of depth by processes of cracking, isomerization and alkylation. The high content of light fractions in crude oil will allow producing more than 30 % of gasoline (in absence of jet fuel production). It is possible the processing of middle distillates into jet and diesel fuels without hydrotreating processes. Such a variant may be considered as the first part of SR.

On tentative estimations the cost of SR construction (capacity up to 3 million tons/years) is approximately 0.7-1 billion $ (4-6 billion rubbles). With such capacity of SR, it is necessary to consider the variant of compound feed with oil from Tomsk region. A possible building site for SR should be the populated area with the usual infrastructure, building capacities, railway, etc. The most suitable candidates are Kuibyshev, Barabinsk and Novosibirsk.

For the final decision concerning the case of development of oil refining in Novosibirsk region, the special FEASIBILITY REPORT should be done. It should include the arguments for the capacity of refinery, its technological scheme and cost.

PP-D-14

# TESTING PROCEDURE AND DATA BASE OF HYDROTREATMENT CATALYSTS

**N.M. Ostrovskii, K.S. Gulyaev, O.N. Semyonova, V.K. Duplyakin**
Boreskov Institute of Catalysis SB RAS, Omsk Department, Omsk, Russia

Last 7-10 years in oil processing the tendency to decrease the contents of sulfurorganic compounds (RS) in motor fuels is kept. It is caused by acceptance in many countries of the acts limiting the content of sulfur in fuels at a level 0.05 and even 0.01 % wt. In Russia the standards on ecologically clean fuel (TU 38.1011348-90) are also accepted.

To solve this problem many companies develop new catalysts and processes of deep hydrodesulfurization (HDS), and also improve the methods of catalysts testing. The HDS process peculiarity is, that the testing procedure requires 5-7 days. The nowadays technique of tests (OST 38 01130-77) in Russia does not allow to estimate catalysts of deep hydrodesulfurization.

At development of a technique submitted in the given report, the authors take into consideration the following basic rules determining suitability of the catalyst for deep hydrodesulfurization:

1. The most difficult to destroy (in reaction of hydrogenolysis) sulfurorganics are dibenzthiophenes with alkyl substitutes, concentrated in a fraction of feed which is boiling within temperature range 315-360 $^0$C.
2. The modern catalyst should provide deep hydrodesulfurization at temperature above 370 $^0$C, at pressure lower 40 atm, and space velocity of feed - not lower than 2 $h^{-1}$ and with the contents of sulfur in feed (diesel fuel) not less than 1 %.
3. The procedure of preparation of catalysts (presulfiding) should be such that did not worsen property of potentially active catalysts.
4. The realization of standard procedure (OST 38 01130-77) does not provide reliable discrimination of catalysts on activity when the conversion is high (in hydrodesulfurization conversion of RS not less than 90 %).

The development of a technique includes a substantiation such as standard feed, procedure of tests, conditions of reaction and sequence of their changes, choice the criteria of efficiency of catalysts, and also procedure for catalyst presulfiding.

As standard feed for tests was chosen the diesel fraction boiling within temperature range 240-350 $^0$C, with sulfur content of 1.0-1.2 %.

# PP-D-14

The testing procedure includes drying and presulfiding of the catalyst, the catalyst pretreatment at P = 40 atm, T = 350 °C and LHSV = 4 $h^{-1}$, and following test of activity on one of the programs (short or complete) with regulation of $H_2S$ concentration in recycling hydrogen - contained gas (HCG).

The tests should be carried out in flowing isothermal reactor with obligatory circulation HCG. With each combination of T and LHSV, the liquid products are collected within 4-th hours. The part of a product is divided on a fractions boiling before and after 315 °C. The analysis of the residual contents of sulfur should be carried out both in all product samples, and in its fractions.

The optimum way of presulfiding is the submission on the catalyst of the hydrodesulfurized feed with addition of easy destroyable sulfurorganic compounds.

Following criteria of catalyst efficiency are accepted:

1. Minimal temperature ($T_{MIN}$) providing the residual content of sulfur in a product less than 0.05 % wt. at LHSV = 4 $h^{-1}$.
2. Maximal space velocity of feed ($LHSV_{MAX}$) ensuring with T = 350 °C the given degree of desulfurization - no more than 0.05 % wt. sulfur.
3. The stock of catalyst bed temperature ($\Delta T_{MAX} = 370 - T_{MIN}$), which being the characteristic of its potential stability.
4. Conversion of sulfurorganics in a fraction is boiling at temperature higher then 315 °C.
5. Decrease of sulfurorganics conversion by the end of tests with return to initial conditions T = 350 °C and LHSV = 4 $h^{-1}$.

The technique is tested using a number of foreign and domestic catalysts and has demonstrated "high sensitivity" to their quality. The conditional level of lag for industrial domestic catalysts from best foreign catalysts is estimated at 15-20 °C. The best domestic catalyst GO-70 with a special procedure of presulfiding is approach to better foreign samples.

In Omsk department of Boreskov Institute of Catalysis the necessary experience is saved and there is an experimental base (installations OL-105 and OL-120) for realization of comparative tests of catalysts of deep hydrodesulfurization. Their results can be a basis for acceptance of the decision about operation of the catalyst.

**PP-D-15**

# TECHNOLOGY OF "ACID" GASES CONVERSION FOR PETROCHEMISTRY

Z. Pai, A. Yermakova, O. Akmalova

*Boreskov Institute of Catalysis, Novosibirsk, 630090, Russia*

Liquid-phase purification methods accompanied by sulfur recovery appear to be feasible for processing low concentrated sulfurous exhaust gases or small volumes (400-6000 $m^3/h$) of concentrated ($\geq 20$ vol.%) hydrogen sulfide.

Thus, performance of the Claus process [1].

$$2\,H_2S + SO_2 \rightarrow 3\,S + 2\,H_2O$$

in the liquid phase seems to be rather promising.

Though the stoichiometry of $H_2S$ interaction with $SO_2$ is the same for both aqueous and gas Claus reactions, the chemistry of the process differs considerabby in these media, since different intermediates are responsible for sulfur generation during the reduction processes.

A series of studies concerning the mechanism and kinetics of the Claus process in aqueous medium was carried out in Boreskov Institute of Catalysis during recent years. As a result, a new catalytic SLP-method (Simultaneous liquid purification) was developed [2].

The aqueous solution of ammonia salts of orthophosphorous acid possessing buffer properties serves as a sorbent in SLP. The solution also contains ammonia thiosulfate and a homogeneous catalyst.

The developed compositions of contact solutions and optimal conditions of SLP passed pilot and large scale tests (loading with respect to $H_2S$ was 250 $m^3/h$ of 23% vol. gas ).

At present a set of technology for the processing of sulfurous gases with respect to their composition is suggested for commercial implementation. The main desing of the process equipment has been accomplished. A general scheme is suggested for the processing of gas containing more than 20 vol.% of hydrogen sulfide and admixtures of $CO_2$ and $H_2O$.

Thus, the considered SLP technology providing a high sulfur removal from the unit of reaction volume appears to be competitive with the gas-phase Claus process and possesses a series of advantages. In particular, it allows us:

- - to maintain the accuracy of the $H_2S$: $O_2$ ratio control at the thermal Claus stage and essentially simplify the technological scheme of the process and its performance;
- - to attain a high efficiency in the process producing a gas with $H_2S$ content below 5÷10 ppm;
- - to improve the process reliability in comparison to the gas-phase Claus process.

## REFERENCES

1. A new regenerable FGD process// Sulfur.-1993. -v. 228, Sep-Oct. P. 47-48.
2. Z.P. Pai, A. Yermakova, N.N. Kundo and V.A. Kirillov. Sulfur Production in the Processes of Purification and Conversion of Hydrocarbon Raw Materials. // Chemistry for Sustainable Develop. 2(1), (1994) P. 219-223.

PP-D-16

# PHYSICO-CHEMICAL FOUNDATIONS OF OIL PREPARATION PROCESSES

N.A. Svarovskaya
*Tomsk Polytechnical University, Russia*

The wells product is a three-phases system consisting of gas, liquid and solid (mechanical admixtures) components. The knowledge about inner structure of components, search for functional interconnections of properties between them is a necessary investigation stage of predicting raw oil preparation processes.

"Oil – gas – water" – is not an ideal multi-component system. It can be characterized by a representative set of macroscopic and technological parameters, which present average characteristics of the structure and construction. On the other hand, the compounds contained reflect physico-chemical laws of formation conditions and genesis of oil systems.

The analogy of reaction ability of various compounds must be first of all the base of systematization of oil, hydrocarbon compound and properties observed. The indicators of reaction ability may be values, which characterize stability or activity of substances, molecule-structure peculiarities of composition and also the processes, occurring in oil system itself, such as formation of complex substances, supermolecular structures and others.

The investigations previously carried out and aimed at oil systematization including hydrocarbon composition of Western Siberia deposits [1], and at searching of functional interconnections between their properties [2], enabled us to specify the most informative indicators, responsible for processes occurring in oils (including raw oils) and characterizing them.

Thus, it is the density distribution function well correlated to electron characteristics of molecular structure that attracts the most attention. The value of total doublet moment of molecules, which numerically reflects the polarity of the system is chosen as a factor evaluating intensity of intermolecular interactions, affecting durability of oil emulsion. The value of polarity enables us to predict the technology of oil preparation units.

The analysis of the set of parameters (gas-content, output of light fractions) together with density evidences stable or unstable condition of our system and may serve as basement of stabilization processes development.

Therefore the following set of indicators is necessary for preliminary estimation of the processes: the density of oils; the content of sulfur, solid paraffins, pitches and asphaltens; output of fraction prior to 300 °C; volume of gas, water, type of water and mineralization.

## *Bibliography*

1. Kravtsov A.V., Svarovskaya N.A., Marsanova I.V. Physico–chemical questions of oil systems hydrocarbon systematization. – Tomsk: Preprint TPU, 1997 – 56 p.
2. Kravtsov A.V., Svarovskaya N.A. and others. Functional interconnection between properties of oils and oil products of Western Siberia deposits. – Tomsk: Preprintr TF SFAS USSR, 1988. – 36p.

**PP-D-17**

# THE REACTORS BLOCK SIMULATION SYSTEM OF TECHNOLOGICAL LINE FOR HIGH TEMPERATURE PYROLYSIS

N. Svarovskaya, I. Zelenko

*Tomsk Polytechnic University, Tomsk, Russia*

In the industry the homogeneous process of the high temperature pyrolysis is realized in tubular furnaces.

The basic technological problem for pyrolysis furnaces is universality in relation to raw materials, which may vary from gases (ethane and others) up to the liquid.

The problems of reactors reprofiling and redesigning appearing thereby are solved with the use of contemporary intelligent computer system of the process in question.

The Info-Simulation System (ISS) of pyrolysis technology basic unit (block of furnaces) has been developed at the faculty of fuel chemical technology at Tomsk Polytechnic University. This system will be gradually improved up to intelligent expert system of the whole technological line.

ISS includes several blocks, each of which represents a package of software and data files:

◆ the block of mathematical models consists of: kinetic models library of pyrolysis of gas-like (ethane-propane fractions, $C_4$ – fraction, LFLH) and liquid raw materials (petroleum fractions, and rafinates), models of pyrolysis furnaces such as SRT-1, SRT-2 (SRT-3,4);

◆ physico-chemical data bank;

◆ graphics block contains: the schemes of reactors (SRT-1, SRT-2 furnaces) and the whole technological line;

◆ the «SOSTAW» block for assembly of initial raw material composition made of 2 and more hydrocarbon fractions;

◆ the «MS» block which forms pyrolysis furnaces unit simulation system;

◆ results-displaying block.

The «MS» block is basic. The variables are set in it (the quantity of furnaces in the block, using liquid or gas-like raw materials; structure of raw materials, loads, design parameters of coil pipes for each furnace) and that is where the calculations are carried out as well.

Because of the difference in the design of coil pipes the calculations are carried out zone by zone. For each zone its own diameter, longitude and quantity of pipes are given.

The functional abilities of ISS are defined by how much its mathematical models are sensitive to the change in chemical structure of raw materials. The models are based on physico-chemical laws of processing phenomena and include component-by-component structure of raw materials and products.

The questions of designing determined kinetic models and pyrolysis process reactors are in detail described in works [1,2,3].

With the help of the represented ISS of reactors block the following production problems may be solved:

1. Estimating the suitability of hydrocarbon raw materials offered for pyrolysis;
2. Selecting technological mode and capacity;
3. Giving out recommendations on using minor and waste products as a mixture or as basic raw material;
4. With the purpose of reprofiling to another kind of raw materials to carry out the calculations of pyrolysis furnaces in action;
5. During reconstruction of furnaces (replacement one kind of coil pipe to another) to calculate the necessary characteristics for their operation and processing.

### Bibliography

1. Physico-chemical problems of developing determined models for hydrocarbon raw materials pyrolysis. /Kravtsov A.V., Svarovskaya N.A., Zelenko I.U.; TPU, Tomsk, 1997.—32p., ill. – Bibliography: 42 names. – Russ. – Dep. in VINITI. -- № 1059 – B97.
2. The computering reference book. Physico-chemical processes in gas and plasma. 2 parts. – M.: Publishing office of MSU, 1992, part 1: The dynamic of physico-chemical processes in gas and plasma.
3. Kravtsov A.V., Svarovskaya N.A., Trizna A.G., Zelenko I.U. Physico-chemical basis of nonisothermal reactors simulation using petroleum pyrolysis example. Chem. Industry, 1995, №2, p. 36-38.

**PP-D-18**

# TOPOCHEMICAL CONTROL OF THE ACTIVE LIQUIDS FILTRATION UNDER THE WATER-FLOODED OIL RESERVOIR CONDITIONS

Telin A.G., Dolomatov M.U., Safuanova R.M., Zainetdinov T.I.

VNIITS "Neftegastechnologia", Ufa, Russia

It is known that the filtration of chemically active liquids under the water-flooded oil reservoir goes according to the classic topochemical relationships like Avraami - Yerofeyev equation. The multiple experiments provided by the authors and the results of other researchers showed that when the active liquid is filtered the permeability is not only the geometrical characteristic of the porous media but depends on the properties of the liquid. The relationship was found that describes the kinetics of filtration process independently from the nature of the physical and chemical interactions.

The change in permeability and active component concentration goes under the equations (1-2) as follows:

$$K = K_0[\exp(-kt^n)], \qquad (1)$$

$$\alpha = 1 - \exp k't^{n'}, \qquad (2)$$

where $K$ и $K_0$ are the current and the initial permeability;

$t$ is time;

$\alpha$ is the conversion of active component;

$k$, $k'$, $n$, $n'$ are kinetic constants.

We suppose that physical meaning of shown phenomena is in formation of a surface with a new nature and properties between the solid phase and the liquid, that is the subject of topochemistry.

Such processes are usual in oil recovery. The injection of water containing the traces of oil, reagents and particles of the solid phase leads to the change in the oil, water and porous media properties. The reservoir treatment with aggressive substances like acids and alkalines, injection of polymers, surfactants, hydrocarbon solvents and gel systems for oil recovery enhancement is supposed to change the properties of oil, water and rock.

As we think the development of this scientific direction will permit to study in detail the mechanism of processes taking place in porous media during the active liquids filtration and find out the meaning of kinetic parameters recovered from the experiments.

The practical use of the kinetic constants already gives the opportunity to choose the appropriate compositions for the well treatment in carbonate collectors, calculate the optimal volumes and injection rate of biocide to clean the reservoir from biological pollution.

**PP-D-19**

# REGULATION OF THE RATE OF REACTION OF HYDROCHLORIC ACID WITH WATER- AND OIL-SATURATED CARBONATE ROCK

A.G. Telin, I.P. Kraikina, T.I. Zainetdinov, A.E. Lepilin

*VNIITS "Neftegastechnologia", Russia*

Nowadays the acid processings are the basic geologic-physical measures which provide the increase in rate of oil production from carbonate collectors. The special additives - reducers of the acid and the carbonated rock reaction rate are applied to extend the acid processings efficiency, which ensures deeper penetration of an acid into a layer. At the same time the industrial data analysis shows that the successfulness of acid influence on the "old" areas does not exceed 30%. The main reason of acid processings low efficiency is that while filtered through the treated well zone of a layer acid penetrates mainly into the intervals with a high water saturation. Thus the rate of a hydrochloric acid reaction with water-saturated carbonate rock exceeds one with oil-saturated rock because of diffusion difficulties.

Presented work offers the methods of regulating the rate of reaction of hydrochloric acid with water- and oil- carbonated porous media by inserting additives - mono- and poly-nuclear alcohols, organic solvents and surfactants. The results of researches established that macrokinetics of reaction of a hydrochloric acid with rock is well described by the Avrami-Erofeev equation:

$$v_t = v_o(1 - e^{-kt^n}) \qquad (1)$$

which depicts the kinetics of topochemical process. In equation (1) n is the measure of the media anisotropy. The results of some experiments are given on fig.1 and in table 1.

The occurrence of an induction period in oil-saturated porous media is explained by low speed diffusion of an acid through a film of oil. The estimation of diffusion influence on the reaction rate is carried out using the factor of inner-diffusional braking, which in our case is equal to the ratio of a maximum rate of reaction between the pure hydrochloric acid and the water-saturated rock to a maximum speeds of the other processes. The influence of the various reagents adding to an acid was the same way estimated.

The application of the surfactants, solvents and alcohols additives allows to align the rate of reaction of an acid with carbonate rock in water- and oil- saturated intervals, that in practice results in substantial growth of acid processings efficiency.

# PP-D-19

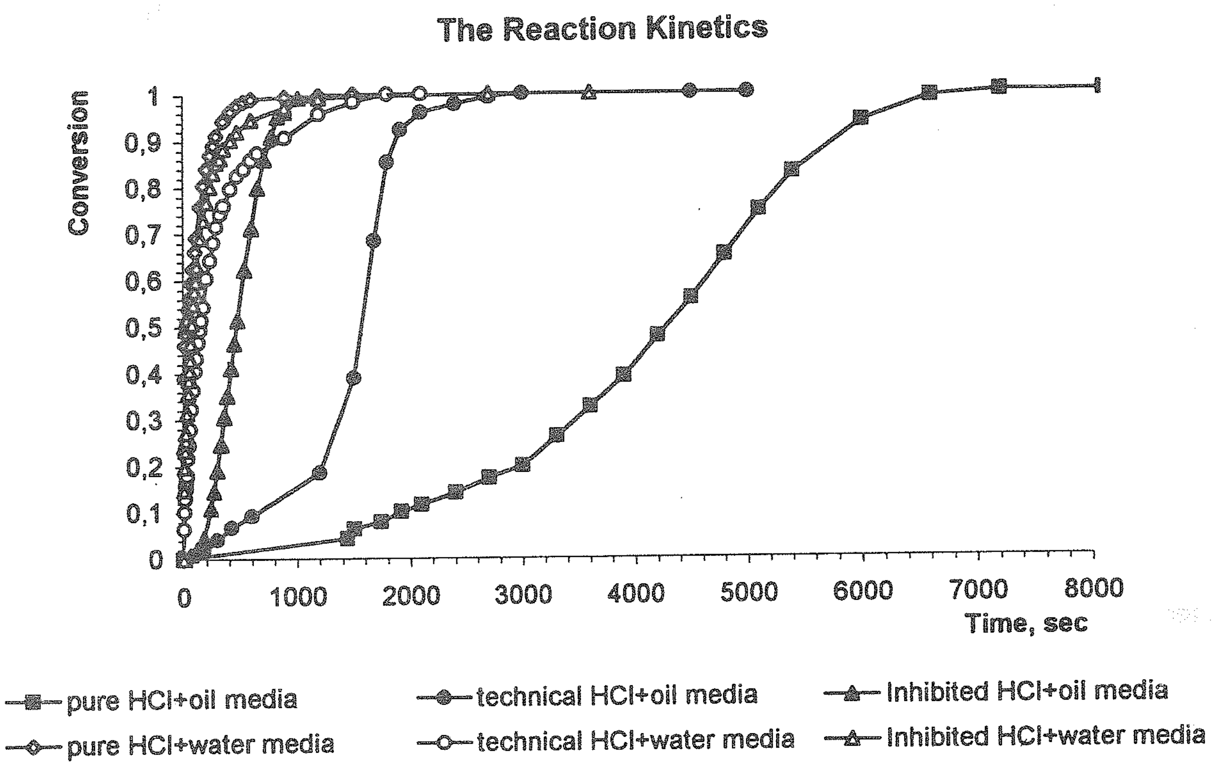


Fig. 1.

Table 1.

**Kinetic parameters and diffusional braking factors of reaction between the acid compositions and carbonate rock**

| System | k | n | $f_D$ |
|---|---|---|---|
| pure HCl (water-saturated media) | -0.9514 | 0.5001 | 1.00 |
| pure HCl (oil-saturated media) | -0.0002152 | 1.9248 | 79.99 |
| technical HCl (water-saturated media) | -0.3387 | 0.781 | 3.72 |
| technical HCl (oil-saturated media) | -0.0002645 | 2.50 | 14.61 |
| inhibited HCl (water-saturated media) | -0.5961 | 0.701 | 1.75 |
| inhibited HCl (oil-saturated media) | -0.003832 | 2.5186 | 8.73 |
| technical HCl + butanol (water-saturated media) | -0.2599 | 0.6684 | 5.77 |
| technical HCl +butanol (oil-saturated media) | -0.1287 | 1.027 | 7.32 |
| inhibited HCl + butanol (water-saturated media) | -0.3311 | 0.6118 | 5.14 |
| inhibited HCl + butanol (oil-saturated media) | -0.05518 | 1.122 | 15.34 |
| technical HCl +polyglycerin (water-saturated media) | -0.6341 | 0.3558 | 0.91 |
| technical HCl + polyglycerin (oil-saturated media) | -0.000222 | 2.2935 | 22.83 |
| inhibited HCl + polyglycerin (water-saturated media) | -0.3676 | 0.3427 | 3.55 |

# CONTENT

PLENARY LECTURES

ORAL PRESENTATIONS

## POSTER SESSION

# LIST OF PARTICIPANTS

**Андреев Всеволод Владимирович**
Чувашский Госуниверситет
Московский пр., 15
Чебоксары 428015
Россия
e-mail: main@chgu.chuvashia.su

**Аншиц Александр Георгиевич**
Институт химии и хим. технологии СО РАН
г. Красноярск
Россия
тел.: 3912 439431
факс: 3912 275384

**Ахметов Арслан Фаритович**
Уфимский государственный нефтяной
технический университет
ул. Космонавтов, 1
Уфа 450062
Россия
тел.: 3472 431535
факс: 3472 431535

**Ахундов А.А.**
Институт теоретических проблем
химической технологии АН Азербайджана
370000 Баку
Азербайджан
e-mail: ITPCHT@lan.ab.az

**Бальжинимаев Баир Сыдыпович**
Институт катализа им. Г.К. Борескова
Пр. акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 3832-34-47-70
факс: 3832-34-37-66
E-mail: iccct@catalysis.nsk.su;
balzh@catalysis.nsk.su

**Барелко Виктор Владимирвич**
Институт физической химии Черноголовки
Черноголовка, Моск. обл.
Ногинский р-он
Россия
E-mail: viktor@barelko.chg.ru

**Белоусова Ольга Юрьевна**
Уфимский государственный нефтяной
технический университет
ул. Космонавтов, 1
450062 г. Уфа
Россия

**Бесков Владимир Сергеевич**
Российский химико-технологический
университет им. Д.И.Менделеева
Миусская пл. 9
Москва 125047Россия
тел.: (095) 978-91-45
факс: (095) 200-42-04
e-mail: bes@mhti.msc.su

**Бибин Владимир Николаевич**
Институт катализа им. Г.К.Борескова
пр. Акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 3832 341278
факс: 3832 341878
e-mail: root@reverse.nsk.su

**Боброва Людмила Николаевна**
Институт катализа им. Г.К.Борескова
пр. Акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 3832 341278
факс: 3832 341878
e-mail: bobr@reverse.nsk.su

**Боронин Андрей Иванович**
Институт катализа им. Г.К.Борескова
пр. Акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 3832 344789
e-mail: boron@catalysis.nsk.su

**Быков Валерий Иванович**
Красноярский Государственный Технический
Университет
Красноярск 660036
Россия
тел.: 3912 494724
факс: 3912 439830
e-mail: bykov@cc.krascience.rssi.ru

**Вайман Александр Маркович**
Институт нефтехимии и катализа
Уфа 450096
Россия
тел.: 3472 313521
факс: 3472 236680
e-mail: root@vayman.ufanet.ru

**Верниковская Надежда Викторовна**
Институт катализа им. Г.К.Борескова
пр. Акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 3832 341278
факс: 3832 341878
e-mail: nady@reverse.nsk.su

**Водянкина Ольга Владимировна**
Томский Госуниверситет
пр. Ленина, 36
Томск 634050
тел.: 3822 424257
факс: 3822 415579
e-mail: galanov@xf.tsu.tomsk.su

**Воронцов Александр Валерьевич**
Институт катализа им. Г.К.Борескова
пр. Акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 3832 344573
e-mail: voronts@catalysis.nsk.su

**Герасев Александр Петрович**
Институт катализа им. Г.К.Борескова
пр. Акад. Лаврентьева, 5
Новосибирск 630090
Россия
факс: 3832 341878
e-mail: gerasev@reverse.nsk.su

**Гогин Леонид Львович**
Институт катализа им. Г.К.Борескова
пр. Акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 3832 341278
факс: 3832 341878
e-mail: gogin@reverse.nsk.su

**Горбачевский Андрей Ярославович**
МГУ
Воробьевы горы
Москва 119899
тел. 095 939 32 07
факс:095 932 88 46
E-mail: GORBA@RADIO.chem.msu.ru

**Гуляев Константин Станиславович**
Омский филиал Института
катализа СО РАН
ул. Нефтезаводская, 54
Омск 644040
Россия
тел.: 381-2- 66-44-74
факс: 381-2-64-61-56

**Добрынкин Николай Михайлович**
Институт катализа им. Г.К.Борескова
пр. Акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 3832 341751
факс: 3832 341878
e-mail: dobr@reverse.nsk.su

**Доломатов Михаил Юрьевич**
ВНИИЦ «Нефтегазтехнология»
Ул. Ленина 102-41
Уфа 450006
Россия
тел.: 3472 524922
E-mail: DMU@mts.bashkiria.su

**Дуплякин Валерий Кузьмич**
Омский филиал Института
катализа СО РАН
ул. Нефтезаводская, 54
Омск 644040 Россия
тел.: 381 2 66-44-50
факс: 381 2 64-61-56

**Елохин Владимир Иванович**
Институт катализа им. Г.К. Борескова
Пр. акад. Лаврентьева, 5
Новосибирск 630090
Россия
e-mail: elokhin@catalysis.nsk.su

**Ефимова Елена Витальевна**
Институт катализа им. Г.К. Борескова
Пр. акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 3832-39-73-00
факс: 3832 34-37-66

**Жукова Ольга Петровна**
Институт Угля и Углехимии СО РАН
ул. Рукавишникова, 21
Кемерово 650610
Россия
тел.: 3842 365561

**Заварухин Сергей Григорьевич**
Институт катализа им. Г.К.Борескова
пр. Акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 3832 397310

**Зайнетдинов Тимур Имберович**
ВНИИЦ «Нефтегазтехнология»
а/я 24
Уфа 450006
Россия
тел.: 3472 520623

**Замулина Татьяна Владимировна**
Институт катализа им. Г.К. Борескова
Пр. акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.:3832-34-12-97
факс: 3832-34-30-56
E-mail: zam@catalysis.nsk.su

**Зеленко Ирина Юрьевна**
Томский политехнический университет
Томск, Россия
тел.: 415443
e-mail: mart@tpu.ru

**Золотарский Илья Александрович**
Институт катализа им. Г.К. Борескова
Пр. акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.:3832-34-44-91
E-mail: zol@catalysis.nsk.su
факс: 383-2-34-18-78

**Иванов Евгений Алексеевич**
Институт катализа им. Г.К.Борескова
пр. Акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.:3832 397308
e-mail: eugene@sirius.catalysis.nsk.su

**Иванчина Эмилия Дмитриевна**
Томский политехнический университет
Томск, Россия
тел.: 415443
факс: 223995
e-mail: tpu@tpu.edu.ru

**Каренгин Александр Григорьевич**
Томский политехнический университет
Томск 634061
Россия
тел.: 3822 419143
факс: 3822 419143
e-mail: orlov23@phtd.tpu.edu.ru

**Кашкин Виталий Николаевич**
Институт катализа им. Г.К. Борескова
Пр. акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 383-2-34-44-91

**Керженцев Михаил Анатольевич**
Институт катализа им. Г.К. Борескова
Пр. акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел. 383-2-34-21-54
факс: 383-2-39-73-52
E-mail:ma_k@catalysis.nsk.su

**Кожевников Игорь Викторович**
Чувашский Госуниверситет
Московский пр., 15
Чебоксары 428015
Россия
тел.: 8350 423432
факс: 8350 428090
e-mail: main@chgu.chuvashia.su

**Кондратьев Николай Александрович**
Восточная Нефтяная Компания
Наб. реки. Умайки, 24
Томск
Россия
тел.: 3822-22-14-73

**Корниенко Андрей**
Восточная Нефтяная Компания
Наб. реки. Умайки, 24
Томск
Россия
тел.: 382-2-221-442

**Кравцов Анатолий Васильевич**
Томский политехнический университет
Томск, Россия
тел.: 415443
факс: 223995
e-mail: tpu@tpu.edu.ru

**Крайкина Ирина Петровна**
ВНИИЦ «Нефтегазтехнология»
Уфа, Россия
тел.: 3472 520623

**Краснов О.С.**
СНИИГГиМС
Новосибирск
Россия

**Курзина Ирина Алексеевна**
Томский Госуниверситет
пр. Ленина, 36
Томск 634050,
Россия
тел.: 424257
факс: 415579

**Куркина Елена Сергеевна**
МГУ им. М.В.Ломоносова
Воробьевы Горы
Москва 119899
Россия
тел.: 095 9394079
факс: 095 9392596
e-mail: kurkina@cs.msu.su

**Ламберов Александр Адольфович**
Казанский государственный
технологический университет
ул. К.Маркса, 68
Казань 420015
Россия
тел.: 8432 365892
факс: 8432 365892
e-mail: kataliz@cnit.ksu.rus.ru

**Левашова Альбина Ивановна**
Томский политехнический университет
Томск, Россия
тел.: 3822 415443
факс: 3822 223995
e-mail: tpu@tpu.edu.ru

**Лепилин Андрей Евгеньевич**
ВНИИЦ «Нефтегазтехнология»
Уфа, Россия
тел.: 3472 520623
e-mail: lepiandr@ufanet.ru

**Малоземов Юрий Витальевич**
КТИ «Цеосит» СО РАН
Новосибирск 630090
Россия
тел.: 3832 355763
e-mail: yura@batman.ict.nsk.ru

**Мезенцев Александр Николаевич**
Восточная Нефтяная Компания
Наб. реки. Ушайки, 24
Томск, Россия
тел.: 382-2-22-40-16

**Могильных Юрий Иванович**
Институт катализа им. Г.К.Борескова
пр. Акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 3832 397310
e-mail: ggk@catalysis.nsk.su

**Москвин Владимир Сергеевич**
Томский Политехнический Университет
пр. Ленина, 30
Томск 634004, Россия
тел.: 3822 412232
факс: 3822 412723
E-mail: root@oms.cp.tomsk.su

**Мустафина Светлана**
Государственный колледж образования
ул. Коммунистов, 85 - 126
Стерлитамак 453125
Россия
тел.: 3473 240725

**Нагирняк Алексей Тарасович**
КАООТ «Азот»
Кемерово 650099
Россия

**Назаренко Ольга Брониславовна**
НИИ высоких напряжений
пр. Ленина, 2а
Томск 634050, Россия
тел. 3822 41-91-55, 3822 41-91-01
e-mail: admin@admin.hvri.tpu.edu.ru

**Низов Василий Александрович**
Секция «Химические технологии» СО РИА
Красноярск 660025
Россия
тел.: 3912 439431

**Новиков Александр Автономович**
Томский политехнический университет
Томск, Россия
тел.: 3822 415443
факс: 3822 223995
e-mail: tpu@tpu.edu.ru

**Носков Александр Степанович**
Институт катализа им. Г.К. Борескова
Пр. акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 3832-34-18-78
факс: 3832-34-18-78
E-mail: Noskov@catalysis.nsk.su;
alex@reverse.nsk.su

**Овсиенко Петр Викторович**
НИИ химических технологий
ул. Дзержинского 1
Северодонецк 349940
Луганская область
Украина
тел.: 06452 29373
факс: 06452 25367
e-mail: root@himn.etalon.lugansk.ua

**Орлик Владимир Николаевич**
Институт газа НАН Украины
Киев, Украина
тел.: 044 4460324
e-mail: orlyk@gas.freenet.kiev.ua

**Орлов Алексей Алексеевич**
Томский политехнический университет
Томск, Россия
тел.: 3822 419143
e-mail: ott@phtd.tpu.edu.ru

**Оружейников Александр Иванович**
Омский филиал Института
катализа СО РАН
ул. Нефтезаводская, 54
Омск 644040
Россия

**Осадчий Олег Георгиевич**
Ачинский Нефтеперерабатывающий завод
Ачинск
Красноярский край
Россия

**Островский Николай Михайлович**
Омский филиал Института
катализа СО РАН
ул. Нефтезаводская, 54
Омск 644040
Россия
тел.: 3812 664474
E-mail: ostr@omsk.net.ru

**Островский Юрий Владимирович**
НГПИИ ВНИПИЭТ
ул. Б.Хмельницкого, 2
630075 г. Новосибирск
Россия
тел.: 3832 769635
e-mail: ost@pri.sib.ru

**Пай Зинаида Петровна**
Институт катализа им. Г.К.Борескова
пр. Акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 3832 341746

**Пармон Валентин Николаевич**
Институт катализа им. Г.К. Борескова
Пр. акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 383 2 34-32-69
факс: 383 2 34-32-69
e-mail: parmon@catalysis.nsk.su

**Пацков Вадим Петрович**
НТУЦЭТ НАН и Минэнерго Украины
252115, г. Киев-115
Украина
тел.: 044 4166915
факс: 044 4162510
e-mail: root@dhtec.kiev.ua

**Писаренко Елена Витальевна**
Российский химико-технологический
университет им. Д.И.Менделеева
Миусская пл. 9
Москва 125047
Россия
тел. 095 978-91-78
факс:095 200-42-04
E-mail: pvn@MHTJ.msk.su

**Покровская Светлана Афанасьевна**
Институт катализа им. Г.К.Борескова
пр. Акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 3832 341278
факс: 3832 341878
e-mail: svetlana@reverse.nsk.su

**Принь Елена Маратовна**
Научно-исслед. институт ХИМТЕХНОЛОГИЯ
Северодонецк
Украина
тел.: 0 645 29-38-29
E-mail: prin@ixt.sed.lg.ua

**Пряхин Алексей Николаевич**
МГУ им. М.В.Ломоносова
Воробьевы Горы
Москва 119899
Россия
тел.: 095 9394524
факс: 095 9394575
e-mail: knn@cge.chem.msu.su

**Расулов Вугар Аббас оглы**
ИТПХТ АН Азербайджана
пр. Г.Джавида, 29
Баку 370143
Азербайджан
тел.: 8922 94159
e-mail: itpcht@lan.ab.az

**Решетов Петр Николаевич**
Восточная Нефтяная Компания
Наб. реки. Умайки, 24
Томск, Россия
тел.: 382-2-22-40-18

**Решетников Виктор Николаевич**
Восточная Нефтяная Компания
Наб. реки. Умайки, 24
Томск
Россия
тел.: 382-2 221-442

**Решетников Сергей Иванович**
Институт катализа им. Г.К.Борескова
пр. Акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 3832 397310
E-mail:resh@catalysis.nsk.su

**Романов Юрий Владимирович**
Институт Угля и Углехимии СО РАН
ул. Рукавишникова, 21
Кемерово 650610
Россия
тел.: 3842 365561

**Савенков Анатолий Сергеевич**
Госуд. политехнический университет
Харьков, Украина
тел.: 0572 400-258
e-mail: root@polyt.kharkov. ua

**Садовская Екатерина Михайловна**
Институт катализа им. Г.К.Борескова
пр. Акад. Лаврентьева, 5
Новосибирск 630090
Россия

**Сазонов Владимир Андреевич**
Институт катализа им. Г.К. Борескова
Пр. акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.:383-2-34-17-71
факс: 383-2-39-73-52
e-mail: sazonov@catalysis.nsk.su

**Салимоненко Дмитрий Александрович**
Уфимский государственный
авиационный технический университет
ул. Мингажева 19/а
Уфа 450000
Россия
тел.: 3472 235244
факс: 3472 236680
e-mail: root@vayman.ufanet.ru

**Сафуанова Резеда Мавлетьяновна**
ИОХ УНЦ РАН
Достоевского 102/2-2
Уфа 450077
Россия

**Сваровская Наталья Алексеевна**
Томский политехнический университет
Томск, Россия
тел.: 3822 415785
факс: 3822 279080

**Семендяева Наталья Леонидовна**
МГУ
Воробьевы горы
Москва
Россия
E-mail: slinko@cs.msu.su

**Софронов В.Л.**
Северский технологический
Институт Томского политехнического
университета
Северск
Россия

**Спивак Семен Израилевич**
Башкирский государственный университет
Уфа 450096
Россия
тел.: 3472 236162
факс: 3472 236680
e-mail: spivak@bsu.bashedu.ru

**Спиридонов Алексей Алексеевич**
Институт катализа им. Г.К. Борескова
Пр. акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 3832-39-73-09
факс: 3832-34-30-56
e-mail: pub@catalysis.nsk.su

**Степанов Виктор Георгиевич**
КТИ «Цеосит» СО РАН
Новосибирск 630090
Россия
тел.: 3832 396251

**Стефогло Евгений Федорович**
Институт Угля и Углехимии СО РАН
ул. Рукавишникова, 21
Кемерово 650610
Россия
тел.: 3842 365561
e-mail:sorbent@sorben.kemerovo

**Сыропятов Владимир Яковлевич**
НИИТ Автопром
Москва, Россия

**Телин Алексей Герольдович**
ВНИИЦ «Нефтегазтехнология»
ул. Менделеева 171/3-41
Уфа 450080
Россия
тел.: 3472 520623

**Томилов Виктор Николаевич**
Институт катализа им. Г.К.Борескова
пр. Акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 3832 344491
факс: 3832 341878
e-mail: vic@sirivs.catalysis.nsk.su

**Ушева Наталья Викторовна**
Томский политехнический университет
Томск, Россия
тел.: 3822 415443
факс: 3822 223995
e-mail: tpu@tpu.edu.ru

**Фомин Андрей Анатольевич**
Институт химической физики Черноголовки
Черноголовка, Моск. обл.
Россия

**Хитрина Людмила Юрьевна**
Институт катализа им. Г.К.Борескова
пр. Акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 3832 333561
e-mail: khitrina@domain.com

**Цырульников Павел Григорьевич**
Омский филиал Института
катализа СО РАН
ул. Нефтезаводская, 54
Омск 644040
Россия
тел.: 3812-662275
факс: 3812 646156
e-mail:tsir@incat.omsk.net.ru

**Чесноков Борис Борисович**
НИИ СИНТЕЗ
Москва, ул. Угрешская
Россия
E-mail: olches@olches.ps.msu.su

**Чумакова Наталья Алексеевна**
Институт катализа им. Г.К. Борескова
Пр. акад. Лаврентьева, 5
Новосибирск 630090
Россия
тел.: 3832-341278
факс: 3832-34-18-78
e-mail: chum@catalysis.nsk.su

**Чумаченко Виктор Анатольевич**
ОАО «Катализатор»
ул. Тихая, 1
Новосибирск 630052
Россия
тел.: 383-2-32-94-45
E-mail: vic@katcom.nsk.su

**Emilian Angelescu**
Univ. of Bucharest
Dept. of Chem. Techn. and Catal.
BD. CAROL I, No. 13
Bucharest
**ROMANIA**
phone: 4016503289/101
e-mail: m-alifanti@chim.upb.ro

**Paolo Cuzzato**
Ausimont R/D
via Della Chimica 5
30175 Porto Marghera
**Italy**
phone: 39412912686
e-mail: pcuzzato@tin.it

**Elenko Georgiev Dimitrov**
«NEOCHIM» SA, Institute for Low Tonnage
Chemical Products
6400 Dimitrovgrad
**Bulgaria**
fax: 359391

**Ravindra Dixit**
The Dow Chemical Company
**USA**
fax: 1-409-238-3840
E-mail:ravindra@dow.com

**Dario Duca**
ICTPN-CNR
via U. LaMalfa 153
90146 Palermo
**ITALY**
phone: 39916809370
fax: 39916809399
e-mail: dduca@cuc.unipa.it

**Ralf Doepper**
Institute of Chemical Engineering
EPFL-LGRC
Lausanne CH-1025
**Switzerland**
fax: 41-21-693-3190

**Pio Forzatti**
Technical University of Milan
Piazza L. da Vinci 32,
20133 Milano
**Italy**
fax: 39 (0) 2-70638173
E-mail:pio.forzatti@polimi.it

**Gilbert Froment**
University of Gent
**Belgium**
fax: (32) 9 264 49 99
E-mail: gilbert.froment@skynet.be

**Rosa M. Quinta Ferreira**
Departamento de Engenharia Quimica
Faculdade de Ciencias e Tecnologia
Universidade de Coimbra, Largo Marques de Pombal
3000 Coimbra
**PORTUGAL**
fax: 351-(0) 39-841138
E-mail: eq1rq@eq.uc.pt

**Zlatka Kostadinova Hagjiivanova**
«NEOCHIM» SA, Institute for Low Tonnage Chemical Products
6400 Dimitrovgrad
**Bulgaria**
phone: 359391/27576

**Lioubov Kiwi-Minsker**
Swiss Federal Institute of Technology
LGRC-EPFL
CH-1015 Lausanne
**Switzerland**
tel.: 41-21-693-3182
secr: 41-21-693-3175
41-21-693-3192
fax: 41-21-693-3190
41-21-693-6161
e-mail: kiwi@igcsun3.epfl.ch

**Stefan Kupiec**
Zaklady Azotowe w Tarnowie-Moscicach S.A.
Glowny Technolog
ul. Kwiatkowskiego 8
33-101 Tarnov
**Polska**
fax: 0480140332678

**Alexei Lapkine**
Department of Chemical Engineering
University of Bath
Claverton Down
BA2 7AY
**UK**
fax: (0) 1225 826894
e-mail: cesal@bath.ac.uk

**Miriam Lorenzi**
Institute of Chemical Engineering
EPFL-LGRC
Lausanne CH-1025
**Switzerland**
fax: 41-21-693-3190

**Aura Matei**
Univ. of Bucharest
Dept. of Chem. Techn. and Catal.
BD. CAROL I, No. 13
Bucharest
**ROMANIA**
phone: 4016503289/238
e-mail: m-alifanti@chim.upb.ro
fax: 4013159249

**Bastien Monnerat**
Institute of Chemical Engineering
EPFL-LGRC
Lausanne CH-1-25
**Switzerland**
fax: 41-21-693-3190

**Jerzy Nosek**
Zaklady Azotowe w Tarnowie-Moscicach S.A.
Glowny Technolog
ul. Kwiatkowskiego 8
33-101 Tarnov
**Polska**
fax: 0480140332678

**Albert K.E. Renken**
Institute of Chemical Engineering
EPFL-LGRC
Lausanne CH-1025
**Switzerland**
fax: 41-21-693-3190
E-mail: renken@igcsun3.epfl.ch

**Andre Rouge**
Institute of Chemical Engineering
EPFL-LGRC
Lausanne CH-1025
**Switzerland**
fax: 41-21-693-3190

**Ioan Sandulescu**
Univ. of Bucharest
Dept. of Chem. Techn. and Catal.
BD. CAROL I, No. 13
Bucharest
**ROMANIA**
phone: 4016503289/238
e-mail: n_maxim@chim.upb.ro
fax: 4013159249

**Steve Tennison**
Department of Chemical Engineering
University of Bath
Claverton Down
BA2 7AY
**UK**
fax: (0) 1225 826894
e-mail: s.perera@bath.ac.uk

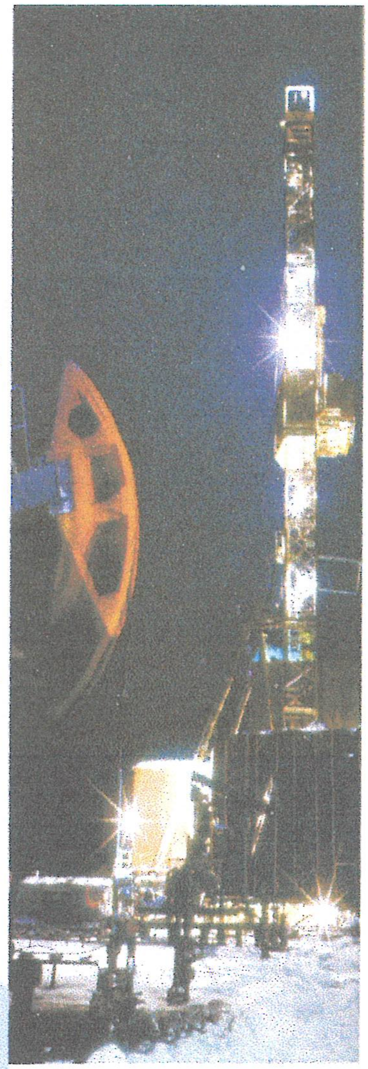
**John James Witton**
Cranfield University
**UK**
fax: 44(0)1234 750 728
E-mail: j.j.witton@cranfield.ac.uk

**Rodica Zavoianu**
Univ. of Bucharest
Dept. of Chem. Techn. and Catal.
BD. CAROL I, No. 13
Bucharest
**ROMANIA**
fax: 4013159249

АКЦИОНЕРНОЕ ОБЩЕСТВО
ВНК
ВОСТОЧНАЯ НЕФТЯНАЯ КОМПАНИЯ

# EAST OIL COMPANY

**Providing the prospecting of oil and gas deposits; organizing the oil extraction and transportation; oil and gas processing, petrochemicals production; external economic operations; oil and petrochemicals realization, sale of products from hydrocarbons and other raw materials; investment activity including the operation sale with securities. East Oil Company has a stable and steady state on oil market of Russia, possess the status of Government agent in oil and petrochemical providing the row of regions of Siberian area.**



The JOINT STOCK COMPANY EAST
OIL COMPANY, EOC, Tomsk, RF
(3822) 23-32-91
fax 22-22-30, 22-25-33

# NOTES

# XIV International Conference on Chemical Reactors

# CHEMREACTOR-14

Editor: Professor Alexander S. Noskov

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. 30,5 Заказ 76 Тираж 100

---

Отпечатано на полиграфическом участке издательского отдела
Института катализа СО РАН
630090, Новосибирск, пр. Академика Лаврентьева,5