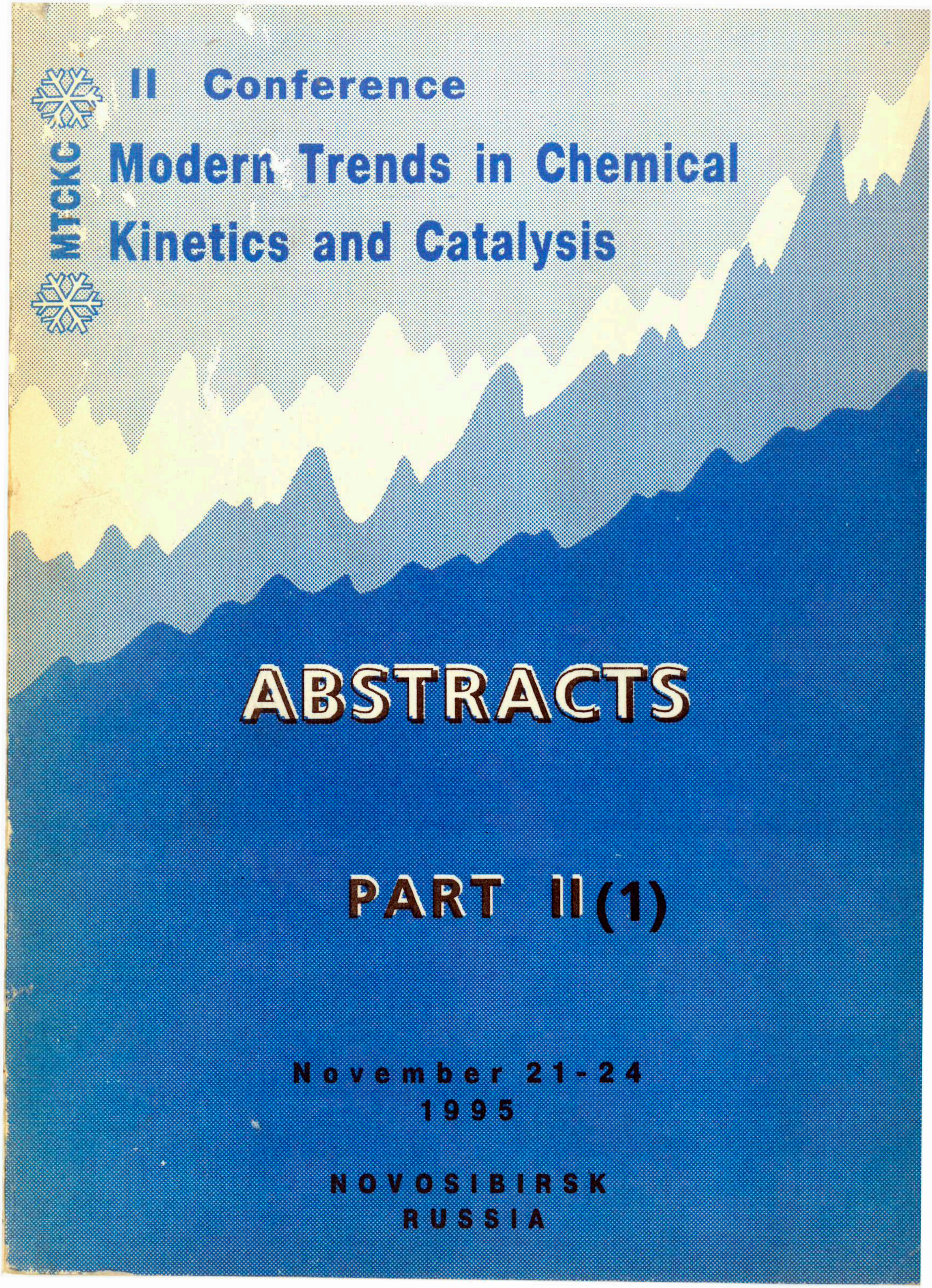

MTCKC

II Conference
Modern Trends in Chemical Kinetics and Catalysis

ABSTRACTS

PART II(1)

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CATALYSIS
POSTERS

PPC-1 – PPC-94

Application of Computer Simulation Analysis to Study Structure of Catalysts with Electric Conductivity Measurements

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It is generally accepted that the activity and efficiency of a catalyst system are not determined by its chemical and electronic properties only — the geometrical and topological structure is of tremendous importance. The formation of a catalyst structure depends on many factors and includes a number of topochemical and physical processes. The goal of the present report is to demonstrate capabilities of computer simulations as a method to analyze the catalyst structure, identifying characteristic features of a solid catalyst on various stages of its biography. We use the electroconductivity as a probe of the phase-structure state of a catalyst because this transport property depends critically on the geometrical structure and intergranular contacts. To get a theoretically understandable correspondence between the geometrical and the electrical characteristics we have developed a versatile program package based on Monte-Carlo approach [1]. The analyzing power of electroconductivity has been tested for several model and real objects, each with some notable peculiarities in their behaviour. We have considered both monodisperse and polydisperse multi-component solid systems. The conductivity of dispersed solids belongs to percolation phenomena. It is essentially governed by the spatial distribution of the conducting phase and by the intergranular contact barriers. The experimental characteristics of the concentration dependence of conductivity are the position of percolation threshold (where conductivity grows sharply from the bad-conducting phase level) and the slopes of the graph below and above this threshold. On the theoretical side, for monodispersed systems, we have developed several MC models. In these models the physical space is represented by a three-dimensional discrete lattice, whose sites may be occupied by either of the considered species. The bonds connecting neighboring sites represent electrical contacts with conductivities defined according to the model assumptions. The input model parameters are the mean value and the range of intergranular barrier conductivities, the degree of friability, measured by the average number of contacts per grain, and the degree of inhomogeneity, either introduced by a conventional parameter or simulated by means of special MC procedure.

For a series of oxide mixtures (Fe_3O_4+MgO, Fe_3O_4+NiO, Ni+ZrO_2) we succeeded in an interpretation of the experimental data with the above model parameters [2]. An example of such analysis is given below, based on the concentration dependence of conductivity σ of a Fe_3O_4+NiO system. We observed a relatively high percolation threshold $X_c \approx 0.5$, which contrasts with ordinary homogeneous mixtures ($X_c \approx 0.3$). This may be explained by the inhomogeneity of phase distribution. A simulation with the use of "disaggregating" MC procedure leads to a perfect agreement with the experimental results. Another feature of the conductivity graph is its negative slope in the below-threshold region. It means that heterophase contacts are even worse conducting than homophase bad-conducting phase barriers. This also gives evidence for the absence of chemical interaction between the components, since the possible product, nickel ferrite, would manifest in an enhanced conductivity. A detailed discussion of some other interesting properties of monodisperse mixtures may be found in paper [2]. We emphasize that the considered models not only give a qualitative theoretical picture, but describe the real physical systems quantitatively.

Now we consider some polydisperse systems, dealing mainly with supported catalysts. We call the low and high dispersed phases as supporting and supported phases, respectively. Since the geometrical scales of the supported phase, the support and the whole sample differ by many orders of magnitude, we perform the simulations in two stages. We simulate the properties of individual grains at the first stage, and then use the obtained results as input to simulate the whole sample (composed of many grains) at the second stage. We analyze the cases of small, moderate and large intrinsic surface area of the support. We study the dependence of the net conductivity on the conducting coverage fraction X. For definition, we assume the supported phase to be the conducting one ($\sigma=1$) and the support to be isolating ($\sigma=0$). When X achieves some critical value X_c, the overall conductivity appears and then grows monotonically with growing X. The conductivity behaviour depends both on the structure of the support and the distribution of the supported phase. If the supporting phase has a continuous structure (a single grain, a sintered film, a sponge, etc.) then the role of the surface area manifests in the position of percolation threshold and in the behaviour of conductivity in the nearby threshold region. A large intrinsic surface of the support may lead to opposite consequences depending on the structure of pores. As compared with a smooth surface ($X_c \approx 0.27$), the open pores provide extra paths for current, thus enhancing the conductivity and lowering the percolation threshold ($X_c \approx 0.15$). The blind pores accumulate the conducting material in dead-ends, thus suppressing the conductivity and rising the percolation threshold ($X_c \approx 0.42$).

If the supporting phase has a granulated structure, the intergranular contacts play the major role. Then only the way of localization of the supported phase is important, while the surface area has only a little influence. When comparing the random uniform distribution and the distribution correlated with contact points (i.e., every intergranular contact belongs to supported phase), we observe that not only the percolation threshold shifts but the shape of the curve changes generally. These cases may thus be discriminated experimentally. Hence, if located in contact regions, even a small amount of supported phase may lead to visible effects in conductivity character. Since a chemical interaction or a phase transformation usually starts at intergranular contacts, many important processes of catalyst biography (such as reduction of oxides, formation of new compounds during its preparation or exploitation, etc.) may be detected at their very early stages.

Thus, if combined with proper MC analysis, the electric conductivity may be used as a sensitive probe of the geometrical and physical structure of a catalyst.

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^{119}SN PROBE-ATOM MOSSBAUER SPECTROSCOPY APPLIED TO STUDY TIN-DOPED SESQUIOXIDES OF CORUNDUM STRUCTURE: NEW POSSIBILITIES FOR SURFACE RESEARCH

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Our previous investigations concerning two simple antiferromagnetic oxides, Cr_2O_3 and V_2O_3, as well as related solid solutions, have permitted to find experimental conditions assuring the location of tin dopant atoms in two different valence states, Sn(II) or Sn(IV), immediately on the surface of sesquioxide grains. The *insertion* of tin atoms (doping rate: < 1 at.%) into such a material is evidenced by magnetic hyperfine interactions appearing in ^{119}Sn spectra in going through the Néel temperature of the oxide under investigation. On the other hand, the *surface location* of the tin is attested by the following facts: (i) observed ^{119}Sn hyperfine parameters imply a low coordination of the dopant atoms, in striking contrast with the octahedral anionic environment of the metallic site in the bulk of the corundum structure; (ii) at room temperature, the tin is shown to react rapidly with various gas molecules, such reactions, prohibited for bulk-located atoms, being easily detected by Mössbauer spectra; (iii) XPS analysis shows an "abnormally" high concentration of tin in 20-30 Å surface layers explored by this characterization technique.

The mentioned tin-doped sesquioxides appear, therefore, to be particularly appropriate systems for studying the features of chemical bonding and local surroundings of surface-located atoms by means of conventional transmission Mössbauer spectroscopy. Recent examples of such researches are discussed in this communication. Moreover, we report new results concerning individual dynamic characteristics (i.e. Mössbauer lattice temperature and vibrational anisotropy) of the tin located in different surface-sites as well as its interactions with H_2S molecules. Finally, for Cr_2O_3 which is known to be catalytically active for various reactions, our recent results permitting to elucidate the effect of tin additives revealed in both processes the oxidation of CO by O_2 and dehydrogenation of ethyl-benzene, are also reported.

The described research was made possible in part by Grant № NBG300 from the International Science Foundation and Russian Gouvernment.

PPC-3

THE ELECTROCATALYTIC PROPERTIES OF ULTRAFINE HYDROGEN-SORBING INTERMETALLIDES

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It is known that hydrogen-sorbing intermetallides are the high-effective catalysts of the process of the hydrogen electroreduction in alkaline solutions.

The present work is devoted to the investigation of the pecularities of ultrafine (crystalline and amorphous) intermetallides ($LaNi_5$, $CeCo_3$, TiFe) preparation by a method of high-energy mechanical action at planetary mill and to the study of their electrocatalytic and hydrogensorbed properties.

It is known that the crystalline powders with particle size of ~ 0.1 mcm can be obtained by a high-energy action on preliminarily hydrogenembrittling intermetallides and their hydride phases at small ball loading and milling time. The increase of internsity and milling time leads to an "amorfization" of intermetallides and later on to their disintegration.

The density of exchage current in electrocatalytic reaction of hydrogen cathode evolution on investigated powders of intermetallides with an increase of ball loading and the time of high-energy treatment is changed not monotonously: at first it increases (maximum in 4 times for $LaNi_5$) up to a study of the existence of amorphous intermetallides, and then it lowers sharply in a field of their disintegration.

Hydrogensorbed capasity of intermetallides, unlike their catalytic activity, decreases monotonously with a increase of milling intensity, and a slope of the phase transition β-hydride$\rightleftharpoons\alpha$-hydride plato increases up to the plato disappearance.

The optimal conditions of the production of ultrafine intermetallides with improving electrocatalytic characterizations were determinated.

This work was carried out with the support of the Russian Foundation for Fundamental Research (project no.95-03-09566).

Study of New Catalytic Systems in Polyphenylene Synthesis by Means of Oxidative Polycondensation

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New co-catalysts for oxidative polycondensation method of polyphenylene synthesis with $CuCl_2$ as an oxidant were checked. Liquid monoalkoxy substituted aluminum chlorides $AlCl_2OC_9H_{19}$, $AlCl_2OC_2H_5$, $AlCl_2OCH_2CF_2CF_2H$ were shown to be inactive in this reaction probably due to their liquid state which leads to insufficient oxidation potential. The use of solid co-catalyst $(CF_3)_2CHOAlCl_2$ results in polyphenylene formation.

Adding fluorinated sulfonic acid with long substituent $CF_3-CF_2-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3H$ to the standard Kovacic catalytic system ($AlCl_3-CuCl_2$) leads to the growth of the degree of polymerization of the PP up to 66. It was shown the acid added reacts with $AlCl_3$ with white soft substance formation.

Acknowledgment

The research described in this publication was made possible in part by Grant M10000 from the International Science Foundation

PPC-5

PHOTOSTIMULATED METHANE CONVERSION ON TITANIUM AND NIOBIUM OXIDE COMPOUNDS

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It is resulted from probable mechanism for the photo adsorption of methane and for the formation of ethane and higher hydrocarbons [1] that photo generation of hole centers of the O type is one of the necessary conditions of its molecule activation. Now it is clear [2] that formation of similar holecenters occurs effectively on surfaces of so called supported systems. Furthermore the polyfunctional surface is needed to close the catalytic cycle., Because of this the photo induced reactions of methane has been studied using two groups of samples: 1) niobium oxides supported on high-pure silica - air-silica gel (they were prepared according the scheme of molecular layering, when ethanolic solutions of niobium (V) chloride and water vapor were used), 2) titanoniobates, in particular, protonic oxide with layer structure (HTiNbO) and its derivatives (Li, Zn, Fe). These investigations were carried out both according traditional technique using high vacuum without-oil equipment and in conditions of flow reactor at atmospheric pressure. For samples of the first group (niobium surface content was more than 2.7 percent) absolute quantum efficiencies for methane photo adsorption have been studied in detail. In the temperature range 170-450 K under action of quanta with energy 2.5-4.1 eV an extreme character both of temperature and spectral dependencies of absolute quantum efficiency values of methane photo adsorption has been established. Maximal values have been observed under light irradiation with quantum energy equal to the beginning of oxide optical absorption in the long-wave range. This effect may be explained by the present of niobium (IV), which has an absorption band in the same region. Photo adsorption of oxygen was not observed on this type of samples. Appreciable short-wave shift (0.5 eV versus bulk niobia) in absorption spectra of these samples gives evidence of low dimension state of niobium oxide particles. On samples of the second group the photostimulated mild, oxidation of methane to methanol as the main product is carefully investigated at 290-390 K.

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PPC-6

THE OXIDATIVE ADDITION OF METHANE TO $Pt(Cl)_2(PH_3)_2$ AND $Pt(Cl)_2(PH_3)$ COMPLEXES.

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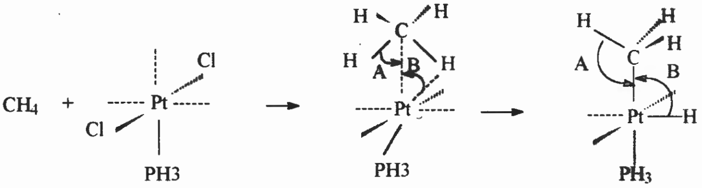
The activation of methane by transition-metal complexes has been analyzed with *ab initio* quantum chemical methods for model reaction:

$$CH_4 + Pt(X)_2(L)_n \rightarrow (H)(CH_3)Pt(X)_2(L)_n \qquad (1)$$

with planar complex (n=2) and T-complex (n=1), (X=Cl, L=PH_3,).

The calculations were performed with GAUSSIAN92 package of programs by RHF/MP2/LANL1DZ method. For reaction (1) main electronic parameters was determined, including optimized geometry, frequencies in stationary points on the potential energy surface for reactants (R), transition state (TS) and product (P). Reaction path connected R/P and TS has been determined also. It was shown that reaction (1) with n=1 proceeds through a bifurcated η^2-CH_4 complex :



T-complex η^2-CH_4 complex Product

For n=2 the energy barrier of oxidative addition of methane to planar complex is so high (47kcal/mol) that one could hardly expect significant activation C-H bond.

Main energetic and geometry parameters of reaction are given in Table 1, where energy of isolate reactants were represented as zero . The analysis of these parameters as well as the change of intermediate structure along the reaction path were shown an important role of donor-acceptor ligands in decreasing of the transition state energy. In particular, in case n=2 it was shown that in close to TS one of phosphin group leaves the first coordination sphere of complex, thereby the T-structure of complex was stabilized with acceptor Cl-ligands and the second PH_3 -ligand regulates formation of the Pt-H bond.

Table 1.

Parameters	n=2			n=1		
	R	TS	P	η^2- CH_4	TS	P
Energy (kcal/mol)	0	47	27	-12	21	17
Bonds (Å)						
Pt-C	4.64	2.20	2.10	2.77	2.12	2.09
Pt-P	2.44	2.63	2.70	2.35	2.65	2.70
Pt-H	4.10	1.59	1.54	2.39	1.54	1.51
Pt-Cl	2.45	2.44	2.44	2.43	2.42	2.41
Angle (degree)						
A	55.2	96.1	108.6	56.4	100.0	105.0
B	12.4	47.7	80.7	22.9	62.0	78.0
CPtP	90	165	171	180	157	176

Thus the calculations predicted that the oxidative addition of CH_4 to the 14-electronic $Pt(Cl)_2(PH_3)$ (T-complex) is possible with marked rate because the TS-energy is decreased substantially (21 kcal/mol) as compared with the planar $Pt(Cl)_2(PH_3)_2$ complex.

The research described in this publication was made possible in part by Grant № RBH-300 from the International Science Foundation and Russian Government.

PPC-7

UNIFORM MULTIAPPLIED CATALYTIC SYSTEMS ON WOVEN SILICA BASE-NEW CATALYSTS' GENERATION

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Catalyst's structure and shapes of the catalytic elements.

The catalyst is the material woven of the amorfous silica filaments in the form of the breadths or of the grids. These elements contain the catalytic components from the wide row of metals - Pt, Pd, Rh, Au, Ag, Ni, Cr, Mn, Co, Fe et. al.

The catalyst may be used both in the shelf and tube catalytic reactors. In the first case catalytic elements are laid on the shelves of the reactor as a "carpet", in the second one they are pressed into the tubes of the reactor in the form of the "roll".

Some information about the technology of the catalyst production.

The catalysts active phase is formed not by the traditional ways of depositing of the metallic layer on the surface of the support but by implantation of catalytic elements in any assigned collection and correlation into its body with a special technology.

This technology provides high stability of the catalytic phase: the metal component is strongly retained by the matrix and doesn't undergo destruction, reconstruction and mass loss during the reaction.

This technology allows to provide a high catalytic activity while a very low concentration of metal (for example, for such a valuable metals as Pt, Pd, Rh, - while the their concentration is much less 0.1% the activity is comparable to one of the metal gouzes).

The technological process of the industrial manufacturing of these catalysts is uninterrupted. It is based on introduction of several additional operations in the present known technology of the silica woven materials, that will not break its continuity. The industrial base necessary for serial production of these new catalysts have formed to present time.

Fields for new catalysts application.

1. The contact stage of the nitric acid production: the silica elements containing 0:01-0.1% of Pt or Pd will allow to reduce in 2-3 times the amount of the platinum group metals in the catalytic packet of the reactor and to reduce their losses in the same extent.

2. The contact stage of the sulfur acid production: exchange of the vanadium catalyst to the silica one with content of platinum 0.001-0.01% will allow to reduce the temperature of the contact, to increase the conversion and to decrease the amount of sulfur dioxide in the gas exhausts.

3. The automobile exhaust neutralization in the converters with the new catalytic elements will allow to decrease the used quantity of platinum metals in 1.5-2 times while retaining the demanded level of purification and to simplified theirs production technology.

4. The use of the new catalysts with silver component in the processes of soft oxidation of the hydrocarbons (production of formaldehyde from methanol, of ethylene-oxide etc.) will allow to increase the reducing of the product on the unit of silver's mass in 10- 20 times with retaining of the high selectivity.

5. The new catalysts may be useful in the petrochemical processes, the proceesses of hydrogenation of hydrocarbons (e.g.plant oils), in the catalytic generators of heat and gases, in the catalytic microengines.

PPC-8

NEW APPROACH TO PREPARE Pt/ALUMINA CATALYSTS: DESIGN OF SURFACE PLATINUM DISTRIBUTION OVER PORES

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In the course of catalysts preparation diffusive-sorption processes at impregnation stage control movement and platinum macrodistribution in the support. Nine characteristic platinum distribution types in a granule are known [1]. Migration of adsopbed precursors in pores of different size with the subsequent ancoring of active substance in these pores takes place simultaneousely with the platinum movement over the granule diameter. Different concentration of the metal in micro- and macropores are predicted because of the diffusion processes. In practice this question is not settled because of complexity of definition of pore size interval where active component ancores.

Correlation between impregnetion conditions of alumina by chloroplatinum acid and platinum surface distribution in the alumina porous structure is investigated in this work.

The catalysts in the shape of spherical granules of 1,5-2 mm size were prepared by the adsorption of H_2PtCl_6 on γ-Al_2O_3 (S_{BET}=180 m^2/g, V= 0,6 cm^3/g, R=7 nm). Competitive acids HCl, CH_3COOH of different concentration were added into the saturation solution. Thus, it was stated that a number of diffusive chemical processes while platinum solution moves in the alumina grain defines complex, heterogenuous type of platinum particle distribution (of active phase deposit) in the catalyst's porous structure. Heterogeneity of dispersed platinum in Pt/Al_2O_3 was taken into consideration while analysing experimental data: metal platinum particles (Pt^o) in the environment of electron defficient platinum atoms Pt^σ (specific, "non-metallic " platinum state) .

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Effect of activation by substrate of hydrogenation catalytic system based on Pd(Acac)$_2$·PPh$_3$ and sodium hypophosphite.

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Selective catalytic hydrogenation of acetylene hydrocarbons has received much attention as in connection with a necessity of a solution of a number of oil chemistry and fine organic synthesis problems as much as of theoretical problems of activation of hydrogen molecule and substrates. [1]

Study of behavior of a new metal complex catalytic system based on bis-acetylacetonato(triphenylphosphine)palladium and sodium hypophosphite in hydrogenation of unsaturated compounds has permitted to reveal a number of features of it.

An activation phenomena of catalyst in hydrogenation process of model compound-phenylacetylene has been obtained. This phenomena is consisted in dramatic jump rise of triple bond hydrogenation rate and increasing of selectivity of catalyst under hydrogenation of a new portion of substrate. The change of the nature of active palladium complexes as a result of the interaction of initial form of catalyst with one of reaction products - styrene is shown to be a reason of the activation. The activation of catalyst by styrene increases its activation an order in hydrogenation of other acetylene derivatives too.

The formation of a symmetric complex of type [Pd$_3$(PPh$_2$)$_3$(PPh$_3$)] as a result of the interaction between the components of catalytic system and modifying during styrene hydrogenation has been proposed on the base of ^{31}P NMR spectra data.

A formal kinetic scheme including the complexation of initial catalyst with phenylacetylene following by hydrogenation or oligomerization of latter and formation of a new type of active palladium complexes with which proceeds selective hydrogenation either of forming styrene or of a new portion of phenylacetylene is suggested. Numerical simulation data have indicated agreement between suggested scheme of the reaction and experimental data. The equilibrium constant and rate constants of individual stages have been calculated.

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PPC-10

MONOCOMPONENT ORGANOTITANIUM CATALYSTS FOR ROMP AND ZIEGLER-NATTA POLYMERIZATION

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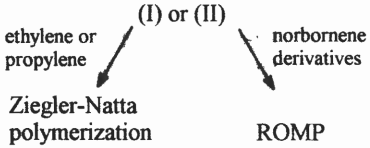
It has been shown that stable organotitanium compounds (I) and (II)

$$Cl_3Ti\,CH_2\overset{CH_3}{\underset{R}{Si}}CH_2\,\overset{CH_3}{\underset{R}{Si}}Cl$$

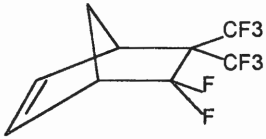
(I R= —CH_3, II R= —CH_2CH_3)

can act as monocomponent catalysts for two kinds of the monomers:



We have examined the high stability of these catalysts for ethylene and propylene polymerization. For example, organotitanium compounds have shown the permanent activity for ethylene polymerization when it has been kept for 24 hr after the reaction with C_2H_4. Moreover, these catalysts produced blockcopolymers of ethylene and propylene when propylene was added after the reaction of ethylene.

ROMP of norbornene derivatives



and

took place with a small yield in the presence of (I).

The formation of active sites from organotitanium precursors are under discussion.

PPC-11

SELECTIVE OXIDATION OF GLYCEROL WITH AIR ON METAL CATALYSTS

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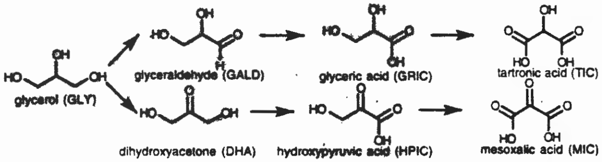
The transesterification of triglycerides extracted from oilseeds used to obtain the so-called "green diesel fuel" yields up to 14% by weight of glycerol. The present glycerol market would not be sufficient to absorb a large glycerol surplus so new outlets for glycerol have to be found. In the present investigation we have used glycerol as a feedstock for the synthesis of valuable oxidation products such as dihydroxyacetone, (presently obtained via costly biotechnology processes) and glyceric acid (prepared by environmentally harmful, nitric acid oxidation). More specifically, we wanted to selectively oxidize the primary or secondary alcohol functions to obtain the following products :



Oxidations of aqueous solutions of glycerol (10wt%) were carried out with air in a well-stirred batch reactor at 50°C under controlled pH and with a metal catalyst in suspension. The composition of the reaction medium was analyzed by HPLC. Catalysts Pd/C and Pt/C (5wt%) were obtained by impregnation of an active charcoal with acidic solutions containing $PdCl_6^-$ or $PtCl_6^-$ ions and then reduction with formaldehyde. Bimetallic PtBi/C catalysts were obtained by electrodeless deposition of Bi atoms on Pt/C catalysts. Particle size and composition were measured by TEM and analytical STEM.

Figure 1 shows that the selectivity to glyceric acid can be as high as 70% at 100% conversion. The reaction mechanism involves an oxidative dehydrogenation of a primary alcohol function to give transiently the hydrated aldehyde which then undergoes a second oxidative dehydrogenation to glyceric acid.

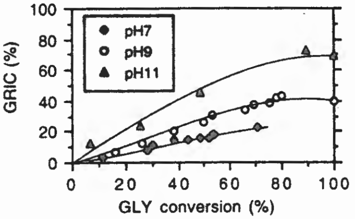


Fig. 1 Glyceric acid yield on Pd/C

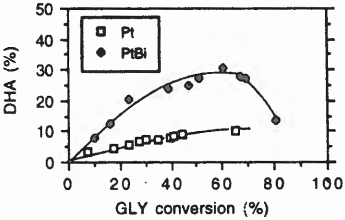


Fig. 2 Dihydroxyacetone yield on Pt/C promoted or not with bismuth (pH 2)

On Pt/C catalyst, glyceric acid was still the main product (55% selectivity) but its selectivity can be tuned by deposition of Bi atoms to produce interesting yields in valuable dihydroxyacetone and hydoxypyruvic acid as shown in Figure 2. The preferential oxidation of the secondary alcohol function induced by the bismuth promoter can be explained by the mechanisms discussed by Mallat and Baiker (1) for the oxidation of other polyols.

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PPC-12

CYCLODEXTRIN INFLUENCE ON KINETICS OF HYDROLYSIS AND SMILES REARRANGEMENT OF SALICYLIC ACID ESTERS

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The hydrolysis of salicylic acid esters proceeds with the intramolecular general base assistance of the deprotonated *ortho*-hydroxyl group. Recently the ability of cyclodextrins to affect the rates and equilibria of intramolecular transformations was demonstrated.. We report here the change in the mechanism of intramolecular hydrolysis of salicylates in the complexes with the β-cyclodextrin and the acceleration of the rate of Smiles rearrangement in the presence of .β-cyclodextrin.

Both esters *p*- and *m*-nitrophenyl form complexes with cyclodextrin with binding constants of their undissociated forms 200±40 M^{-1} and 330±40 M^{-1} respectively. The binding of these esters provides the acceleration of water hydrolysis ca. 10 times but the mechanism of the hydrolysis changes: cyclodextrin-bound ester cleavages through the nucleophilic attack of the deprotonated β-cyclodextrin hydroxyl group at the neutral substrate molecule. This fact is confirmed by the isotopic effect (for water hydrolysis $k_H/k_D=2.0$, but for cyclodextrin catalyzed one $k_H/k_D=1.02$) and deacylation step of the reaction (k_{deac} for both substrates is about 5×10^{-5} s^{-1}). In addition we found some difference in behavior of *p*- and *m*-nitrophenyl esters in presence of β-cyclodextrin. For example, for *m*-substituted substrate the shift of pKa consisted 0.6, but in the case of *p*-substituted ester pKa did not change. It is worth to mention here that Tee et al[1] envisaged different mode of incorporation of *m*- and *p*-nitrophenyl acetates into β-cyclodextrin during their hydrolysis and supposed that the hydrolysis of the latter proceeds without of aryl group inclusion into cyclodextrin cavity. But β-cyclodextrin inhibits or has no effect, depending on pH, on the hydrolysis of methyl salicylate. These results are in general agreement with observations of different authors which demonstrate much more pronounced catalytic effects on the hydrolysis of esters with good leaving groups as compared to those with poor leaving groups. A possible explanation of this difference is that the cyclodextrin hydroxyl groups can not compete with more basic aliphatic alcoholate leaving groups in, but readily expel less basic aromatic phenolate leaving groups from the tetrahedral intermediate.

p-nitrophenyl salicylate undergoes simultaneous Smiles rearrangement which is actually an intramolecular aromatic nucleophilic substitution leading to *o*-carboxyphenyl p-nitrophenyl ether. The initial state of the reaction is anionic with the negative charge localized on the deprotonated *ortho*-hydroxyl group and in the transition state this charge is delocalized on the nitroaromatic ring. Reactions of this type should be accelerated on passing from water to less polar media. In presence of β-cyclodextrin this reaction is accelerated probably due to low polarity of cyclodextrin cavity.

Thus our results reflect the general conclusion about the higher relative effectiveness of intramolecular nucleophilic reactions as compared to the intramolecular processes which involve the transfer of proton.

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PPC-13

Synthesis of Mono-, Di-, and Trisilylated Olefins Based on Rh(I) Catalyzed Hydrosilylation of Methylenecyclopropanes

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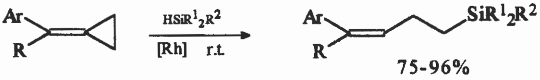
Hydrosilylation of methylenecyclopropanes in the presence of $Rh(PPh_3)_3Cl$, $Rh(CO)(PPh_3)_2Cl$, and $[Rh(C_4H_6)_2Cl]_2$ provides a new synthetic route to silylsubstituted alkenes.

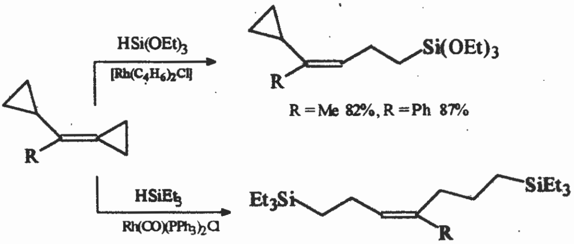
Interaction of arylmethylenecyclopropanes with silanes proceeds at room temperature selectively with ring-opening to form silylated styrenes in excellent yields. The reaction rate depends on the substrate and catalyst nature.



$R^1=R^2=Et$, $R^1=R^2=OEt$, $R^1=Me, R^2=Ph$

$Ar=Ph, R=H$ $Ar=p\text{-}MeOPh, R=H$, $Ar=Ph, R=H$

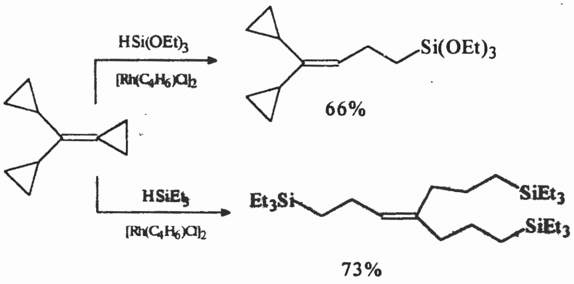
Hydrosilylation of cyclopropylsubstituted methylenecyclopropanes leads to the selective formation of mono- or disilylated olefins. The direction of the reaction is influenced by catalyst and silane.



R = Me 82%, R = Ph 87%

R=Me	$Rh(CO)(PPh_3)_2Cl$	80°C	8 h	66%
R=Ph	$Rh(CO)(PPh_3)_2Cl$	80°C	6 h	73%
R=Ph	$[Rh(C_4H_6)_2Cl]_2$	20°C	100 h	89%

Trisilylated alkene is obtained as the only product of the reaction of dicyclopropylmethylenecyclopropane with triethylsilane in the presence of $[Rh(C_4H_6)Cl]_2$. With triethoxysilane the monoadduct is exclusively produced



Di-μ-chlorotetrakis[η^2-methylenecyclopropane]dirhodium is more active catalyst for hydrosilylation of methylenecyclopropanes than other rhodium complexes. Reactions with different silanes proceed at room temperature in good yields.

The mechanism of methylenecyclopropane hydrosilylation is discussed.

For arylmethylenecyclopropanes, the cyclopropylmethylrhodium intermediate resulted from the addition of $HRhSiR_3$ to the double bond undergoes ring-opening.

In the case of cyclopropylsubstituted methylenecyclopropanes, the vinylcyclopropane fragment is coordinated to rhodium as a bidentate ligand to yield the products of opening of two or three cyclopropane rings.

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PPC-14

CERTAIN OF THE KINETIC MODELS USED IN SCR SIMULATION

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At the beginning of the 70s, Selective Catalytic Reduction of nitrogen oxides by ammonia (SCR process) first commercialized in Japan is the most successful technology for removal of NO_X of stationary sources. In spite of the rapidly growing commercial applications and the large number of studies focusing on various aspects of these reactions, there is still no agreement on the mechanism of the SCR process. This brings up an empirical approach of the overall kinetics of catalytic reactions. So, under some excess of ammonia at 250-350 ^0C, to sufficient accuracy the rate of nitrogen oxides reduction can be expressed by the equation of the first order for NO and zero one for NH_3. The dependence of this sort has been applied in modeling the reactor and operation régime of the first industrial unit for off-gases purification from nitrogen oxides by SCR under unsteady-state conditions arising from periodical reversal of the flow to be purified through catalyst bed (REVERSE-NOX process) [1]. To describe the behaviour of the process within wide area of NH_3/NO_X and temperatures the rate of NO_X reduction is given by

$$r_{NO_x} = k \times C_{NO_x}^{n1} \times C_{NH_3}^{n2} \qquad (1)$$

or

$$r_{NO_x} = \frac{k \times C_{NO_x} \times C_{NH_3}}{1 + K \times C_{NH_3}}. \qquad (2)$$

The rate law of ammonia oxidation is

$$r_{NH_3} = k \times C_{NH_3} \qquad (3)$$

Fig.1 shows the conversion of nitrogen oxides and ammonia as well as maximum temperature as a function of the time between reversals (the rate equation (2)).

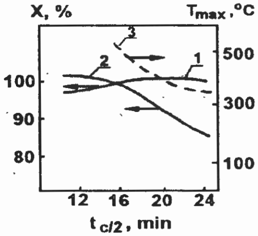

Fig.1. Conversion of the NO_X(1) and NH_3(2), maximum temperature(3) as a function of the time between reversals of the gas flow.

It is known the catalyst being used have the essential adsorption capacity as to ammonia. Operation of industrial reactors associated with start-up and shut-down of the plant, as well as with variations of the load, reagents content or temperature along the catalyst bed, is being performed in transient conditions. Simulation of the reactor behaviour calls nonstationary kinetic model for mathematical description to be fit adequately. The simplest mechanism has been used in a few papers [2, 3, 4] concerning the dynamics of the SCR process.

1. $NH_3 + [\ ] \Leftrightarrow [NH_3]$,
2. $NO_x + [NH_3] + O_2 \Leftrightarrow N_2 + H_2O + [\ ]$.

The rate equation is

$$r_{NO_x} = k_{NO_x} \times C_{NO_x} \times \Theta_{NH_3}\ , \tag{4}$$

where ammonia surface coverage Θ_{NH_3} is described by

$$a\frac{\partial\Theta_{NH_3}}{\partial t} = r_a - r_{NO_x}\,;$$

the rate of reversible adsorption of NH_3

$$r_a = k^+ \times C_{NH_3} \times (1-\Theta_{NH_3}) - k^- \times \Theta_{NH_3},$$

a - catalyst surface capacity.

Using this model one can consider how the storage capacity of ammonia over a catalyst surface affects the efficiency of SCR. Fig.2 shows the behaviour of nitrogen oxides and ammonia concentration in outlet under cyclic changes of NO at the inlet (Fig.2A). Fig.2B illustrates the curves calculated using the nonstationary model (4), fig.2C - with the rate law (2) (Calculations has been made by E.S.Borisova).

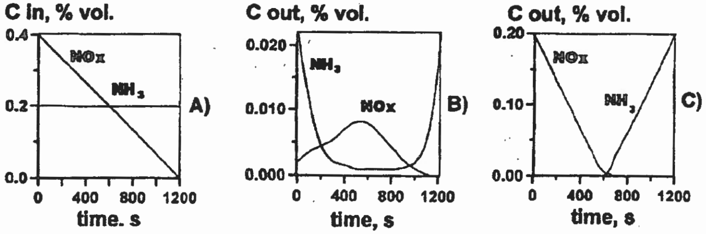

Fig.2. Nitrogen oxide and ammonia content at the inlet (A) and outlet (B, C) of the catalyst bed. B - model (4) has been used, C - model (2); T = 260°C.

Recently Dumesic et.al. have [5] shown that the simple two-step Eley-Rideal mechanism is not consistent with all data. Here it has been proposed that adsorbed ammonia first must undergo an "activation step" before reaction with NO. In the paper that follows [6] the authors attempted to support the suggestion by experiment. In their opinion SCR reaction is initiated by an adsorption equilibrium involving V^{5+}–OH sites. Transformation of the adsorbed ammonia occurs via involving monomeric terminal vanadyl species:

$$V^{5+}\text{-}ONH_4 + V^{5+}{=}O \Leftrightarrow V^{5+}\text{-}ONH_3H^+\text{-}O\text{-}V^{4+} \tag{5}$$

There is the contention regarding the form of adsorbed ammonia and the active site, whether V=O or V–OH. Overview of the experimental evidences we believe strongly suggest that the activation of adsorbed ammonia is due to the interaction summarized of surface structures.

To simulate of the transient regimes of SCR process and reactor dynamics under typical industrial conditions the postulated steps are as follows:

1. $NH_3 + [\ ] \Leftrightarrow [NH_3]$
2. $NH_3 + [V_2O_5] \Leftrightarrow [NH_3\text{–}V_2O_5]$
3. $[NH_3\text{–}V_2O_5] \Leftrightarrow [NH_2\text{–}V_2O_4\text{–}OH]$
4. $[NH_2\text{–}V_2O_4\text{-}OH] + NO + 1/4O_2 \Leftrightarrow N_2 + H_2O + [V_2O_5]$

Ammonia is adsorbed on two type of sites (steps 1 and 2). Step 1 and 2 represent respectively the species assigned to the lower part of TPD spectrum at maximum temperature 120-150 °C and the medium one at 200-280 °C [6]. The activated ammonia capable or reacting appears to be relative to the high-temperature part of TPD spectrum is given by step 3. Gaseous NO and O_2 react with ammonia activated, yielding the reaction products and vanadium species regenerated (step 4).

Preliminary simulation of the transient regimes of SCR process with the differential reactor model has demonstrated the reasonable behaviour of the substances in the gas phase.

Acknowledgments

The author would like to thank colleagues specifically Dr. A.S.Noskov for united results and very useful discussions.

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CARBONYLATION OF 1-SUBSTITUTED-1-ARYLETHANES and ETHENES: VARIATIONS IN REGIOSELECTIVITY

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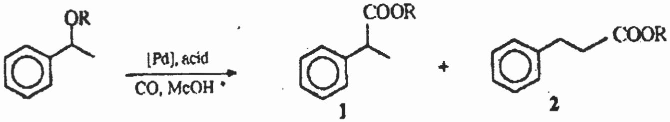
Carbonylation of 1-arylethanols under mild conditions provides an attractive short route to arylpropionic acids which are used as non-steroidal anti-inflammatory drugs:[1]



We have examined the behaviour of different starting 1-substituted-1-arylethanes for this carbonylation and reported large changes in the product regioselectivity by variation of the substituents and reaction conditions, and the nature of the catalytic system based on palladium:[2]

-1-phenylethyl propionate could be carbonylated (P_{CO} = 50bar) to the esters **1**, **2** (R = OMe) in the presence of methanol, $Pd(PPh_3)_2Cl_2$ and $HBF_4 \cdot OEt_2$ as a co-catalyst. This system favours the formation of the linear ester (**1**/**2** = 0.21). Monitoring of the reaction shows that the carbonylation process proceeds through 1-phenylethanol or the corresponding methyl ether 3.

-ether **3** is slowly converted under similar conditions to the same products (**1**/**2** = 0.23).

-1-phenylethanol is extensively consumed, but the formation of **3** is favoured over the production of the expected esters (**1**/**2** = 0.21). A study of the influence of the phosphine and co-solvent shows practically no influence on the yield of esters and the regioselectivity. The use of other acids provides significant modifications: an increase in the yield of the esters is observed with soluble sulfonic acids (**1/2** = 0.22). Addition of LiCl depress 1-phenylethanol conversion but enhances the regioselectivity (**1/2** = 0.50). As expected,[1] the use of HCl increases the regioselectivity (**1/2** = 0.73), but, again, at the expense of the yields. The best results are obtained with the use of sulfonated resins (Amberlyst 15) in methanol or water. The reaction has been extended to other 1-arylethanols with noticeable variations observed on yields and selectivities with the nature of the aryl group.

Finally, alkoxycarbonylation of styrene under the same conditions has been examined.[3] The regioselectivity is much higher (**1/2** = 0.45 to 0.82) and is, at variance with the alkoxycarbonylation of 1-phenylethanol and 1-phenylethyl propionate, influenced by all the factors examined.[4]

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4. Work supported by CAPES, Brazil (ALM) and CNRS.

NEW ASPECTS OF PREPARATION OF CATALYSTS BASED ON THE PHTHALOCYANINES HETEROGENIZED ON SILOCHROME SURFACE.

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The use of silica (SiO_2 in itself and its modified form) became one of the heterogenating ways of metal complexes classic. In case of phthalocyanines the possibility of developing various types of catalysts on the ground of this carrier may be rather wider as the carrier makes it possible to realize all the main methods of forming surface structures: by adsorptive interactions, coordination linking and chemical graft.

In present investigation methods are realized and compared from the example of cobalt phthalocyanine (PcCo).

The use of the PcCo solutions in nonpolar solvents (octane, toluene) is the only way for the adsorptive coating of the complex (on unmodified SiO_2); it ensures rather noticeable hydrophobic interactions "adsorbent-adsorbate". On the base of the analysis of kinetic data and adsorption isoterms we consider that in this case structures are formed from parallel surface by the orientation of the PcCo molecules; such systems catalyze selectively reactions by whose mechanism a triple complex is not supposed to be formed (for example the RSH oxidation).

The attempt to make surface layers by means of merely nonpolar interactions was unsuccessful (SiO_2, hydrophobizied by propyl groups).

Method of coordination linking (gamma-aminopropyl-silochrome) allows structures of two types to be prepared. 1-The PcCo molecule is coordinated with the NH_2-group through the Co_2+ ion; such adducts interact weakly with each other and are highly effective in the prosses of the O_2 activation; 2-linkage forming owing to the protonation of amine groups (if the phthalocyanine molecule has acidic substituents, for example HSO_3^-).

Calculation, confirmed by experimental and spectral data, allows a decision to be made concerning the preferable formation of 1 type linkages when having both possibilities at the same time.

For the "PcCo- -aminopropylsilochrome" systems the isoterm form depends on carrier specific surface: -for the carrier with SS=120 m^2/g it accords with the Langmuir isotherm and is easely straightened in the coordinates of the Langmuir equation; -for the carrier with SS=80 m^2/g the isotherm has a complex form: its initial part is described by Langmuir equation and the next one-by BET equation.

Both isoterms have part of irreversible adsorption of Pc molecules (up to 35% of monolayer capacity), meaning the strong interaction adsorbate-adsorbent.

The isoterm analysis shows that PcCo molecules form laers with the parallel orientation to the surface.

The chemical graft of the complex can be realized by treating the carrier (- aminopropylsilochrome) with the solution of PcCo sulfochloride. The maximum coating of the surface is 70% and obviously that is really reachable for the PcCo molecules. The part of the molecules in the formed layer has an inclined arrangment; at the same time there are apparently structures where PcCo molecules are linked in addition with the surface by the coordination linkage. Such systems have not only all the advantages of the immobilized metal complexes but are also bifunctional catalysts and may be used in the processes of the oxidation of acidic substrates in case of need of the preliminary dissociation of the reacting molecule (for example RSH).

So systems with different structure of the active phase and different catalytic properties can be prepared by changing the conditions of the heterogenation of the phthalocyanine complex and the properties of the silica surface.

Kinetic features of the nitrogen desorption in CO+NO reaction on Iridium

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The kinetics of NO+CO reaction on iridium has been investigated by XPS and TDS. N_2 and CO_2 appeared to be the products of this reaction, while N_2O formation was not detected in mass−spectra. N_2 desorption proceeds through NO dissociation with the subsequent recombination of nitrogen atoms. The reaction kinetics study of NO reduction by CO at $P(CO,NO)=10^{-7} - 10^{-5}$ mbar over a wide range of partial pressures has shown that the reaction starts to rise at temperatures 400 K up. Our experiments on adsorption of N_2 activated by high−frequency discharge in the gas phase have proved the absence of the N_2 desorption from the atomic nitrogen adlayer at $T<700$ K. In this case the temperature of the maximum desorption peak is located at $T=750$ K. So, the mechanism of nitrogen activation and the low temperature desorption of N_2 are likely to be responsible for the activity of the CO+NO reaction at $T<700$ K. The formation of subsurface oxygen, following NO decomposition at $T>400$ K, activates the adsorbed atomic nitrogen, thus providing a sharp increase of N_2 desorption. As a result of the $N_{ads} - O_{subsurf}$ interaction the low temperature desorption peak of N_2 appears near 550 K.

The proposed kinetic scheme includes the steps of the formation of subsurface oxygen and diffusion of nitrogen atoms to the surface sites activated by $O_{subsurf}$. Using this kinetic model and the experimentally determined constants of the elementary steps we have numerically simulated thermodesorption spectra. Simulation showed that a low temperature desorption of nitrogen from the $N_{ads} + O_{ads}$ layer takes the place. The numeric calculations with variation of different parameters has been also performed.

This work was supported by Russian Fund of Fundamental Investigations, grant N 95−03−09676.

PPC-18

DESIGN OF POLYFUNCTIONAL CATALYTIC SYSTEMS FOR ALKYNE OXIDATIVE CARBONYLATION

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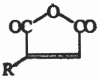
Reactions of alkyne oxidative carbonylation can be used for the synthesis of a number of products [1,2]. Among these products, derivatives of alkynylcarboxylic acid esters (I) and maleic anhydride (II) are of principal interest:

$$\mathrm{RC{\equiv}CH + CO + R'OH + Ox \rightarrow Red + 2[H] + RC{\equiv}CCOOR'} \qquad \text{(I)}$$

$$\mathrm{RC{\equiv}CH + 2CO + H_2O + Ox \rightarrow Red + 2[H] +}$$  (II)

The data obtained during last 5 years [3–7] enabled us to suggest that the mechanisms of these reactions have common features and to approach the choice of catalytic system for putting them into practice.

A key intermediate of reaction (I), palladium(II) σ-ethynyl complex can be generated via three mechanisms: (1) the oxidative addition of a C–Hal bond of halogenated acetylene to reduced palladium; (2) the transmetalation with Cu(I), Ag(I), or Hg(II) ethynyl complexes, which can be generated more readily; (3) the oxidative addition of acetylene C–H bond to reduced palladium. The composition of a catalytic system affects the reaction pathway. Variant 1 is predominant when the system contains iodide or bromide ions. Variant 2 is predominant when the system contains chloride ion and Cu(I), Ag(I), or Hg(II). Variant 3, which did not gained sufficient evidence yet, is practicable when variants 1 and 2 are hardly possible.

Hydride complexes are most probable intermediates, which are formed simultaneously with the target product via the cleavage of ethynylcarbonyl σ-organometallic compound as a consequence of the nucleophilic attack of alcohol, although there is no direct evidence for the formation of hydride complexes in system (1). The oxidant function reduces to the transformation of hydride complexes into initial catalyst entity. The problem consist in that the oxidant should not be strong enough to oxidize the reduced palladium (variants 1 and 3) or Cu(I) (variant 2).

It was shown that, in the case of $PdCl_2$–CuCl system, the problem can be solved by the use of oxygen and the choice of reaction conditions (p_{CO}/p_{O_2} and pH). The process can be conducted continuously with the selectivity to methyl phenylpropionate of ~85% and productivity of 50 g/(L h) (R = Ph, R' = CH_3) [5,6].

In the case of reaction (II), which is catalyzed by Pd(I), the situation is much similar. In the absence of oxidant under the same condition, reaction (III) replaces reaction (II):

$C_2H_2 + 2CO + H_2O \rightarrow$  (III)

The key intermediate of reaction (III) is the maleic anhydride coordinated with palladium hydride complex [8]. Palladium hydride complex was monitored by the ^{1}NMR method. The introduction of an oxidant results in the induction period (the Pd(I) →Pd(II) oxidation), increase of the rate of maleic anhydride formation, and then while the oxidant is reduced, increase in the rate of succinic anhydride formation. Oxygen is an efficient hydride acceptor. Its oxidation potential can be varied by altering its partial pressure in the gas mixture [8]. However, the presence of oxygen and acetylene in the reacting mixture is not desirable from the standpoint of explosion safety. Thus, the problem reduces to the choice of an oxidant or a catalyst of oxidation that make it possible to separate acetylene from oxygen or decrease the oxygen partial pressure to the value lower than the explosion limit. At the same time, they should not oxidize Pd(I) compounds to a detectable extent.

We failed to find the oxidant that possess the desirable oxidation potential. It was shown that, if oxygen partial pressure is low (<0.05 atm), phthalocyanine transition metal complexes can be used as catalysts of oxidation.

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DETERMINATION OF THE NUMBER OF ACTIVE CENTERS AND THE PROPAGATION RATE CONSTANT FOR ETHYLENE POLYMERIZATION ON SUPPORTED Ni-CATALYSTS BY ^{14}CO

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Ethylene polymerization on NiL_n/MgH_2 and $NiL_n/Al(i\text{-}Bu)_3/SiO_2$ catalysts [1] by ^{14}CO as the inhibitor for determining the number of active centers (AC, Ni-polymer bonds) is studied. After introducing $^{14}CO/Ni = 0.5 \div 1$ (mol) the polymerization rate decreases sharply. The removal of ^{14}CO from polymerization medium recovers the catalyst activity, but the polymerization rate is lower than one before ^{14}CO introduction.

The interaction of catalytic system with ^{14}CO at the various time (τ_{CO}) and molar ratio CO/Ni is studied. The number of labels in the polymer and liquid phase (hexane) proportionally depends on the ^{14}CO concentration and the catalyst activity (number of AC). Number of labels in the polymer increses with τ_{CO}; but the rate of the label accumulation during short τ_{CO} (≤ 5 min) is essentially higher than the successive one. In the absence of ethylene the number of labels in the polymer does not increase with τ_{CO} and the number of labels in the liquid phase is lower than one in the ethylene presence. The slower increase of the number of labels with τ_{CO} seems to be due to slow copolymerization of ethylene with ^{14}CO. Maximal number of labels in the polymerization system (polymer + hexane) in our experiments exceeded half of Ni content in the catalyst.

Catalyst activity and the number of AC (in the range of $1.5 \div 6\%$ of Ni content) with the polymerization time decrease several times. The values of the propagation rate constant (k_p) are maximal at the short polymerization time ($5 \div 15$ min) and equal to $(2 \div 3) \cdot 10^3$ l/(mol·s) at 65^0C. With increasing polymerization time the k_p values determined by ^{14}CO decrease slightly (by a factor of ≈ 1.5).

This study was carried out due to the financial support by ISF (grant RBF 300).

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XPS STUDY OF OXYGEN ADSORPTION ON SILVER: FROM SINGLE CRYSTALS TO SUPPORTED PARTICLES.

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The use of bulk silver samples such as single crystals or foils as objects for surface science studies of the silver-catalyzed ethylene epoxidation [1-3] has provided a breakthrough in the specification of the types of adsorbed oxygen states and their reactivity towards C_2H_4. On the other hand, practical catalysts represent silver supported on α-alumina. The discrepancy between the nature of the bulk and supported metal known as "the material gap" problem creates the difficulties for approximation of the model data to real catalysts. So, in this work we have carried out a comparison of the adsorbed oxygen states which are formed as a result of O_2 adsorption at $T = 470$ K in a following row of silver samples:

Ag(111) - Ag(110) - Ag powder - Ag on graphite - Ag on α-Al_2O_3.

To clarify the nature of oxygen states we have used X-ray photoelectron spectroscopy (XPS) which has proved to be one of the most effective method to study adsorbed species.

Ag(111) and Ag(110) single crystals. Oxygen adsorption both on Ag(111) and on Ag(110) single crystals results in a O1s line with BE = 528.1 - 528.2 eV indicating the appearance of atomically adsorbed oxygen with presumably ionic character of Ag-O bond. The O_2 pressures of 1 Pa or 10^{-3} Pa are necessary to saturate the Ag(111) and Ag(110) surfaces by this oxygen state, respectively. This is in accordance with Campbell's data [1] about O_2 initial sticking probability on these planes: ~ 10^{-6} for Ag(111) and ~ 10^{-3} for Ag(110). Further raising the O_2 pressure up to 100 Pa does not provide additional states of adsorbed oxygen.

Appearance of oxygen state with presumably covalent character of Ag-O bond characterized by O1s line with BE = 530.5 eV is observed after treatment of the clean Ag surfaces by a $C_2H_4 + O_2$ reaction mixture. This process is accompanied by dissolution of oxygen and carbon atoms in subsurface region of the silver. Apparently, namely subsurface oxygen facilitates the formation of the "covalent" oxygen.

Ag powder. The detection of both atomically adsorbed oxygen states after O_2 adsorption at P = 1 Pa on surface of Ag powder confirms this suggestion. Indeed, the powder contains considerable amount of subsurface oxygen even after heating in vacuum up to 800 K. It should be noted that the formation of the "covalent" oxygen occurs only after appearance of the "ionic" one.

Ag on graphite. To study adsorbed oxygen states on dispersed silver we have used Ag particles prepared by evaporation of silver on a cleaned graphite surface over a wide range of the Ag particle sizes: from small clusters (~ 20 Å) to large particles (> 300 - 500 Å). Only the "covalent" oxygen is formed after O_2 adsorption at pressures up to 100 Pa on the silver particles with the mean sizes below 100 Å, while the larger silver particles are characterized by both the "covalent" and "ionic" states of atomically adsorbed oxygen.

Ag on α-Al_2O_3. Decrease in the "ionic" oxygen concentration below XPS sensitivity limit (< 3 -5 % from a monolayer) for the small Ag particles (≤ 100 Å) seems to explain the drop of ethylene epoxidation rate by more than one order of magnitude revealed by us [4] for Ag/Al_2O_3 supported catalysts in the same range of Ag particle sizes (size effect). This explanation is based on our concept about the necessity of both the adsorbed oxygen states to proceed the ethylene epoxidation [2,3]: the "ionic" oxygen creates the sites (Ag^+) for ethylene adsorption, and the "covalent" one reacts with the adsorbed ethylene to produce ethylene oxide. Indeed, the influence of the "ionic" oxygen on ethylene adsorption changes the rates both of epoxidation and of total oxidation of ethylene.

Studying the silver electronic properties in two latter systems (Ag/C, Ag/Al_2O_3) shows that disappearing the "ionic" oxygen on the Ag particles with the mean sizes below 300 - 500 Å is most likely to be determined by worsening of the silver internal conductivity occurring in the same range of the sizes. Indeed, only the "ionic" state of adsorbed oxygen is formed on the single crystals with their perfect conductivity. The "covalent" oxygen formation needs the subsurface oxygen which, most probably, provides the formation of local electronic states in subsurface silver layers. The possible mechanisms for the formation of all oxygen states are also discussed.

The authors acknowledge a financial support from Russian Science Foundation (Grant No 94-03-08294) and International Science Foundation (Grant No RP8000).

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PPC-21

APPLICATION OF ANGULAR DEPENDENT XPS TO STUDY CESIUM OVERLAYERS AT Ag(111) SURFACE

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The fact that the cesium is a main promoter of silver catalysts for ethylene epoxidation explains the attention of researchers to study the Cs overlayers at different silver surfaces [1]. However, the most of these surface science studies have dealt with the bulk samples of silver such as single crystals or powders, while the commercial catalysts represent silver supported on alumina. To avoid this contradiction we have carried out comprehensive XPS and TPD studies of Cs species both on silver supported catalysts and on Ag(111) single crystal [2]. It has been shown that there are two Cs species which are common to both types of the samples studied. One of them is characterized by a $Cs3d_{5/2}$ line with binding energy of 724.2 eV and desorption temperature of about 600 K. The second species ($BE(Cs3d_{5/2})$ = 724.9 eV) is desorbed at much higher temperatures (~ 800 K). The detection of the same Cs species at Ag(111) surface as those on supported silver makes a possible the use of this model system to study their structure. In this work we present the application of angular dependent XPS to tackle this problem.

ADXPS deals with the measurement of the core level XPS intensities when the take-off angle of photoelectrons is changed. Following numeric restoration of the measured angular dependencies of relative XPS intensities to depth concentration profiles has proved to give a quantitative information about structure of subsurface layers. The physical basics and mathematical expressions of this method have been described by us earlier [3].

Before the measurement of ADXPS data we have developed methods of the Cs deposition which allow us to prepare presumably one of the above mentioned Cs species. The Cs deposition on clean Ag(111) surface in vacuum ($P_{base} < 10^{-7}$ Pa) at T = 470 K followed by O_2 adsorption at P = 10 Pa and T = 470 K has been used to produce the low temperature Cs species, while the high temperature species has been prepared by the Cs deposition in O_2 atmosphere ($P = 10^{-2}$ Pa) at T= 470 K followed by heating in vacuum up to 650 K. Special attention was paid in order to obtain identical cesium coverages.

Angular dependencies of the Cs3d$_{5/2}$/Ag3d$_{5/2}$ and O1s/Ag3d$_{5/2}$ intensity ratios have been measured for both species as the samples have been kept at T = 470 K in vacuum. The results of the following restoration of the experimental ADXPS data to depth concentration profiles for Cs, O and Ag are presented in Figure 1.

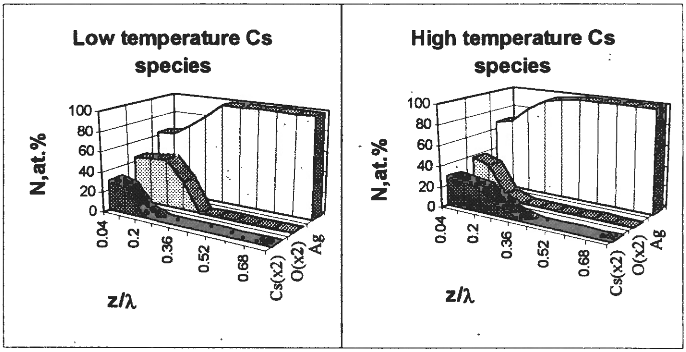

Fig.1. Depth concentration profiles of Cs, O and Ag in terms of at.% for the Cs overlayers at Ag(111) surface.

One can see that although cesium and oxygen have a surface location with respect to silver for both species, however, the relative depths of their distribution are varied. If the oxygen layer for the low temperature species is thicker than the cesium one, so controversial situation is observed for the high temperature species. This fact together with the Cs3d$_{5/2}$ binding energy values allows us to suggest the following structure of these species: the cesium atoms in the former case are bonded with silver surface through oxygen, while direct bonds of the Cs-Ag seem to be formed in the latter case. These results show usefulness of the ADXPS to study the structure of subsurface layers in the model catalytic system.

We would like to acknowledge a financial support form Russian Science Foundation, Grant No. 93-03-4851.

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Experimental and theoretical study of the structure of amorphous and poorly crystallized catalysts by vibrational spectroscopy methods

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Many amorphous or poorly crystallized catalysts obtained via low-temperature synthesis, mechanical activation, etc. cannot be studied by direct (diffraction) structural methods. On the other hand, one can extract a unique structural information from the vibrational spectra after appropriate theoretical analysis. Moreover, vibrational spectroscopy is known to be more sensitive than diffraction methods.

Identifying catalysts with the known structure using their vibrational spectra is the commonly used practice. A wide collection of IR and Raman spectra of reference catalysts was accumulated.

There are empirical relationships correlating changes in the vibrational spectra with those of structural parameters of the compounds under consideration. However, currently most of such relationships have no theoretical substantiation. The latter would allow us to use the vibrational spectra in determining the structure of new compounds.

In connection with catalysis, the theoretical analysis of the spectra has several aspects:

1) factor-group analysis of the perfect structure and simulating the number of IR- and Raman-active vibrations at different occupations of the unit cell sites; simulating different structural defects and their spectral manifestation;

2) analysis of the normal vibration characteristisity and determining the spectral domains responsible for the definite structural fragments;

3) simulating the separate structural fragments by the corresponding molecular models and *ab initio* quantum-chemical calculation of their vibrational frequencies; studying the short-range environmental effects.

Using both theoretical and experimental vibrational spectroscopy allowed us to determine the structure of real catalysts prepared in the Boreskov Institute of Catalysis.

Under special conditions of synthesis the oxide catalysts may include residues of anions. The latter are formed during the catalyst treatment by the reaction medium or originate from the parent phases. The presence of extra anions determines structural features as well as cation distribution in the compound and its catalytic activity.

For instance, under calcining the crystalline goethite, the residual OH-groups hinder the perfect hematite structure (α-Fe_2O_3) formation, the latter occurs through the intermediate metastable phase ("protohematite") containing tetrahedrally coordinated iron atoms. This way of hematite formation is also realized under thermolysis of salts and mechanochemical activation.

The spinel $ZnCo_2O_4$ synthesized at low temperatures starting from the corresponding salts contains residues of their anions. The latter were shown to affect the phase transition temperature and the cation distribution characteristic for the normal spinel.

The cation distribution in the spinel $CuCr_2O_4$ was studied. The Cu^{+2} cations in the tetrahedral sites were shown to disappear as a result of the catalyst reduction.

The formation mechanism of the spinel Co_3O_4 was studied. Effect of the calcination temperature on the cation distribution and the arrangement of extra Co cations in the catalyst structure was determined.

The structure of amorphous product of iron sulfate hydrolisys (being a catalyst in the water oxidation) was determined. One showed that sulfate anions don't enter the first coordination sphere of iron but are retained in the structure by the H-bond system.

The products of mechanochemical activation of copper hydroxocarbonate were studied. This process was shown to be accompanied by the reversible elimination of OH-groups from the first coordination sphere of copper.

Using the vibrational spectroscopy methods to investigate the catalyst structure would be extended provided that the correlations "spectrum - structure" will be substantiated theoretically and the databank of interpreted IR and Raman spectra of catalysts will be created.

This research was made possible in part by Grant No. RAD 000 from the International Science Foundation.

INVESTIGATION OF ACTIVE CENTRES OF NOVEL METAL-CARBON CATALYSTS FOR THE SELECTIVE HYDROGENATION OF UNSATURATED HYDROCARBON

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Up to now, carbonaceous deposition on catalysts has been considered as a harmful process and serious efforts are made to suppress this process. However, now the catalytic carbon is in large demand as a valuable material. Properties of this material depend on the morphology and structure of carbon.

Carbon is deposited as filaments from methane on the nickel-containing catalysts (Ni/Al_2O_3; $Ni-Cu/Al_2O_3$).

The filamentous carbon is used as a catalyst for the selective hydrogenation of unsaturated hydrocarbons. The catalyst consists of carbon filaments and metal monocrystals at their ends.

High resolution electron microscopy (HREM) and X-ray method were used to study the mechanism of a filamentous carbon formation. Metal particles with a 50-500 A diameter initiate the growth of filamentous carbon. Metal crystals are oriented relative to the filament in a partcular way. Diffusion of carbon atoms through the particle is the key step in the mechanism of the filamentous carbon growth. Different faces of Ni crystal act differently during the carbon formation. Thus, (100) and (110) faces initiate the formation of carbon atoms from methane, while the graphite structure is produced at a (111) face.

The hydrogenation properties of filamentous catalysts change as the carbon content varies. At a low C/Me ratio, the catalysts perform the comlete hydrogenation, providing a 100% conversion at room temperature. Raising the C/Me ratio increase the selectivity of the butadiene and acetylene hydrogenation towards alkene.

The reasons of the high selectivity of these catalysts were studied using electron microscopy and x-ray photoelectron spectroscopy (XPS). It has been shown that the shape of nickel particles changes as the C/Ni ratio increases. At low C/Ni, the crystallographic planes (100) and (110) are avialable for the gas reagents. At high C/Ni , only (110) planes are open for the gas reagents, since (100) planes disappear. In both cases, (111) planes are blocked by carbon. The specific mechanism of the filamentous carbon formation causes these changes in the nickel monocrystal faces. At C/Ni >20, the defectiveness of the nickel crystallite enhances. The catalytic activity of such catalysts increases at the approximately constant selectivity. Changes in the shape of nickel particles are accompanied by changes in their electronic properties. Raising the C/Ni ratio results also in the increase in the $Ni2p_{3/2}$ core level binding energy.The Auger parameter conserves. The changes of electronic properties is due to the defectiveness of metal particles. The increase the in Ni2p binding energy may be the reason the observed increase in the hydrogenation rate.

Acknowledgement

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CATALYTIC PROPERTIES OF IONIC/ELECTRON CONDUCTORS INTERFACE AT LOW TEMPERATURE

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In the recent years the number of papers, in which the ionic/electron conductors interface in the environment of various gases is studied, has significantly grown. This is due to advanced application of such systems in heterogeneous catalysis (Non-faradic Modification of Catalytic Activity) and solid electrochemical gas sensors. However, almost all studies were performed at high temperatures.

In this work we studied the effect of composition of ionic (proton and sodium conductive electrolytes) and electron (metallic and semiconducting electrodes) conductors on the rate and mechanism of the processes occurred on three phase ionic conductor/electron conductor/gas boundary at temperature close to the ambient one.

The potential of platinum electrode contacting a protonic conducting solid electrolyte in hydrogen/argon mixture can be described by the Nernst equation for the reaction of hydrogen ionization, is in equilibrium, and is independent of the solid electrolyte composition. In air we found significant deviations from the Nernst dependence caused by formation of the mixed hydrogen-oxygen potential. Both the magnitude of the steady potential and the time of its establishment depend on the composition of the solid electrolyte. All studied protonic conductors can be arrayed in the order of decrease in relaxation rate as follows: heteropoly compounds (HPC) > antimony acid > flavianic acid > hydrated tin dioxide. The highest catalytic activity in the reactions of electrochemical hydrogen oxidation was found in heteropoly acids and their salts with high protonic conductivity. The role played by solid electrolyte is the control of the oxidation degree of platinum that is in contact with it.

In oxygen-free environment the potential of the platinum/HPC interface is practically independent of the carbon monoxide concentration. In air both the rate and mechanism of the processes on three-phase boundary are principally defined by the dispersed condition of platinum. When platinum niello is used, two values of the potential are established. They correspond to oxygen reduction to H_2O and H_2O_2. The change in concentration of carbon monoxide results in jumpwise transition between these states. When spongy platinum or platinum coated on tin dioxide are used, the potential vs concentration of carbon monoxide in air is described by the Nernst equation. In both cases the potential defining process is electrochemical reduction of oxygen to hydrogen peroxide followed by chemical oxidation of carbon monoxide to dioxide.

Electrocatalytical phenomena were also found on interface between sodium conductive solid and semiconducting electrolytes in the presence of carbon dioxides, sulphur, and hydrogen sulfide. Both ionic and electron conductors affect the rate and mechanism of the interaction between gas and solid electrolyte/semiconductor interface. When solid solutions on the base of tin dioxide are used, the adsorption and catalytic properties are cymbate. It was shown that the mechanism of the processes is primarily defined by acidity of electrode surface whereas the equilibrium potential in air depends on the electrode ability to exchange with the bulk of solid electrolyte by minor charge carries (ionized oxygen).

From the preceding results the ways of activating electrochemical processes on three-phase solid electrolyte/electron conductor/gas boundary and the possibilities of using such electrocatalytical phenomena in low temperature electrochemical solid gas sensors are discussed.

The work is supported by the Russian Fundamental Research Foundation, Grant 95-03-0884 .

PPC-25

Silylformylation, and Hydrosilylation of Alkynes Catalyzed by Di-μ-chlorotetrakis[η^2-methylenecyclopropane]dirhodium.

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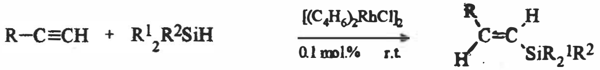
Hydrosilylation of alkynes catalyzed by transition metal complexes yields vinylsilanes, which are the important substances for organic synthesis. There is great interest in silylformylation of alkynes to provide an efficient method for the synthesis of polyfunctional alkenes. Relatively little complexes are known to catalyze this reaction.

Di-μ-chlorotetrakis[η^2-methylenecyclopropane]dirhodium[1,2] was found to be very efficient catalyst for hydrosilylation and silylformylation of alkynes with different silanes.



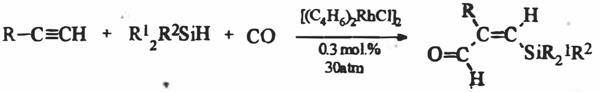
R = Ph, $R^1 = R^2 = Et$
$R^1 = Me$, $R^2 = Ph$
R = $MeOCH_2$, $R^1 = R^2 = Et$
$R^1 = Me$, $R^2 = Ph$

For example, the reaction of phenylacetylene with dimethylphenylsilane is complete in 15 min at room temperature to produce the β-adduct exclusively (Z-/E-=1:2).

The activity of silanes follows the order $PhMe_2SiH \gg Et_3SiH > (EtO)_3SiH$.

Hydrosilylation of internal alkynes occurs rapidly and selectively to form Z-vinylsilanes.

Silylformylation of alkynes in the presence of rhodium complex with methylenecyclopropane proceeds at 30 atm. CO to form two stereoisomeric β-formylvinylsilanes in good yields and a high degree of chemo- and stereocontrol.



R = Ph,	$R^1 = R^2 = Et$	50°C	20h	83%
	$R^1 = Me$, $R^2 = Ph$	20°C	3h	74%
R = C_5H_{11},	$R^1 = R^2 = Et$	80°C	5h	96%
R = $MeOCH_2$,	$R^1 = R^2 = Et$	80°C	5h	68%
	$R^1 = Me$, $R^2 = Ph$	20°C	7h	90%

Dimethylphenylsilane is more active than triethylsilane. In general internal alkynes are less active in silylformylation.

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PPC-26

Novel Catalytic Reactions of Oxidative P–C, P–O, P–N Coupling of Tetraphosphorus to Alcohols, Amines and Nitriles

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The solutions of ROH–ArH–Py, RH_2N–ArH–Py and RCN–ArH–$C_4H_8O_2$ contaning $CuCl_2$, CuL_2, $PdCl_2$, $HgCl_2$, $PtCl_4$, $PtCl_2$ (MY_2) or $AgNO_3$ at 40–90°C rapidly (in 2–8 min) and selectively oxidize even trace (< 10^{-2} mol/l) amounts of tetraphosphorus to give the products of oxidative P–C, P–O and P–N coupling depending on nature of metal and subrate.

$$P_4 + 10CuCl_2 + 16ROH \xrightarrow[-10Cu]{} 4(RO)_3P{=}O + 4RCl + 16HCl \quad (1)$$

$$P_4 + 6CuL_2 + 12ROH \xrightarrow[-6Cu]{} 4(RO)_3P + 12HL \quad (2)$$

$$P_4 + 6CuCl_2 + 12i\text{-}PrOH \xrightarrow[-6Cu]{} 4(i\text{-}PrO)_2HP{=}O + 4i\text{-}PrCl + 8HCl \quad (3)$$

$$P_4 + 10CuCl_2 + 16RCN \xrightarrow[-10Cu]{} 4(RClC{=}N)_3P{=}NCCl_2R \quad (4)$$

$$P_4 + 10CuCl_2 + 16RH_2N \xrightarrow[-10Cu]{} 4(RHN)_3P{=}NR + 20HCl \quad (5)$$

$$P_4 + 10PtCl_4 + 16ROH \xrightarrow[-10PtCl_2]{} 4(RO)_3P{=}O + 4RCl + 12HCl \quad (6)$$

$$P_4 + 10PtCl_4 + 16RH_2N \xrightarrow[-10PtCl_2]{} 4(RHN)_3P{=}NR + 20HCl \quad (7)$$

$$P_4 + 10PtCl_2 + 20RCH_2OH \xrightarrow[-10Pt]{} 4(HOCHR)_3P{=}O + 4(RCH_2)_2O + 20HCl \quad (8)$$

$$P_4 + 10HgCl_2 + 20RCH_2OH \xrightarrow[-10Hg]{} 4(HOCHR)_3P{=}O + 4(RCH_2)_2O + 20HCl \quad (9)$$

$$P_4 + 10HgCl_2 + 16RCH_2OH \xrightarrow[-10Hg]{} 4(HOCHR)_4PCl + 16HCl \quad (10)$$

$$P_4 + 10HgCl_2 + 16RH_2N \xrightarrow[-10Hg]{} 4(RHN)_3P{=}NR + 20HCl \quad (11)$$

$$P_4 + 10PdCl_2 + 20RCH_2OH \xrightarrow[-10Pd]{} 4(HOCHR)_3P{=}O + 4(RCH_2)_2O + 20HCl \quad (12)$$

$$P_4 + 6PdCl_2 + 12i\text{-}PrOH \xrightarrow[-6Pd]{} 4(i\text{-}PrO)_2HP{=}O + 4i\text{-}PrCl + 8HCl \quad (13)$$

$$P_4 + 10PdCl_2 + 16RH_2N \xrightarrow[-10Pd]{} 4(RHN)_3P{=}NR + 20HCl \quad (14)$$

$$P_4 + 20AgNO_2 + 16RCH_2OH \xrightarrow[-20Ag]{} 4(HOCHR)_4PNO_2 + 16HNO_2 \quad (15)$$

$$P_4 + 20AgNO_3 + 16RH_2N \xrightarrow[-20Ag]{} 4(RHN)_3P{=}NR + 20HNO_3 , \quad (16)$$

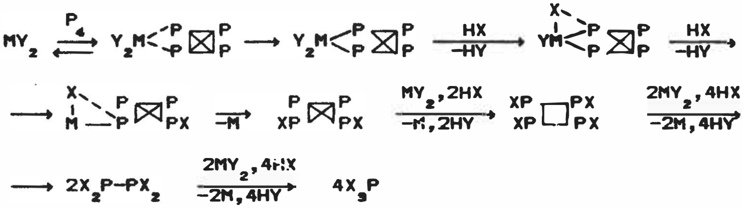
R = Me, Et, Pr, Bu, i–Bu, Am, i–Am, Oct; L = CH_3CO_2, $C_3H_7CO_2$, $C_{17}H_{35}CO_2$; RCN = PhCN, MeCN; RH_2N = i–$PrNH_2$, $C_6H_{11}NH_2$, $PhNH_2$; $PtCl_4$ = Na_2PtCl_6; $PtCl_2$ = Na_2PtCl_4.

Reducted metals are regenereted by O_2(1–4), mixture O_2–HNO_2 (11,12,14), 1,4$C_6H_4O_2$ (7–9), $NaBrO_3$ (6) and electric current. Optimal conditions, kinetics, mechanism, products and intermediates were investigated by ^{31}P NMR–, IR–, UV–, XPS–spectroscopy, GC, redox – potentiometry and methods of chemical modelling, ingibition of radicals, orbital simmetry, CNDO, etc.

Despite of the extremely stressed structure the non-polar tetrahedral P_4 molecule is inert in heterolytic conversions. Tetraphosphorus can be activated by low-valence transition metals as a result of distortion upon η^2-coordination where the edge linked to the metal is lengthened by 11%. High-valence d-metals activate P_4 by means of the P-P bond cleavage resulting in tetraphosphide.

Alkoxyd RO^-, amid RHN^- and imid $RClC{=}N^-$ ions produced from alcohols, amines and nitriles in coordination sphere of $CuCl_2$, CuL_2, $PtCl_4$ react with tetraphosphide-ion to give the products of P-O and P-N coupling excited by complemental reduction of central atom. In coordination sphere of $PtCl_2$, $HgCl_2$, $PdCl_2$ hydroxyalkyl $HOCHR^-$ ions have been formed from alcohols. P-C coupling of tetraphosphide-ion to $HOCHR^-$-ion is stimulated by the synchron complemental demetallation of intermediate complexes.

Mechanistically, the reactions of P-C, P-O, P-N coupling proceed *via* formation of X_3P (17) followed by oxidative phosphorylation (in the case of alcohols) or oxidative imination of latter (in the case of amines and nitriles) (18).



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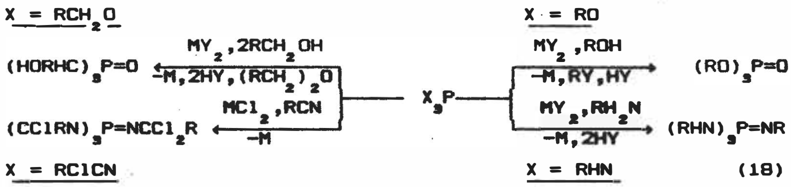

(18)

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PPC-27

BIOMIMETIC OXIDATION OF METHANE TO METHANOL: KINETIC ISOTOPE EFFECT

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Remarkable operation of enzyme monooxygenases (MO) relates to their unique power of oxygen activation over Fe containing sites. MO generated oxygen species can readily incorporate, at ambient conditions, into inactivated alkanes to produce selectively alcohols. Methane monooxygenase (MMO) is a particular case being the only one enzyme of this kind capable of oxidizing even the most inert CH_4 molecule. Progress in understanding the mechanism of MO oxidation greatly depends on developing new biomimetic models. Recently, Fe clusters stabilized in ZSM-5 zeolite matrix have been successfully demonstrated as MMO mimic [1]. They produce, at N_2O decomposition, a new highly reactive form of the surface oxygen (called α-oxygen) providing fast and selective oxidation of methane to methanol at room temperature. In the present work, in order to reveal further similarity to MMO, kinetic isotope effect ($KIE = k_H/k_D$) was measured for the stage of methane interaction with $(O)_\alpha$ preloaded on the surface from N_2O:

$$CH_4 + (O)_\alpha \rightarrow (CH_3OH)_\alpha$$

Experiments were carried out in a vacuum static unit in the temperature range from -50°C to 100°C. Measurements of both intermolecular KIE using $CH_4:CD_4 = 1:1$ mixture and the intramolecular ones using CH_2D_2 mixed isotope were performed. In the latter case the product methanol was extracted from the surface and analyzed for the isotope composition by NMR technique. KIE value was found to very from 6.0 to 1.9 depending on the reaction temperature. Its activation energy (1,2 kcal/mol) corresponds to the difference of zero energies of C-H and C-D bonds whose cleavage occurs at the rate limiting step. Such a high KIE value is typical for monooxygenases, thus confirming a biomimetic type of the oxidation mechanism with α-oxygen.

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Design of Metal Polymer Complex Catalysts with Memory for Catalyzed Substrates

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Macromolecule metal complex catalysts have witnessed a growing interest for the last several years as they combine high activity and selectivity of homogenous complexes with technological advantages of heterogeneous complexes with technological advantages of heterogeneous catalysts.

A number of metal polymer complexes specially prearranged for catalyzing substrate have been obtained and used as selective catalysts. The general principle is based on the use of memory of polymer composition and consists in interaction of non-croslinked complexes with hydrocarbon substrate in solution, i.e. under conditions when macromolecules are still mobile enough. The next step is fixation of the structure of the active centres by intermolecular crosslinking and the third step is removal of the template substrate from the crosslinked system. Crosslinked macromolecules might "keep in mind" conformations advantageous for the template substrate and this should lead to an essential increase of activity and selectivity of metal polymer complex catalysts.

Using this principle a number of metal polymer complex catalysts containing phosphorylic, carboxylic, pyridine, amine and imine functional groups have been prepared and they have been prearranged for catalyzing of liquid phase oxidation reactions of ethylbenzene, isopropylbenzene, cyclohexanone, n-decane and hydrogenation of allyl alcohol. The use of ESR spectra for investigation of polymer complexes has shown significant changes in the structure of prearranged complexes compared with complexes prepared without such prearrangement. Prearrangement provides formation of uniform complexes with structure close to that of their low-molecular analogues in solution.

It has been shown that prearrangement results in significant increase of catalytic activity and selectivity of metal polymer complex catalysts

PPC-29

ADSORPTION AND DYNAMIC BEHAVIOR OF FLUIDS IN MICRO- AND MESOPORES OF CATALYSTS

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The phase composition and diffusion of components adsorbed in micro- and mesopores of catalysts are of particular importance for heterogeneous catalysis. With this regard it is necessary note the increasing role of computational methods of molecular-statistical mechanics [1,2].

This work presents a new version of Grand Canonical Ensemble Monte Carlo (GCEMC) which allows to model simultaneously gas and adsorbed phases in any heterogeneous adsorption and catalytic systems. A conventional GCEMC modeling of adsorption on thermodynamically open surface essentially depends on the volume ratio of gas and adsorbed phases. That is, to model adsorbed layer alone one should regulate the height of simulation box minimizing the gas volume and thus producing almost homogeneous fluid [3]. However, such approach is unsuitable for studying adsorption and catalytic processes in pores because pore geometry dictates the size of simulation box.

With the help of proposed GCEMC version we have selected the parameters of effective potential of the Lennard-Jones (LJ) pair interactions for nitrogen. These parameters are valid for a wide range of surface coverage during nitrogen mono- and multimolecular adsorption. It turns out, however, that at a monolayer coverage below 0.65 it is impossible to select fixed energy e_{sf} of the LJ interaction between nitrogen molecule and support molecule to reproduce adequately the experimental adsorption isotherm on the non-porous solid. We explain this phenomenon by a quadrupole moment of real nitrogen molecule, absence of spherical symmetry and inadequate account for real dispersion and electrostatic interactions (N_2-N_2" and "N_2 - support molecule") of the third and higher order.

The second advance of the present work is an adjusted semiempirical dependence between e_{sf} and the monolayer coverage of carbon surface G, when the latter is below 0.65. The obtained function allows to reproduce in numerical experiment the isotherm of nitrogen adsorption on carbon black "Vulcan" at 77.4K and at relative N_2 pressures varying from 10^{-6} to 0.99.

We used the new version of GCEMC together with obtained $e_{sf}(G)$ function to study nitrogen adsorption and capillary condensation at 77.4K in the slit micro- and mesopores with walls possessing graphite properties. Such experiments are important for the practical characterization of porous structure of carbon-based catalysts and supports by nitrogen low-temperature adsorption. With this approach we show quantitatively and, in part, qualitatively that the popular nonlocal density functional theory is somewhat inadequate [4]. In particular, numerical adsorption experiments in micropores prove the absence of a "layering" transition before capillary condensation reported in [4]. The irreversible capillary condensation starts in larger pores and occurs at higher adsorbate vapor relative pressures (P/P_S), than is predicted in [4]. Moreover, adsorbate density in micro- and mesopores is stable and does not raise starting from some definite P/P_S value, in contrast to [4].

We were the first to observe and thoroughly verify a new phenomenon: in micropores with a size of 1.8-2.2 nitrogen LJ diameters, starting from some P/P_S, a stable solid film forms which comprises strictly localized molecules. We have shown that this phenomenon really occurs by molecular dynamic experiments with the GCEMC produced molecular configurations. Moreover, the foregoing range of slit pore sizes can be divided into some subintervals. For each of them the number of molecules in micropores remains the same. In going from one subinterval to another the number of molecules in a micropore changes stepwise: the number of molecules added or removed is strictly specified for the two given neighbouring subintervals.

We obtained the table of relative pressures at which the smallest mesopores are filled. One can use this table to calculate the pore size distributions of carbon-based catalysts and supports.

Authors thank financial support from RFSF (project 93-03-4809).

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PPC-30

LOW-TEMPERATURE CATALYTIC OXIDATION OF H_2S ON METAL-CONTAINING VION-FIBRE

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The new catalysts providing oxidation of H_2S into elementary sulfur at room temperature with high velocity has been proposed. This catalyst contains transition metals sulfide complexes immobile on the synthetic fibre in swollen state.

Catalysts were investigated at 291 to 333 K, space velocities were adjusted up 10^4 h^{-1} and H_2S concentration range was 0,1-10 vol.%. pH of swollen state catalysts was varied from 6 to 12. IR and ESR methods were used.

The catalytic activity, kinetics and oxidation mechanism has been investigated. At high H_2S concentration the catalytic activity has been reduced exponentially because of geometrical blocking of active catalytic sites by sulfur atoms. This process is reversible.

These studies showed that homogenous reaction mechanism takes place at low temperature catalytic oxidation of H_2S on metalconteining VION-fibre. Catalysts containing Mn, Cu, Ni - sulfide complexes have activity and mechanical resistance to wear.

"Correlation of peroxide radical formation rate with the number of paramagnetic centers (PC) on the surface of massive oxides of IVth period transition metals (IVptm) "

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During the oxidation of normal alcohols over the surface of the IVtpm oxides, the rate of desorbed radicals formation, W_{RO2}, increases, if the partial pressure of hydrocarbon exceeds that of oxygen. The rate increases at most, when hydrocarbon/oxygen ratio is 1/1 [2]. Some preliminary investigations of catalysts subjected to the reaction show that as the IVtpm oxide is reduced in reaction, the number of active sites increases [1,2]. It is known that the oxides can be divided into two groups. The first group comprises hardly reducible oxides. Reduction affects only a few surface levels. We explored such ZnO, Cr_2O_3 and TiO_2, belonging to this group. The second group unites easy reducible oxides. The reduction of these oxides causes not surface changes alone, but also a new phase formation. To this group such oxides as V_2O_5, MnO_2, Fe_2O_3, Co_3O_4, NiO and CuO belong, that we studied as well. The oxide reduction produces localized electron states, which are supposed to relate to some active sites forming during the reaction. These sites are often paramagnetic.

In this work we use the ESR method to explore the correlation of W_{RO2} with the number of PC on IVtpm oxides, activated in reaction course. These PCs were activated during the oxidation of n-propanol. Activation was made by oxygen with the reagent ratio 1/1 at 500C and total pressure 0.1 torr. The use of ESR technique has an inherent limitation. The oxides must have an insufficient quantity of biographical PC after the treatment. (The treatment consists in exposing the catalyst to oxygen at 520C and 1 torr for 1 hour.) Due to the limitation we choose ZnO and TiO_2 among the first group oxides and MnO_2, Co_3O_4 and NiO among the second group ones. To preserve the active sites we quickly cooled the catalyst after reaction in the reaction mixture to room temperature and vacuumed it to 10^{-3} torr. The ESR spectra were recorded at 300K or at 77K. In order to determine the place of PC localization, the registration was conducted both with oxygen and without it. The concentration of PC and spectral parameters were measured using Mn^{+2}/MgO standards. The PC, formed during reaction on ZnO and TiO_2 could be identified as O_2, stabilized in the anion vacancies on the catalyst surface. The increase of their concentration correlates with the increase of W_{RO_2}.

The reduction of NiO and Co_3O_4 causes a fast formation of conductive phase. Due to this fact we failed to investigate a time correlation of W_{RO_2} with these changes.

It was found that the MnO_2 reduction goes much slower. Like other oxides of the second group this catalyst undergoes some structural transformation: $MnO_2 \Rightarrow Mn_2O_3 \Rightarrow Mn_3O_4 \Rightarrow MnO \Rightarrow Mn$ [3]. The free energy change for the last step (79kcal) exceeds the total free energy change of three previous steps (45kcal). Such a change is probably not reimbursed by the free energy of product formation, since a single line of Mn^{+2} ion was observed in the spectra during whole experiment. During the first 4 hours of reaction the line width decreases from 80 mT to 60 mT. During this time only a 0.001 part of ions transforms to Mn^{+2}. The integral intensity of ESR signal also increases synchronously with the W_{RO_2} increase in this case. The possible nature of sites active in the RO_2 formation is discussed.

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OXIDATION OF 1,3-PENTADIENE TO 2-METHYLFURAN: A MODEL REACTION TO MODIFY BI- AND POLYCYCLIC DIENES

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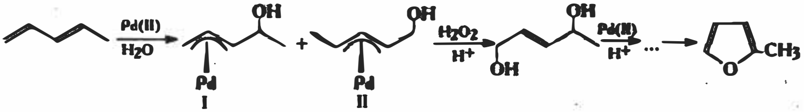
Bi- and polycyclic dienes such as the products of allylation of 2,5-norbornadiene are useful auxiliaries for organic synthesis and may act as accumulators of solar energy. Modification of these compounds by partial oxidation is an interesting process from both practical and mechanistic point of view.

One of the simpliest models for such a reaction is Pd(II)-catalysed oxidation of 1,3-pentadiene to 2-methylfuran in aqueous H_2O_2 solution.

The reaction mechanism was studied by a number of physico-chemical methods (GLC, ^1H NMR, mass-spectrometry, IR-spectroscopy, potentiometry) and can be expressed in the form of the following scheme:



Noteworthy, isomeric complexes I and II possess equal reactivity in oxidation to 2-pentene-1,4-diol. Kinetics of this process was investigated within the range of pH=1÷5 [1,2]. In neutral and weakly acid solutions oxidation of I and II proceeds without breaking of Pd-C bond [3]. This remarkable process is likely to include radical intermediates.

The ways and means of obtaining 2-methylfuran with high yield as well as the effect of reaction conditions on regioselectivity of the process will be discussed.

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PPC-33

Study of the Reactivity of Molybdenum Oxide Cluster Ions $Mo_xO_y^+$ with Some Small Molecules in the Gas Phase using Ion Cyclotron Resonance Speectrometry

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Transition metal oxides have a wide variety of industrial applications in electrochemical processes, electronics and catalysis. The importance of these compounds has promoted a growing number of gas-phase investigations of physical and chemical properties of metal oxide ions. For these studies the number of mass-spectrometric methods were used including the ion cyclotron resonance (ICR) spectrometry. Metal oxide cluster ions in the gas phase can be considered as a model of active sites of heterogeneous oxide catalysts. So, the study of reactivity of $M_xO_y^+$ ions can give information on detailed mechanisms of proceeding processes.

A method for generating of $M_xO_y^+$ ions in ICR cell using the effusion chamber (Knudsen cell) was developed. Knudsen cell (900K) was placed directly on the trapping plate of ICR cell. $Mo_xO_y^+$ ions were formed by electron impact (70eV) of the vapor of the sample of MoO_3. ^{98}Mo (97%) isotope was used to simplify the analysis of ICR spectra.

The combination of high temperature Knudsen cell with standard cubic trapping ICR cell results in formation of polymeric molybdenum oxide ions $Mo_xO_y^+$ ($x = 1$-4, $y = 1$-12) with a great number of oxygen atoms.

The ion-molecular reactions of $Mo_xO_y^+$ ions with carbon monoxide, methane, c-C_3H_6 and ammonia were studied. It was found that molybdenum oxide ions with a great number of oxygen atoms are the most unreactive, probably, due to their coordinate saturation. They exhibit only H atom abstraction reactions in interaction with NH_3, CH_4, c-C_3H_6. Oxygen deficient molybdenum oxide ions react with c-C_3H_6 yielding molybdenum oxo carbenes. The reactivity of $Mo_xO_y^+$ with different number of metal atoms is the same. So, the formation of metal carbenes does not depends on the size of metal particle.

The interaction of $Mo_xO_y^+$ with CO leads to the destruction of polymeric molybdenum oxide ions due to great gain in energy during CO_2 formation.

Molybdenum oxide ions containing three metal atoms react with ammonia via the loss of some oxygen ligands and by formation of some nitrogen containing species up to $Mo_3O_7(N)_2^+$. The detailed study of the mechanism of this reaction can be possibly useful for elucidation of the problem of nitrogen fixation.

RELATIONSHIP BETWEEN ELECTRON-ACCEPTOR PROPERTIES AND SURFACE STRUCTURE OF ALUMINA STUDIED BY ESR AND IR SPECTROSCOPY

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The alumina, especially low-temperature modifications, is widely used as the catalyst component. Some of the important data on the surface properties of alumina were obtained by ESR-spectroscopy of adsorbed 2,2,6,6-tetramethyl-piperidine-N-oxyl (TEMPO) and anthraquinone [1,2] and IR-spectroscopy of adsorbed carbon monoxide [3,4]. However, direct comparison of the ESR and IR data on the Lewis acid sites (LAS) of the alumina has not been made. Nevertheless, it might be very useful for understanding of the LAS structure.

It is known that TEMPO forms a complex with LAS on the dehydroxylated surface of alumina. The ESR spectrum of this complex has hfs from both ^{14}N and ^{27}Al. The similar spectrum is observed in case of the complex TEMPO-$AlCl_3$ formation. On the basis of this coincidence the important conclusion has been made earlier [1]: LAS, which form the complexes with TEMPO on the alumina surface, are three- coordinated Al^{3+} ions. These LAS are non uniform. The value of a_{Al} varies in the range 10.2 -11.7 G [2] with the dehydroxilation temperature and the crystal structure of Al_2O_3.

The IR spectroscopy of adsorbed carbon monoxide is convenient method for investigation on the alumina surface. This method also shows the non uniformity of LAS. The study on adsorption of TEMPO and CO on the equally pretreated alumina samples proved the correlation a_{Al} and ν_{CO} (see Table).

It is known that anthraquinone upon adsorption at 393 K is able to form paramagnetic donor-acceptor complex with coordinatively unsaturated (CUS) Al^{3+} ions. It was shown [2] that anthraquinone and TEMPO formed complexes with the same LAS. We adsorbed CO on the alumina sample with pre-adsorbed anthraquinone. It has been found that there are no IR bands of adsorbed CO (p=5 Torr) in the case of this sample.

Sample	a_{Al}, G	ν_{CO}, cm^{-1}
γ-Al_2O_3, after calcination at 973 K, pyridine adsorption at room temperature and desorption at 573 K.	10.2	2200
0.9 % wt NaOH/γ-Al_2O_3, after calcination at 773 K	10.3	2205 [5]
5.7 % wt H_3BO_3/γ-Al_2O_3, after calcination at 773 K	10.6	2214
γ-Al_2O_3, after calcination at 773 K	11.5	2235
η-Al_2O_3, after calcination at 773 K	11.7 [2]	2242 [3]

Thus, the results of the present investigation allow to conclude that carbon monoxide, TEMPO and anthraquinone form complexes with the same LAS. These LAS are three-coordinated Al^{3+} ions (as determined by TEMPO adsorption). They are disposed regularly and have high local concentrations (as determined by anthraquinone adsorption).

In accordance with the crystallographic model of the structure (proposed by Knozinger et al. [6]), such conditions can be realized on the dehydroxylated (111)A and (110)C planes. We propose that two bands 2230-2245 cm^{-1} and 2200-2215 cm^{-1} in the IR spectra of CO, adsorbed on alumina, can be explained by the presence of two families of three-coordinated aluminium ions, which belong to (111)A and (110)C planes, respectively. The differences in the electron-accepting properties among one family of CUS Al^{3+} ions are determined by the structure of the second coordination sphere, formed by hydroxyls, oxygen atoms and vacancies of the external oxygen layer.

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PPC-35

KINETIC AND MECHANISTIC STUDY OF NORBORNADIENE ALLYLATION CATALYSED BY Ni(0)-PHOSPHITE COMPLEXES

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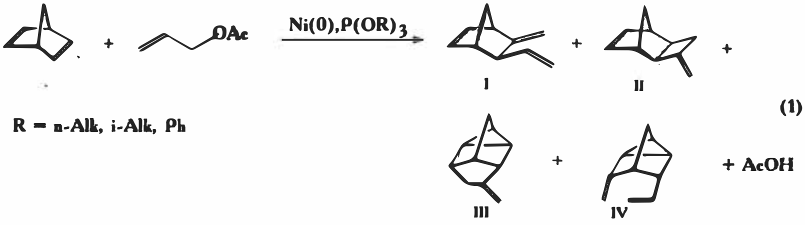
Nickel phosphite complexes are know to be unique catalysts of regio- and stereoselective allylation of 2-norbornenes and 2,5-norbornadienes (NBD) [1,2,3].



$$NiL_4 \rightleftharpoons NiL_3 \rightleftharpoons NiL_2 \rightleftharpoons NiL \qquad (2)$$

$L = P(O\text{-}i\text{-}Pr)_3$, Solvent: benzene

Among the ligands of phosphite series only tertiary ones form catalytically active complexes when coordinated to the nickel center, triisopropylphosphite affording the best results.

^{31}P NMR kinetic study of the allylation elucidated the formation of nickel complexes containing different number of ligands in coordination sphere. The equilibrium (2) was investigated and equilibrium constants obtained showed that NiL_3 species are the most stable. NiL, NiL_2 and NiL_3 selectively catalyse the formation of I, II and III respectively, while NiL_4 is unactive. Adduct IV was obtained in trace amounts. This information enabled us to select the reaction conditions which are suitable for the preparation of each allylation product.

A detailed investigation of the mechanism of reaction (1) by kinetic and spectral methods (^1H NMR, mass-spectrometry) indicated that hydrogen transfer occurs at the key step of the reaction. The study of structures I-IV suggests that the allyl protons (II, III) as well as the proton of norbornadiene ring (I, IV) may take part in hydrogen transfer. It seems possible that hydrogen transfer in compounds I-IV occurs in the presence of nickel catalyst.

The model system $Ni(C_3D_5)$-NBD and $Ni(C_3H_5)$-NBD(D_8) serve to illustrate a elementary catalytic act of reaction (1). A remarkable feature of this step is that the allyl fragment accepts hydrogen forming propylene or its adduct with NBD.

A high value of kinetic isotope effect $K_H/K_D = 3.6$ is the evidence for the intramolecular character of hydrogen rtansfer and the formation of fairly stable hydride intermediate.

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CONCEPT OF MANY-COMPONENT ACTIVE CENTER FOR METALLOCOMPLEX CATALYSTS OF POLYMERIZATION

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From beginning of 1980s fields of research in Ziegler-type catalyst systems, consisting from a organometallic zirconium complex (Zr) and polymethylalumoxane (MAO), are promptly developed. It is due to as high efficiency of such systems in polymerization [1], as to a possibility stereoregular polyolefins [2] and various copolymers to be synthesized [3]. A stimulus for studying such systems is also their solubility, which permits to hope on more detailed, in comparison with heterogeneous systems, studying a structure and ways of formation of active sites.

By now, various models of an active site for this system, as simplified, as approaching on a structure to real catalyst particles, have been advanced and investigated [4-7].

However, from binary (Zr + MAO) models of centres and constructed on their basis kinetic models, which have been suggested, it is not menaged from the uniform point of view to justify all variety of kinetic regularities, unless a new assumption involves for each case.

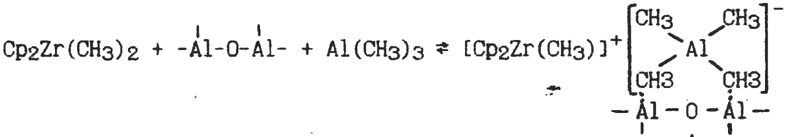
The purpose of the present work is to investigate experimentally this system using a wide range of components concentration, to construct the multicomponent active centre, as well as mathematical models, describing its formation and polymerization kinetics.

The kinetics of ethylene polymerization with (Cp_2ZrCl_2 + MAO) and ($(Cp_2ZrCl)_2O$ + MAO) systems have been studied, the zirconocenes concentration being varied in the experiments a ten thousand times [8]. As the Zr concentration increases the polymerization rate (W) increases, passes through maximum and then decreases. For rising branch of curve W does not depends on MAO and $Al(CH_3)_3$ concentrations, and for descending branch W depends on these parameters. It have been studied the transition regimes of polymerization kinetics which appear on impulsed adding of components in the course of polymerization. On $(Cp_2ZrCl)_2O$ addition at rising branch a new level of quasistationary rate of polymerization is set at intervals of approximately 15 min., and at descending branch - "instantly", less than 1 s.

As a result of alkylating of the zirconocenes under consideration the same "pre"catalyst, Cp_2ZrMe_2, is formed, therefore the rates of polymerization are virtually equal for both zirconocenes [9].

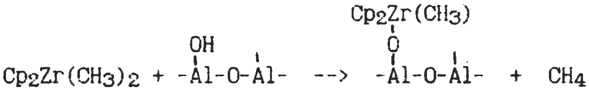
Quantum chemical calculations of models of Al-containing fragments for active site were performed, and composition as well as the pathways of formation of cation-like (A) or protonated (B) active site were proposed.

The center A arises on interacting $Cp_2Zr(CH_3)_2$, $Al(CH_3)_3$ and MAO components:



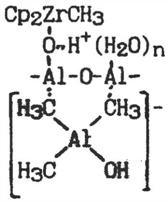
A

The center B is formed on participating fragments $-O-Al(OH)-O-Al(CH_3)-O-$ arising yet at the MAO synthesis (IR-spectrum of MAO used in this study reveals hydroxyls) or on later interacting MAO with H_2O. It is possible to suggest, that at the interaction of $Cp_2Zr(CH_3)_2$ with the OH-containing "active" segment of MAO, the Zr-O-Al bridge arises, being key cell at the process of formation of an active center



$$Cp_2Zr(CH_3)_2 + -\overset{\overset{OH}{|}}{Al}-O-\overset{|}{Al}- \longrightarrow -\overset{\overset{\overset{Cp_2Zr(CH_3)}{|}}{O}}{\overset{|}{Al}}-O-\overset{|}{Al}- + CH_4$$

According to [10], activation of supported catalysts occurs as a result of protonation of bridged oxygen of surface complexes. The similar way of activation can be also suggested in this case. Protonated complex with Zr-O-Al bridge may be assumed to have a such structure:



(B)

Mathematical models describing the process of active center formation from Zr, MAO and additional cocatalysts which are trimethylaluminum and water (specially adding into the system or being contained both in MAO and in other parent components of the catalyst system) as well as kinetics of polymerization have been constructed. This models are enable to describe the set of experimental data: the shape of curves W([Zr],[MAO]), the characteristic properties of the transition regimes, active impurity sensitivity (including sensitivity to incontrollable impurities) of W as well as need in the great excess of MAO (MAO:Zr = 100-10000) for efficient polymerization.

Theory and experiment reveal that the kinetic profile W(t) does not coincide with the kinetics of termination as, for many-component active center, not only forming inactive compounds of a transition metal is of importance, but trapping by these compounds of a portion of cocatalysts should be also taken into account. Particularly, under the certain conditions, polymerization rate and the number of active centers are constant in spite of inactive Zr(III) to form.

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Role of the Acid-Base Centres of SnO_2-catalysts in the Oxidative Dimerization of Methane.

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The oxidative dimerization of methane in one of the most promissing synthetic method for ethylene and fuel from natural gas. There exist an opinion that the methane activation are followed either by the geterolytic C-H bond cracing with participation of surface acid and basic centres or the gomolitic C-H bond cracing tookes place.

In order to detalized the reaction mechanism the acid-basic and catalytic properties of tin(IV) oxide catalysts, modified by K, Na, Li, Ca, Sr, Ba oxides (10%mas) are examined. The surface acid-basic centres are studied by temperatun-programmed desorption method by using probe-molecules CO_2 and NH_3.

The summarized (average) information about surface site properties, found out by potentiometric titration method in unaqueous media.

The IR-Fourier spectroscopy is used to study the adsorbed CO_2 probe-molecules and analysis of UV-absorption bands is made for the basic centers on pure SnO_2 and catalysts prepared basing upon SnO_2.

The IR spectra of CO_2 adsorbed on SnO_2 surface permit to distinguish at least three types of basic centres. Analysis of these spectres demonstrates than on SnO_2 surface bicarbonade compounds characterized by a.b. 1720 sm^{-1} are formed with participation of surface OH^--groups; also, monodentante (v_{asCOO}-1500 sm^{-1}) and bidentante ($v_{asC=O}$ 1610 sm^{-1}) surface complexes are formed with participation of surface basic oxygen

The catalysts on the SnO_2 base containing Li_2O and CaO as promoters are more active and selective for the ethylene synthesis comparing to the pure SnO_2. The most effective and selective Li_2O-SnO_2 catalyst are charactirized by a wide set of basic sities differing in the strenght and nature. There are five types of basic sites on Li_2O-SnO_2 catalyst: surface hydroxel groups and surface basic oxygen in different states.

There is a decrease in frequencies $v_{C=O}$, relating to vibration in bidentante carbonate on the Li-catalyst that indicates a lowering of covalence on the Me-O bonds, that is an increase in basicity of oxygen.

Correlation between catalytic and acid-basic properties of SnO_2 containing catalysts is estimated.

Oxyreforming of methane over Pt electrode in a solid oxide fuel cell.

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In the recent years much attention was given to investigation of catalytic oxyreforming of methane: $CH_4 + 0.5O_2 \rightarrow CO + 2H_2$. This reaction proceeds at high temperatures over supported metal catalysts, including the supported platinum-containing catalysts [1]. Oxyreforming of methane seems to be a promising process to produce a fuel for solid oxide fuel cells (SOFC) utilizing natural gas.

This paper is devoted to the studies of oxyreforming of methane on a platinum electrode-catalyst in a high temperature cell with a solid oxygen conducting electrolyte, *viz.* yttria stabilized zirconia (YSZ). Schematically, such a cell is similar to SOFC:

$$CH_4 + O_2 + N_2, \text{Pt} \mid 0.9ZrO_2 + 0.1Y_2O_3 \mid \text{Pt, air.}$$

The goal of the work was to study properties of the Pt electrode-catalyst with respect to catalytic oxyreforming of methane and electrochemical oxidation of the oxyreforming products (H_2 and CO).

SOFC is a YSZ electrolyte tube, in which porous Pt electrodes containing 5 wt % of YSZ are supported on the inner and outer surfaces. The geometrical area of the electrodes was 3 cm^2, and their thickness was ca.10 μm. The experiments were carried out at atmospheric pressure within the temperature range of 550÷800°C under open and closed circuit conditions. The velocity of the reaction mixture flow, containing 3.5÷12 vol % of methane, was varied between 0.5 and 1 cm^3/s. CH_4/O_2 ratio was 0.6÷2.

The Pt electrode was found to be an active electrode-catalyst for oxyreforming of methane and electrochemical oxidation of the oxyreforming products at 750÷800°C. The typical experimental results are presented in Figs.1 and 2.

Fig.1 shows conversion of CH_4 and yield of CO *versus* the inlet concentration of methane during the methane oxidation at the constant inlet concentration of oxygen under the open circuit condition. Only the reaction of complete oxidation of methane (X_{CH_4}=100%, Y_{CO}=0) is seen to occur at low methane concentrations (or $CH_4/O_2 \approx 0.5$), whereas syn-gas is observed in the reaction products at a higher methane concentration (or $CH_4/O_2 \approx 1÷2$) with the 64% yield of CO and $H_2/CO \approx 2$.

In Fig.2 the cell voltage and concentrations of H_2, CO, and CO_2 are plotted against anodic current (or oxygen flow through the electrolyte into the reaction zone); the values were measured at CH_4/O_2 ratio of 0.75 in the reaction mixture fed to the Pt electrode. Practically 100% conversion of CH_4 and O_2 were observed under the open circuit condition (I=0) due to catalytic oxidation of methane, and only H_2, CO, CO_2, and H_2O were detected in the outlet mixture.

An increase in current up to 220 mA is seen in Fig.2 to result in lower outlet concentrations of CO and H_2, as well as in a higher concentration of CO_2 and an increase in the cell voltage, with respect to their open circuit values. There are observed no carbon monoxide and hydrogen at I=220 mA, and a potential jump is seen in the curent-voltage curve. Upon further increase in current, the concentration of CO_2 reaches a plateau, and oxygen appears in the gas phase.

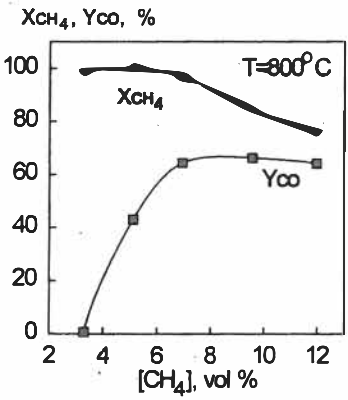

Fig. 1. Effect of inlet CH_4 concentration on CH_4 conversion (X_{CH_4}) and CO yield (Yco) at oxidation of methane over Pt electrode under open-circuit condition. Reaction mixture flow rate is 0.5 cm^3/s, inlet concentration of oxygen is 6 vol %.

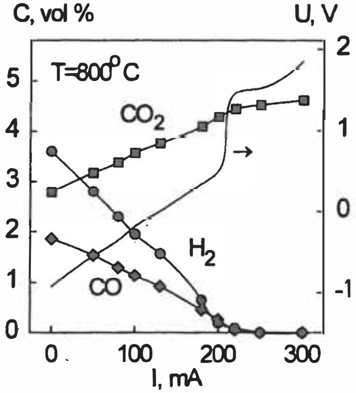

Fig. 2. Effect of anodic current on cell voltage (U) and outlet concentrations (C) of CO_2, CO and H_2 at oxyreforming of CH_4 over Pt electrode exposed to 4.9 vol % CH_4 + 6.5 vol % O_2 + 88.6 vol % N_2 inlet mixture. Reaction mixture flow rate is 0.5 cm^3/s.

An analysis of these results and similar dependences obtained under different experimental conditions allowed the conclusion that during an anodic polarization of the Pt electrode, oxygen supplied to the reaction zone is mainly consumed for electrochemical oxidation of the methane oxyreforming products (H_2 and CO), and only Faradaic increase in the rate of methane conversion is observed. In fact, this is an evidence that the Non-Faradaic Electrochemical Modification of Catalytic Activity effect [2] does not take place in this catalytic system.

The data obtained are the basis for discussions on the mechanism of methane oxyreforming and on the prospects for SOFC with internal oxyreforming of natural gas.

The work was funded by Russian Foundation for Basic Research (Project 93-03-5097) and INTAS (Project 94-3056).

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PPC-39

Hydrodechlorination of Carbon Tetrachloride.

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Hydrodehlorination of hydrocarbons is as a rule non-selective process. That is why the useful utilisation undesirable products are practically important. The problem of utilisation carbine tetrachloride in particular become very actuality because of "The Montreal Protocol on Substances that deplete the Ozone layer" that doesn't allow to use freons. One of the ways of utilisation of carbon tetrachloride is the process of hydrodechlorination. From the other side this process is one of the simplest process of this class, that define the theoretical sense of that investigation.

It's been tested the influence of platinum concentration and of size particle of metal applied on the gamma aluminium oxide on catalytic property of sample. Two samples of catalyst were prepared: F-5 with 0.4% and F-7 with 3 %w. of Pt. Distribution of Pt on catalyst granule, estimated with $SnCl_2$ solution, was homogenous.

Catalytic properties were studied in the flow reactor under the 60-150 C.

It's found that the catalyst F-5 had a low selectivity by $CHCL_3$ (about 40%). $C_2H_3CL_3$ and CH_4 were the main by-side products. Selectivity was about 50% and 10% correspondingly. The additions of water vapours decreased the $CHCL_3$ selectivity.

Under the increasing of Pt concentration (sample F-7) the rate of transformation of $CHCL_3$ per atom of Pt didn't change. But the selectivity by $CHCL_3$ increases till 65% and under the same method of treating of catalyst it can reach 85%.

The result of kinetic investigation combining with data of TPR, TPO and TEM allows to conclude that CCL_4 hydrodechlorination is a structure sensitive reaction.

The data about the kinetics of investigated reaction were got by the flow-circulation method on the samples with about 0.5% w. Pt. The reaction was carried out upon the excess of hydrogen upon the temperatures 60-120 C. The partial pressures of CCL_4 and HCL changed by the variation of flow CCL_4 to the unit and contact time.

The result shows that the rate of reaction is proportional to the concentration of CCL_4 and inversely proportional to the square root of concentration of HCL.

The temperature dependence of rate constant corresponds to the activation energy equal to 9,3 Kcal/mol. The lower value of temperature's dependence that the known from literature (about 19 Kcal/mol) can point to important role of the mass transfer process in granule.

This work is part of INTAS project N 13-1382.

PPC-40

THEORY OF CREEPING FAST AND SLOW HEAT FRONTS IN A CATALYST FIXED-BED WITH A REVERSIBLE REACTION

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A family of unsteady-state processes in fixed catalyst bed reactors using the creeping heat front phenomenon has been developed at BIC. The heat front is a spatiotemporal structure, that can form and exist in the catalyst fixed-bed during the infinite time as a result of self-organization. We have analyzed qualitatively and quantitatively basic regularities for creeping heat fronts in the catalyst fixed-bed, when a single reversible first order reaction proceeds. The simplest pseudo-homogeneous mathematical model used for a theoretical investigation takes into account convective heat and mass transfer, effective axial heat conductivity of the grain bed, exothermal chemical reaction proceeding and fixed-bed heat inertia [1,2].

In a coordinate system moving with the heat front this model is a system of two ordinary differential equations. According to the theory of dynamical systems on plane [3] a bounded solution of the problem under consideration (if it exists) converges in infinity to a singular point of the system - to an equilibrium point. It was proved in the case considered that there is unique inflection point, I, on equilibrium curve. A singular point of the system can be either a saddle point or a stable node.

It has been shown that if the inlet temperature is low enough for chemical reaction rates to be negligible (though chemical reaction affinity is non zero) a heat front forms, whose creep velocity (ω) is less than the heat mark transfer velocity. These fronts are considered as slow heat fronts (SHF). In SHF the reaction mixture comes in a thermodynamic equilibrium state with high temperature. The structure, maximum temperature and velocity of SHF are determined by the heat and mass exchange processes in the catalyst bed and by the chemical reaction kinetics.

If the inlet conditions correspond to a point of the equilibrium curve (T_o, C_o^*), but T_n - the initial temperature of catalyst - is other than T_o, a fast heat front (FHF) forms, whose velocity ω is higher than the heat mark trasfer velocity.

FHF moves only in one direction with the gas stream. If the inlet conditions correspond to inflection point I, FHF shown to exist at any T_n. Otherwise, there is interval of temperatures T_n containing I, where FHF does not exist. FHF velocity ω is calculated directly from the integral laws of mass and energy conservation and does not depend on heat and mass exchange processes in the catalyst bed and on the chemical reaction kinetics.

We have obtained equation for entropy production in the heat front using methods of non-equilibrium thermodynamic. The surface of local entropy production has been studied in the FHF and SHF. We have shown the local entropy production to be equal to zero at plus and minus infinity and to be a positive function in the heat front.

The heat waves classification on FHF and SHF introduced in [1] corresponds to definition of the automodel solutions of the first and the second type used in [4].

ACKNOWLEDGEMENT

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PPC-41

Role of Rotation in Low-Temperature Dissociative Recombination of Electrons with Hydrogen Molecular Ions.

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The dissociative recombination (DR) process

$$e^- + XY^+ \longrightarrow X + Y \tag{1}$$

is investigated at low temperatures of electrons e^- and molecular ions XY^+ with taking into account both direct and resonance (i.e. corresponding to the formation of intermediate Rydberg complex XY^{**}) mechanisms.

The paper seeks to study the influence of molecular rotation and nonadiabatic electron-rotational coupling on the cross section and the rate constant of reaction (1). It seems to be especially important for hydrogen-containing molecular ions (XH^+) which possess the small moment of inertia. The rotational constants of such ions are of the order of magnitude $B \sim 10^{-4}$ a.u. and the first threshold of excitation is reached already at the thermal electron energies.

The problem was solved in the framework of integral variant of Multichannel Quantum Defect Theory (MQDT) where the equations are formulated directly for the collision T-matrix. The particular calculations were carried out for para-modification of H_2^+ ion.

The influence of initial rotational excitation is visually demonstrated in Fig.1 and Fig.2 where the partial cross sections σ_{3N} and the corresponding rate constants $k_3(T_\epsilon, N)$ are presented for vibronic quantum number $v = 0$ and three values of rotational quantum numbers $N = 0, 2, 4$. They are marked by diamonds ($N = 0$), triangles ($N = 2$), and circles ($N = 4$). As it is obvious from the figures, with the increasing of N the cross section function is moved to the left side of electron energy axis. The shift quantity equals to the value of rotational excitation threshold $BN(N+1)$. In addition, the cross section and the rate constant at $N = 2$ are approximately one order of magnitude greater than the ground state ones.

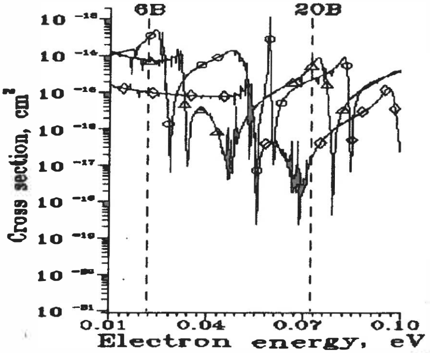

Fig.1

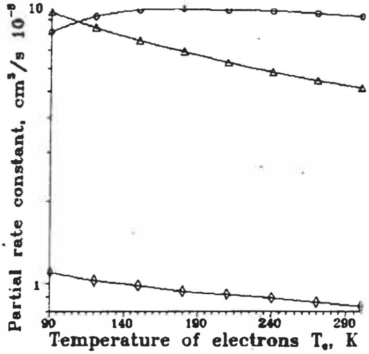

Fig.2

The ion and electron temperature dependences of total rate constant for the reaction $e^- + XY^+$ are shown in Fig.3. It follows from this figure that the total rate constant levels out when the electron temperature increase, i.e. the initial rotational excitation have a weak effect on curve profile. The maximum of these functions is reached at $T_i \simeq 200K$. Further one can see the smooth decreasing which can be explained by the behaviour of rotational partition function for para-modification of hydrogen molecular ion.

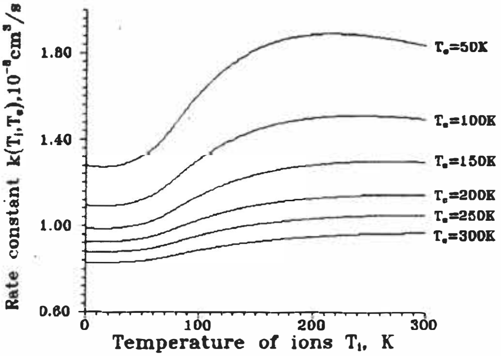

Fig.3

PPC-42

COMBINED CLASSIC AND QUANTUM MECHANIC APPROXIMATION TO CALCULATE SURFACE REACTIVITY OF COVALENT SOLIDS

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Proposed recently the Method of Local Self-Consistent Field (LSCF)[1], giving the possibility of mixed classical and quantum- mechanical calculations on very large molecular systems has been updated on the calculations of adsorption and catalytic properties of a covalent oxides surface at the MNDO-AM1 and the MNDO-PM3 approximations. The original LSCF version has been modified by the transfer of geometric and charge values from quantum-mechanical to classical subsystems.

The parameters of LSCF method are:

i)The characteristics of a strictly localized bond orbital representing two electrons in each bond separating the quantum-chemical subsystem and the neighboring atoms;

ii)the charges of classical atoms;

The parameters are adjusted on bulk of solid by imposing self consistency between the values of charges in quantum and classical subsystems.

The first implementation of the LSCF method has been performed on the calculations of some geometric and energetic parameters of (010) a-cristobalite face. The sets of pre-calculated parameters are defined from the calculations of pseudo-cubes, containing of 1500 -15972 atoms. The conclusions about the influence of the numbers of atoms to the charge values have been done. The geometry of the (010) hydroxylated regular face has been calculated. It was shown that the difference between the data of simple cluster approximation and LSCF method exists. The geometrical and energetic parameters of some adsorption complexes containing water molecule have been calculated.

The general possibility of the irregular surface structure investigations has been shown by the calculations of the geometry of a small hill surrounded by regular surface and of the geometry of a hydroxyl cover placed at the outskirts of crystal. The geometry and adsorption energy with water molecule has been calculated at both cases.

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PPC-43

KINETIC STUDY OF NO+CO REACTION ON PLATINUM RHODIUM BASED CATALYSTS MODIFIED BY CERIUM ADDITION

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Three way catalyst converter is one of the most effective way to control nitrogen oxide from exhaust catalyst. However such process presents several disadvantages related to the utilization of noble metals highly expensive and to an optimizing efficiency obtained near the stoechiometric conditions. Nowadays the different research programs concern mainly the synthesis of novel materials exhibiting the same catalytic properties as the noble metals. A second alternative way is the modification of the existing catalysts by the addition of promoters such as cerium oxide in order to improve the catalyst performances in oxidizing and reducing medium. The success of these different programs is conditionned by a better understanding of the mechanism involved in the NO reduction by CO.

We have investigated the NO+CO reaction by means of kinetic study and infrared spectrometry of CO and NO adsorbed. Two bimetallic catalysts Pt-Rh/Al_2O_3 and Pt-Rh/Al_2O_3-CeO_2 have been studied. The rate law of the overall NO reduction on the first one can be defined by the following expression assuming that NO dissociation on the metal is the determining step of the reaction.

$$V=k\Theta_{NO}(1-\Sigma\Theta)$$

Θ_{NO}: NO coverage on metallic sites
$(1-\Sigma\Theta)$: free metallic sites coverage

The kinetic study on Pt-Rh/Al_2O_3-CeO_2 characterizes two activity domains taking place at different temperatures. In this way the rate law would be the sum of two elementary processes, the first one occuring on the metal whereas the second one would be activated on the cerium oxide support.

$$V = k\Theta_{NO}(1-\Sigma\Theta)+k'\Theta_{NO}(1-\Theta'_{O})$$

Θ'_{O}: Oatoms coverage on CeO_2

Kinetic measurements on Pt-Rh/Al_2O_3-CeO_2 catalyst at elevated temperatures (~300°C) show the same catalytic behaviour as Pt-Rh/Al_2O_3. The NO dissociation reaction would be the determining step of the overall NO reduction. On the contrary at low temperatures (~120°C) the mechanism involving the oxygen atoms on the cerium oxide support would predominate. The rate law could be expressed by the following relation

$$V = k'\Theta_{NO}(1-\Theta'_{O})$$

We thank the "Groupement de Recherche Pot catalytique" for supporting this work.

PPC-44

OXIDATION OF CARBON MONOXIDE ON COPPER-CONTAINING CATALYSTS.

TEMPERATURE EFFECTS

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The oxidation of carbon monoxide was realized by the air excess in automated set KL-2. The reaction was carried out at flow-circulation regime on different copper-containing oxide catalysts (the catalysts obtained from copper-aluminum alloys of different compositions; copper-cement catalysts; copper oxide obtained by decomposition of copper hydroxocarbonate, etc.). The reaction mixture was analyzed gas-chromatografically.

The special peculiarity of the dependencies of CO conversion (*x*) on temperature is the hysteresis: under reactor heating after some temperature point (usually 130-150°C) conversion drastically rose from 0 to 100%, while under cooling the corresponding drastic decreasing of *x* take place at more low temperature. The widths of hysteresis (the difference between the temperatures of drastic rising and drastic falling of *x*) depend on the activity of catalyst: the higher activity the more width. In the case of low active catalyst the hysteresis was practically absent. The hysteresis width also depends on the reaction mixture composition. When the CO percentage in mixture is rise and the reaction rate increased, the hysteresis width is greater. It possible to find such relation between CO and air when after ceasing of heating the reaction on active catalyst is continued to go with $x = 100\%$ even at almost room temperature.

We suppose that the reason of this phenomena is the high exothermity of the reaction (ΔH = 283 kJ/mol). On the active sites it is released the great excess of heat energy that is unable to redistribute and to dissipate during the process. Therefore the local temperature near by active centers is much more than the average temperature in the catalyst layer measured by the thermocouple. The surfaces of catalyst consist of the hot points surrounded by the more cool mass of the carrier and inactive part of copper. The higher the reaction rate (active catalyst, optimal relation of components) the more ununiform is the distribution of temperature on the catalyst surface.

The investigation was carried out under supporting of the Russian Foundation for Fundamental Researches (grant 94-03-08611).

INVESTIGATION OF THE REACTION OF DIRECT OXIDATION OF HYDROGEN SULPHIDE BY OPTICAL AND KINETIC METHODS

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The problem of hydrogen sulphide utilization and processing is one of the most urgent tasks in the creation of environmentally safe processes in gas and oil extracting and processing.

In Boreskov Institute of Catalysis a process of the purification of hydrogen sulphide containing gases has been developed, based on the reaction of direct selective oxidation of H_2S on the surface of solid oxide catalysts. Depending on the process condition, H_2S catalytic oxidation is carried out either in a fluidized bed of spherical catalyst granules or in stationary bed of honeycomb monolithic catalysts [1,2].

The objective of this work is the investigation of the reaction of direct H_2S oxidation to sulphur on a number of oxide catalysts by optical and kinetic methods.

EXPERIMENTAL

The following catalysts were used in experiments: Fe_2O_3/γ-Al_2O_3, $MgCr_2O_4/\gamma$-Al_2O_3, TiO_2-SIO_2-Al_2O_3 and γ-Al_2O_3.

The kinetics of the reaction of H_2S direct oxidation was studied on a flow setup. The temperature was varied in the range of 150-350°C. The initial mixture was 20% H_2S in nitrogen. The reaction was carried out at stoichiometric H_2S/O_2 ratio.

Infrared spectra were recorded on a spectrometer BOMEM MB-102 (Canada). CO adsorption was studied at - 196°C, the adsorption and interaction with surface of H_2S and SO_2 were studied in the temperature range 25-350°C.

ESDR spectra were registered at room temperature using SPECORD M40 (Germany) spectrophotometer.

RESULTS AND DISCUSSION

The study of the reaction kinetics showed that at residence time less than 0,3 sec. 100% selectivity of the reaction to elemental sulphur is achieved an all catalysts studied. This is explained by little contribution to the process of the consecutive reaction of oxidation of formed sulphur to sulphur dioxide. At longer residence time the decrease of the selectivity was observed when the temperature was raised to 250-300^{0}C. The highest activity and selectivity in H_2S direct oxidation is achieved on the catalyst $MgCr_2O_4/\gamma$-Al_2O_3. The kinetic parameters of the reaction were obtained for all catalysts studied.

By the IR spectra of adsorbed CO it was shown that all the catalysts have both Lewis and Brönsted acidic sites on the surface. However the nature, strength and number of sites are all particular for each type of catalyst. This leads to difference in adsorption and interaction with the surface of H_2S and SO_2 on different catalysts.

Basing on IR spectroscopic study H_2S was shown to adsorb to the catalyst surface dissociatively. As temperature is raised H_2S oxidation occurs, this process being most fast on $MgCr_2O_4/\gamma$-Al_2O_3 in accordance with the kinetic data.

ESDR study showed that during the reaction various types of elemental sulphur: S_4-S_8 are formed on the catalyst surface.

The investigation performed allows drawing tentative conclusions about reaction routes: the reaction can proceed both by direct sulphur formation upon H_2S oxidation and by the formation of SO_2 with it subsequent interaction with H_2S to form sulphur. The predominance of either route depends on the catalyst nature.

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Physicochemical Characterization of Solid Superacids Based on Sulfated Oxides Modified by Transition Metals and Reduced Noble Metals

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Recently solid superacids attracted a considerable attention since they are active in the reactions of paraffins as well as in processes of fine chemicals synthesis. It was shown that modification of sulfated zirconia by transition metals influences the activity and stability of catalysts in the isomerization of n-butane. However, the nature of the active sites in sulfated oxides and the electronic state of metals supported on these materials are not perfectly understood. The aim of this work is to clarify the above questions.

EXPERIMENTAL

ZrO_2, TiO_2, Al_2O_3, WO_3-Al_2O_3, and SiO_2 were used as the starting materials for the preparation of solid superacids. The specific surface areas of the samples were 100 - 500 m^2/g. Sulfate anions (5 wt %) were introduced by impregnation of the dried hydroxides with a 1 M solution of H_2SO_4 followed by calcination in an air flow at 720 - 1020 K. Platinum (0.1 - 2.5 wt %) and palladium (0.5 wt %) were supported by wet impregnation of the calcined sulfated samples with further calcination in air at 770 K and reduction in hydrogen at 520 - 570 K. Prior to spectroscopic measurements, the samples were evacuated at the same temperature for 2 h. Diffuse-reflectance IR spectra were measured with a Perkin-Elmer 580 B spectrophotometer. Adsorption of various molecules was carried out at 300 K and pressure of 10 - 20 torr.

RESULTS AND DISCUSSION

IR-spectroscopic study of SO_4^{-2}/ZrO_2, SO_4^{-2}/TiO_2, SO_4^{-2}/Al_2O_3, and other solid superacids showed that modification with sulfate anions changed the distribution of the hydroxyl groups that are present at the surface of oxides. First, the terminal OH groups exhibiting the most strong basic properties disappear and characteristic $\nu(SO_4^{-2})$ bands at 1380 -1340 cm^{-1} appear in the spectra together with the overtone band at 2760 cm^{-1}. The sulfur resistance in the sulfated samples after high-temperature oxidative and reductive treatments was determined by monitoring the intensity of the SO_4^{-2} overtone band.

It was found that for all the samples the modification with sulfate anions results in low-frequency shifts of the bands of the OH stretching vibrations. The enhancement of the acid strength was determined from the frequency shifts for H-bonded complexes with adsorbed molecules (benzene, ethylene, dichloromethane etc.). This may be explained by the inductive effect of sulfate anions on the neighboring OH groups of the oxide. The most distinctive feature of the IR spectra of sulfated catalysts is the appearance of the very broad absorption bands with a maximum at 3300 - 2900 cm^{-1}, depending on the pretreatment temperature and the nature of the oxide. This band has been ascribed to a new type of Brønsted acid sites - delocalized protons connected with the SO_4^{-2} anion.

To characterize the acidic properties of the sulfated oxides, the activity in low-temperature oligomerization of light olefins and cyclopropane was studied by in-situ IR spectroscopy. It was found that the sulfated samples may be arranged according to the acid strength in the following sequence:

$$ZrO_2 > WO_3\text{-}Al_2O_3 > TiO_2 > Al_2O_3 > SiO_2.$$

Brønsted, but not Lewis acid sites were found to be the active centers responsible for the oligomerization activity, which was proved by H-D exchange occurring during the olefin oligomerization.

Modification with SO_4^{-2} anions influences also the properties and distribution of Lewis acid sites: it blocks the least acidic Lewis sites and enhances the strength of the strongest Lewis centers. At a high concentration of the sulfate anions, the total concentration of Lewis acid sites decreases.

To characterize the state of Pt and Pd supported on ZrO_2 and SO_4^{-2}/ZrO_2, IR spectra of adsorbed CO were measured. In the case of Pt/ZrO_2, a partial negative charging of Pt particles was inferred from the low-frequency shift of the CO band for the linear Pt-CO complexes (ν_{CO} = 2040 cm^{-1}), as compared to the neutral Pt(0) species (ν_{CO} = 2070 cm^{-1}). Unlike Pt/ZrO_2, for the sulfated sample, a positive charging of the Pt particles was anticipated, because an opposite (high-frequency) shift of the CO band was observed (ν_{CO} = 2105 cm^{-1}). The extent of modification diminishes with increasing Pt loading. The adsorption of CO molecules on $0.1Pt/SO_4^{-2}/ZrO_2$ suppresses entirely. The spectra of $0.5Pt/SO_4^{-2}/ZrO_2$ show distinctive features attributed only to the partially charged form of Pt, whereas neutral and partially charged states of Pt can be distinguished at a 2.5 wt % Pt loading. The loss of sulfur at reduction temperatures higher than 520 K leads to the neutral state of platinum and finally to its negative charging.

To reveal the pecularities of the metal-support interaction, Pd-containing and Pt-Pd bimetallic systems based on SO_4^{-2}/ZrO_2 were also studied. It was shown that stabilization of charged states of metals and the existence of the partially charged species could be explained in terms of the influence of delocalized protons on metal particles and sulfur poisoning of metal surfaces.

Benzene alkylation with propylene over ferrisilicates: On the nature of active sites

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Ferrisilicate analogs of zeolites proved to be very active and selective catalysts for alkylation reactions [1]. However, little is known about the alkylation mechanism operating on these catalysts and the nature of active sites. The purpose of the present study was to determine the role of Fe ions with different state, coordination and location in overall catalytic activity, as well as to elucidate their transformations during the catalytic reaction. Benzene isopropylation was chosen as a model reaction.

Fe- and (Fe, Al) - analogs of medium (MEL) and large (BETA) pore zeolites with various Fe content were synthesized. All the samples were characterized for phase purity and crystallinity (XRD), chemical composition (EDX), crystal size (SEM) and acidity (NH_3 TPD). The state and coordination of Fe-ions was studied using X-band ESR spectroscopy. The alkylation activity and selectivity were studied in a flow fixed-bed reactor operating at atmospheric pressure. The catalysts were tested at 240 -300°C, WHSV = 5-100 h^{-1} and $C_6H_6/C_3H_6=9$.

The X-band ESR spectra of as-synthesized and freshly calcined samples consisted of two major signals at g=4.3 and g=2.0, respectively; on some of the samples a broad signal at g=2.3 was also detected. The commonly accepted assignments of these signals have been as follows: framework iron, iron in cation-exchange sites and interstitial oxide or hydroxide phases, respectively [2]. These traditional assignments were recently challenged and attribution of g=2.0 signal to framework ions was also considered [3,4]. It was stressed, however, that neither the appearance of the ESR signal at g=4.3, nor the one at g=2.0 can provide unambiguous evidences for framework substitution unless combined with other physical and chemical methods. In our case, the stable behavior of g=4.3 and g=2.0 signals upon the cation exchange or the extraction with strong mineral acids, suggested that these signals may be indeed attributed to different sites in zeolite framework. Moreover, the number of such sites estimated from ESR spectra, corresponded to the amount of acid sites determined from acidity measurements, what confirms our assignment. By contrast, the signal at g=2.3 was found to disappear upon extraction with mineral acids and thus can be attributed to extraframework species.

All the aluminum free ferrisilicates exhibited remarkable selectivity to cumene and diisopropylbenzene (up to 100%). Large pore zeolites were characterized by minimal formation of the most undesirable by-product, i.e., n-propylbenzene (less than 0.05%). However, they showed relatively poor stability of catalytic activity as a function of time on stream, with respect to medium pore zeolites. Addition of small amounts of Al led to significant improvement of the catalytic stability, however it was always followed by decrease of selectivity to cumene.

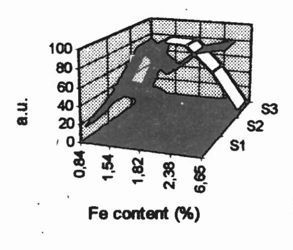

Figure 1. Variation of relative intensity of the ESR signal at g=4.3 (S1), relative intensity of the ESR signal at g=2.0 (S2) and cumene yield (S3) with Fe content in a series of ferrisilicates with MEL structure.

Ferrisilicates of the same structural type (MEL) but containing various amounts of iron showed different activity in alkylation (Fig.1). However, no direct correlation of catalytic activity with total Fe content was observed. Similarly, no correlations were found with Fe sites corresponding to ESR signals at g=2.0 and g=2.3. On the contrary, framework Fe sites characterized by g=4.3 signal showed strong correlation with cumene yields (Fig. 1). The appearance of the signal at g=4.3 was previously associated with Brønsted acid sites, while g=2.0 signal was associated with framework Lewis sites [3]. Basing on this hypothesis, one may conclude that catalytic activity of ferrisilicates in alkylation is due to Brønsted acid sites formed upon isomorphous substitution of Si by Fe. The moderate acidic strength of such centers may further explain an extremely high selectivity of these catalysts.

However, this suggestion was not supported by the ESR results obtained for ferrisilicate catalysts after reaction. Indeed, the intensity of the signals at g=2.0 and g=4.3 was found to decrease drastically during several reaction/regeneration cycles while the catalysts showed stable and reproducible activity and the number of acid sites only slightly decreased. The elucidation of the fate of iron during the catalytic reaction and the nature of active sites under working conditions are discussed.

Acknowledgments

The authors thank INTAS for financial support.

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PPC-48

PHOTOCATALYSIS OF CHAIN SUBSTITUTION REACTIONS IN HALOGENOHYDROXYNAPHTHALENES BY TRIS(BIPYRIDINE) RUTHENIUM(II) COMPLEX.

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On irradiation of tris(2,2'-bipyridine) ruthenium(II) complex the substitution of bromine by sulpho group in 1-bromo-2-hydroxynaphthalene in an aqueous solution of sodium sulphite has been observed. Similarly, chlorine is substituted by sulpho group in 4-chloro-1-hydroxynaphthalene. The initiation mechanism of chain substitution reaction in halogenohydroxynaphthalenes photosensitized by ruthenium(II) complex has been investigated. It has been shown that a chain substitution reaction proceeds by two different mechanisms: through radical anion of halogenohydroxynaphthalene and radical of nucleophile. On interaction of excited ruthenium complex with halogenohydroxynaphthalenes the ruthenium(I) complex and naphthoxy radical are obtained. Ruthenium(I) complex is strong reduced agent which reacts with halogenohydroxynaphthalene giving radical anion of halogenohydroxynaphthalene. Naphthoxy radical reacts with sulphite ion giving sulphite radical anion which participates in propagation step:

$$^{-}OArBr + SO_3^{-\cdot} \xrightarrow{k_R} [^{-}OAr(SO_3^{-})Br]^{\cdot}$$

$$[^{-}OAr(SO_3^{-})Br]^{\cdot} \longrightarrow {}^{\cdot}OArSO_3^{-} + Br^{-}$$

$$OArSO_3^{-} + SO_3^{2-} \longrightarrow {}^{-}OArSO_3^{-} + SO_3^{-\cdot}$$

$$SO_3^{-\cdot} + SO_3^{-\cdot} \xrightarrow{k_0} S_2O_6^{2-}$$

The quantum yield of substitution reaction depends on light intensity: with decrease of light intensity the quantum yield increases. At high intensity the reaction proceeds basically through radical anion of halogenohydroxynaphthalene by $S_{RN}1$ mechanism. At low intensity the substitution reaction proceeds basically by second mechanism through sulphite radical anion. In this connection the quantum yield of substitution reaction at high and low light intensity depends on halogenohydroxynaphthalene concentration by various means. At high light intensity dependence of quantum yield on concentration of halogenohydroxynaphthalene is linear. At low light intensity the quantum yield depends on halogenohydroxynaphthalene concentration to power 3/2. These results are in agreement with proposed mechanisms.

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PPC-49

THE INFLUENCE OF ION-INDUCED DEFECTS ON *CO* ADSORPTION ON POLYCRYSTALLINE NICKEL AND PLATINUM

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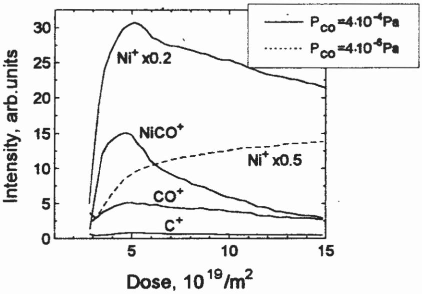
CO adsorption on polycrystalline Ni and Pt foils was studied under the simultaneous surface bombardment with Ar^+ ions using the method of secondary ion mass-spectrometry (SIMS).

Experiments were carried out in MS-7201 (Russia) spectrometer at room temperature and a CO pressures of $(1\text{-}40)\cdot 10^{-5}$ Pa. The bombardment was executed by a Ar^+ beam with E = 4 keV and density of current J = 4 $\mu A/cm^2$. The pressure of residual gases did not exceed $7\cdot 10^{-7}$ Pa, that provided the realisation of experiments in conditions of a dynamically clean surface. Polycrystalline Ni and Pt foils of 99.9 % purity were previously cleaned by annealing at high temperature in a separate vacuum system. The bombardment doses varied from ~ 10^{19} to 10^{21} m^{-2}.

At these doses the concentration of surface defects - vacancies already achieves a stationary level. Subsequently, the steps, kinks and cones are formed on the surface as observed by SEM. In the process of CO adsorption on nickel only Ni^+, $NiCO^+$, CO^+, NiO^+ and C^+ ions were observed in the SIMS spectra. The intensities of these peaks increased during the CO adsorption. Moreover, at the CO pressure higher than 10^{-4} Pa the intensity vs dose curves had maximums (fig.). There were found two states of adsorbed CO with the cross-sections of the ion-induced desorption (σ) - 8 and $15\cdot 10^{-19}$ m^2.

Weakly-bond state of CO with $\sigma = 15\cdot 10^{-19}$ m^2 was attributed to the bombardment induced defects. The state desorption activation energy was

PPC-49



estimated to be ca. 75 kJ/mol. The ion bombardment of this state resulted in the desorption of CO^+ ions and the formation of NiO layers due to the ion-stimulated dissociation.

The effect of the secondary ion emission increase during CO adsorption was quantitatively described within the framework of electron tunnelling model. The best fitness of CO adsorption kinetic was found assuming that sticking probability equalled 0.4. This value is lower than 0.9 found for CO adsorption on smooth surfaces [1]. This fact was suggested to relate to both ion-induced defects and CO adsorption in the strongly-bond state proceeding through the weakly-bond state.

During adsorption of mixture CO + 4% O_2 on Pt foil $PtCO^+$, CO^+ and O^+ ions were observed in the SIMS spectra. Peak intensities vs dose curves were identical to those observed on Ni. The presence of CO^+ ions in the SIMS spectra led to conclusion that CO adsorption occurred through the precursor state.

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HOMOGENEOUS ELECTROPHILIC CATALYSIS IN THE PHOSPHORYLATION OF POLYFLUOROALKANOLS WITH PHOSPHORUS ACID CHLORIDES

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A novel approach to the enhancement of the reactivity of phosphorus acid chlorides toward polyfluoroalkanols through the coordination of an electrophilic catalyst to phosphoryl group has been suggested.

Using the model reaction of 1,1-dihydroperfluorobutanol with phosphoryl chloride as an example

$$3C_3F_7CH_2OH + POCl_3 \xrightarrow[-HCl]{\text{Catalyst, }160^\circ} (C_3F_7CH_2O)_3PO$$

we have considered the problems of catalysis in the phosphorylation of polyfluoroalkanols with phosphorus acid chlorides. A number of electrophilic agents has been studied as the catalysts: metal salts (mainly I and II Group metal salts), some onium type salts (e.g., various organoammonium and phosphonium salts); a series of dipolar compounds having E=O fragment [where E = $C(NMe_2)R$ (R = H, Me, NMe_2), R'_3P (R' = Ph, $CH_2CH_2CF_3$), $R''_nP(OR_F)_{3-n}$ (R" = Me, Ph; R_F = polyfluoroalkyl; n = 1, 2), or Me_2S] that are able to form onium type intermediates in the course of the reaction.

I - VIII Group metal salts have been studied in detail. The effect of cation and anion nature has been investigated. We have studied the effect of the strength of Lewis acids on their catalytic activity. The strongest Lewis acids ($AlCl_3$, $TiCl_4$, $FeCl_3$) were of little utility for the synthesis of polyfluoroalkyl phosphate esters because of side reactions. But Lewis acids of medium and low strength were found to be the most effective catalysts, with the best result beeng obtained when the corresponding salts of carboxy and organophosphate acids were used. The comparison of some pairs of the catalysts of this type showed that weaker Lewis acids were found to be more active catalysts than stronger Lewis acids, for example: $LiClO_4 > Mg(ClO_4)_2$; $LiOCOCF_3 > Mg(OCOCF_3)_2$; $Ca(ClO_4)_2 > Mg(ClO_4)_2$; $SnCl_2 > SnCl_4$; $SbCl_3 > SbCl_5$; $BiCl_3 > SbCl_3$.

Alkyl ammonium and alkyl triphenylphosphonium salts, which are likely to be able to ion-dipole association with phosphoryl group, are less active catalysts, but their activity is sufficient for preparing the esters.

The above dipolar compounds, which were used as the catalysts, are the efficient precursors of homogeneous catalytic systems. Carboxy and phosphoric amides, phosphine oxides, polyfluoroalkyl phosphonates and phosphinates are the typical compounds of such kind, with the catalytic activity of phosphine oxides being comparable with that of the best metal salts of organic acids.

The possible mechanisms of the catalysis are discussed for the various groups of the catalysts.

The findings have been used for the development of facile catalytic methods for the synthesis of a number of types of polyfluoroalkyl phosphorus esters.

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HOMOGENEOUS CATALYSIS BY PHTHALOCYANINES IN OXIDATION REACTIONS: STATE OF ART AND PERSPECTIVES

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Similarity of phthalocyanines (Pc) sructure with active-centers of heme containing enzymes attracts for a long time attention of chemists stimulating the development of enzyme-like catalytic oxidation processes using Pc derivatives as catalysts. Such developments could help to solve the problem of replacement of heavy metal compounds used in industry as oxidants by ecologically pure ones - dioxygen, hydrogen peroxide and peracids.

By our knowledge, there is only one industrial process using Pc as catalyst in oxidation reaction - Merox technology of oil products demercaptanization. Nevertheless, there are a number of scientific publications and patents concerning not only S-H but C-H, O-H and N-H oxidation as well. In this report we present some literature and our own experimental data on the catalysis by Pc and related compounds in oxidation reactions of aromatic hydrocarbons and phenols to quinones, substituted di- and triarylmethanes - to corresponding cationic dyes, cyclohexane - to cyclohexanol and cyclohexanone mixture and so on. The rates of reactions, selectivity and overall turnover numbers of Pc catalysts are rather high for production of several fine chemicals such as vitamins, food preservatives, dyes and so on. The requirements to Pc structure, nature of solvents and oxidants will be formulated depending on reaction type. The emphasis will be done on the development of heterogeneous catalysts based on Pc with the purpose to improve their technological characteristics.

PPC-52

MOLECULAR DESIGN OF CATALYSTS BASED ON FUNCTIONALIZED SOLUBLE POLYMERS

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The concept of attaching metal complexes to soluble polymers seems very attractive since the catalysts on their basis very often lack the drawbacks connected with rigid structure of modifying groups and diffusional limitations. At the same time such soluble catalysts can be separated from the products by various procedures and repeatedly used

Monoethers of polyethylene oxide RE [R= CH_3, C_4H_9 , E = $(CH_2\text{-}CH_2\text{-}O)_n$] or block-copolymers RPE and REP [P = $(CH(CH_3)\text{-}CH_2\text{-}O)_m$] with hydroxyl group only on one end of polymer chain were functionalized by dipyridyl, acetylacetone, catechol, nitrile . Of special interest are the block-copolymers with incompatible blocks characterized by different affinity to solvent. e.g. copolymers of ethylene oxide and propylene oxide. In this case it is possible to design catalytical sites either in hydrophilic or hydroophobic part of copolymer depending on the combination of polyethylene oxide or polypropylene oxide fragments. Macrocomplexes of transition metals have been synthesized by using these ligands. The complexes showed activity as catalysts in oxidation of hydrocarbons of different structure by both hydrogen peroxide and dioxygen. (Table)

Table.

Macromolecular catalysts.

№	Macroligand	Metal	Test reaction
1	RE-acac	Fe,Co,Cu	
2	REP-acac	Fe	Oxidation of ethylbenzene, cyclohexane and
3	RPE-acac	Fe,Co	cyclohexene by dioxygen or hydrogen
4	(RE)2-dipy	Fe	peroxide
5	(REP)2-dipy	Fe	
6	RE-catechol	Fe,Cu,	Hydroxylation of benzene by hydrogen peroxide
7	RE-CN	Pd	Wacker-type oxidation of decene-1

* - Co-catalyst $CuCl_2$, acac- acetylacetone, dipy - dipyridyl

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PPC-53

INFRARED STUDIES OF ACIDIC PROPERTIES OF ZIRCONIUM DIOXIDE MODIFIED BY Sc^{3+}, Y^{3+}, La^{3} CATIONS

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The investigation of donor-acceptor properties of the modified zirconium dioxide surface is the important problem now, because ZrO_2 may be used as a high temperature catalyst or as a base for supported catalysts with stable value of surface area. We have been carried out the systematic investigation of influence of preparation condition on acidic properties of zirconium dioxide surface, modified by Sc^{3+}, Y^{3+}, La^{3+} cations. The samples were obtained with supporting doped cations to the moloclinic zirconium dioxide surface from nitrate solution with successive calcination, and by co-precipitation method from nitrate solution with using NH_4OH one.

Doped oxide containment was varied from 0.1 to 4 % weight for samples, which were obtained with impregnation method, and 1 - 10 % mol. per co-precipitated oxides.

The characterization of this samples was carried out by BET, XRD and IR diffuse reflectance spectroscopy. Acidic properties of modified ZrO_2 surface were investigated by infrared spectroscopy with carbon monoxide as a probe.

The tetragonal or/and amorphous domains origin was obtained on the impregnated ZrO_2 surface.

Several new types of OH-groups were registrated on the surface of modified ZrO_2, which was obtained by precipitation method. Its adsorption band frequencies were different from ones on the pure oxide surface.

It can be proposed, that these bands corresponds to the bridged OH-groups, in which oxigen atom is connected with different cations Zr and Me (Me is Sc, Y, or La). However, the OH-groups of the modified by co-precipitating ZrO_2 surface are similar to the ones on the pure ZrO_2 surface.

According to I.R. data of adsorbed carbon monoxide the

Lewis acidic sites concentration decreases with doped component concentration arise. The presence of Me cations on the modified by impregnation ZrO_2 surface promotes the origin of new basic site types. The I.R. bands of adsorbed CO , corresponding these sites, were registrated in 2050 - 2140 cm^{-1} region. It's supposed, ion pairs (cus cation Me^{3+} - bi-bridged anion O^{2-}) to be such sites.

Similar sites were not observed on the surface of modified ZrO_2, which was obtained by co-precipitation method. It can be explained with low doped cation concentration on the ZrO_2 surface and doped cations different coordination .

It can be concluded, that doped component concentration and modifying technique major affect ZrO_2 surface acid sites formation. By co-precipitation method the modified oxides, which have surface sites similar to pure ZrO_2 sites can be obtained. However, the introduction of doped cations by means of impregnation technique results in formation of surface with new donor-acceptor properties.

This data may be used for creation catalysts on the ZrO_2 base with new properties.

PPC-54

Alkene Epoxidation Catalyzed by Novel Terpenoid-Based Transition Metal Complexes.

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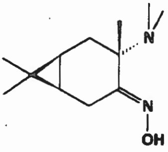
The importance of epoxides in synthetic chemistry and biochemistry stimulates the search for new non-enzymatic catalytic systems for selective epoxidation of alkenes.

We have synthesized a number of new polyfunctional ligands **1-5** using natural chiral terpene molecule as starting material and found that they form stable complexes with many transition metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Fe^{3+}, Ru^{3+}, Pt^{2+}, etc.).



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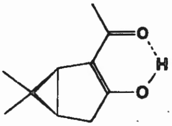

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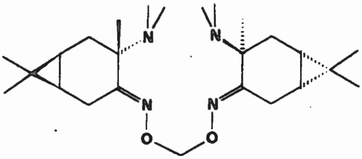

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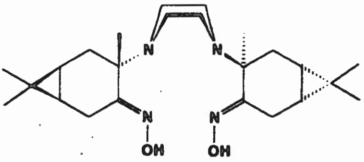

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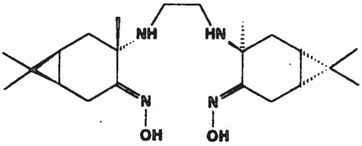

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We have investigated the catalytic activity of a number of these complexes in alkene epoxidation by various oxygen donors such as H_2O_2, *tert*-BuOOH, PhIO and O_2 in the presence of isobutiraldehyde (IBA) using *trans*-stilbene as a model substrate. It has been found that ligands **1,3-5** strongly influence the selectivity of epoxide formation in the reaction with PhIO, catalyzed by Ru-complexes. Thus, when $Na_2[RuCl_5NO]$ is used as catalytic precursor in CH_3CN medium, the selectivity to *trans*-epoxide attains 66 and 43% in the presence of **4** and **5** respectively, while it does not exceed 20% in the absence of the organic ligands, benzaldehyde being the main co-product. The influence of the ligands on the selectivity of the epoxide formation is smaller when *tert*-BuOOH acts as primary oxidant.

The oxidative system O_2-IBA proved to be the most active one, especially with cobalt catalysts. Co^{2+}-complexes with both octahedral and tetrahedral configurations display very high activity in alkene epoxidation, *trans*-stilbene being oxidized in their presence to *trans*-epoxide by air oxygen in 75-85% yield after 0.5-1 h at room temperature. Iron complexes are less active but more selective than the corresponding Co-complexes. Ligand **2**, when coordinated to Fe^{3+}, enhances the yield of the epoxide (90%) as compared to $Fe(acac)_3$ (73%) at 100% conversion of alkene under the same reaction conditions. Dioxygen in the presence IBA exhibits unique oxidative properties in some cases. Thus, well-characterized Pt^{2+} complex with **1**[1] is inactive in stilbene oxidation, when H_2O_2, *tert*-BuOOH or PhIO are used as primary oxidants, whereas O_2 in the presence of IBA produces the epoxide with 81% yield at room temperature and normal pressure.

Mechanistic features and stereochemistry of the above reactions are in progress. Preliminary data show that alkene oxidation with *tert*-BuOOH and O_2 -IBA has an induction period and is inhibited by ionol in most cases. This suggests a free radical mechanism of the reactions rather than a heterolytic pathway that seems to be realized in the oxidation with PhIO.

The research described was made possible in part by Grants RAU000 and RCS000 (the International Science Foundation), and Grants RAU300 and RCS300 (the International Science Foundation, Russian Government and the Russian Fundamental Science Foundation), and Grant 94-03-08063 (the Russian Fundamental Science Foundation).

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PPC-55

POLYFUNCTIONAL CATALYSTS IN POLYMER NETWORKS SYNTHESIS ON THE BASIS OF 2-HYDROXYETHYL METHACRYLATE

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The catalytical action mechanism of vanadium and rhenium compounds in hydrophilic polymer networks (hydrogels) formation followed by low temperature polymerization of 2-hydroxyethyl methacrylate (HEMA) and copolymerization of HEMA with styrene, phenylacetylene and trans-β-methylstyrene has been studied. The electronic structure and coordinative unsaturation of examined metal compounds explain their polyfunctional catalytic action. The generation of the reactive oxygen species is shown to be a result of one electron reduction of molecular O_2 in the coordination sphere of the metal ion and initiates the chain radical polymerization of HEMA. The kinetic behaviour of the paramagnetic HEMA derivative intermediates was studied by ESR-technique without or with the radical acceptor; the part of the radical processes in the common polymerization rate was established.

The formation of polymer network occurs without cross-linking agents. Network parameters were calculated using the elasticity module of equilibrium swollen gels. The number of monomer molecules composing one elastic active chain is 30-50. The structure and properties (swelling, mechanical solidity etc.) of polymers seemed to depend on the concentration of metal compounds. The formation of crosslinks in the network is a result of the reactions connected with Lewis acidity of vanadyl complex as well as rhenium metal organic compound. The high catalytic activity of these compounds is shown in the alcoholysis reactions of epoxides and unsaturated ketones, and in the epoxide formation followed by molecular O_2 oxidation of olefins.

Gas-Phase Studies with Ion Cyclotron Resonance Spectrometry of the C-S and C-H Bond Activation Reactions by VI and VIII Group Transition Metal Ions

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All processes of hydrodesulfurization of oil fraction proceed over the catalysts, that is the composition of Mo (or W) with Ni (or Co) in sulfide form. Due to the efforts of the advanced laboratories the active component of these catalysts are well studied nowadays[1]. But there is a discussion concerning the roles of metals entering the composition of the active component in the activation of the reactive molecules in the reaction of catalytic hydrodesulfurization.

At preset paper the C-S, S-H and C-H-bond activation reactions by the Mo^+, W^+, Ni^+, Co^+, and Fe^+ ions in the various sulfur containing hydrocarbon molecules were studied using the FT ICR method. As was shown Ni^+ and Co^+ attack preferably the C-S bond in all hydrocarbon molecules studied, while Mo^+ and W^+ does not react with this bond. On the other hand, Mo^+ and W^+ react with these molecules through insertion into C-H bond, or rarely into S-H bond, while Ni^+ и Co^+ ions are not active in these reactions. The observed difference in the gas-phase reactivity of the VI and VIII group metals give additional arguments to the early advanced hypothesis[2] concerning the roles of the metals included in the catalysts for hydrodesulfurization. According to it activation of the S-containing molecule and hydrogenolysis of the C-S bond occur on the Ni or Co ions, while activation of the H_2 proceeds on the MoS_2 (WS_2) sites.

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PPC-58

KINETICS EQUATIONS FOR UNSTEADY HOMOGENEOUS AND HETEROGENEOUS CATALYTIC PROCESSES SOLVED BY METHOD OF "FROZEN" COEFFICIENTS

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It is possible to separate in the homogeneous and heterogeneous catalytic processess in the static and dynamic systems a few stages in stationary or unstationary conditions we can separate three stages of catalytic process-the creation accumulation of catalytic complexes in reaction mixture, stationary stage and the spending of one.

It should be noted that tirst and third stages occupy a little time, but exert influence upon interraction of molecule of reagents during chemical process in presence of the catalyst, usually, these two stages don't fail to take into account in time of soluting of differential equations using the Bodenstein's Principle.

Meanwhile the un-steady stages ecxite in the homogeneous systems transformation of hydrocarbon and non hydrocarbon compounds during the stationary stags. Its exert influence upon local and mean distribution of products in reaction mixture.

It may be determine in homogeneous and heterogenious catalytic processes next stages: collision of molecules (in the base or exciting states) with catalysts molecules (or an active centres), creating of catalytic complex, redistribution of atomic or molecular orbital, decomposition of catalytic complex on products and catalyst, deabssorption of product molecules.

The solution of kinetic equations by methode of "frozen" coefficients was make for the kinetic scheme: A+K == AK+B ==AKB--AB+K where A, B, AB, K-molecules of initial, ending subsstences and catalyst.

The solution of equations presented for un-steady conditions in the form of dependence concentration of catalyst and molecule of reagents in the reaction mixture. It is easy to get the equation for stationary condition.

THE MODELLING OF CATALYTIC REACTIONS PROCEEDING IN DIFFERENT REGIMES

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It is known that the peculiarities of proceeding of catalytic reactions are determined by structure of their stage schemes. That is why the analysis of relaxation time for different classes of reactions and sistematization of the mechanisms which describe critical phenomena and auto-oscillation is interested. The solution of these problems is directed on creation of data bank which may be used for investigation of kinetics of concrete reactions. In the report the results of using mathematic modelling methods for analysis of relaxation time and critical phenomena in catalytic reactions are given. For example, the estimation of relaxation time for two-three-and many-stage reactions are generalized. This analysis is based on the program which helps to generalize all the possible mechanisms of different class reactions and also to investigate the roots of characterized equation. At the value of efficient part of maximum root of this equation computer calculates relaxation time for corresponding scheme reaction. On the base of leading analysis the complete sistematization of relaxation times for all investigated class reactions with creation of corresponding part of kinetics data bank was done.

Another important problem of chemical kinetics is sistematization of simple mechanisms which describe critical phenomena as multiplicity steady states (MSS). The selection of these mechanisms was automatized with the help of the program which is based on the special criterion. The criterion represents the system of inequalities on stoichiometric of reactions and allows not only to establish the possibility of MSS existing, but also to estimate the conditions of its realization. The mechanisms which can be used for description such forms of MSS as hystere sises, selfintersections and breaks were investigated. In the deadlines of the most known classes of three-and four-stage reactions the systematization of the mechanisms which describe autooscillating regimes was carried out by us too. For the analysis of the schemes of such reactions the stoichiometric conditions of stability and single steady state were defined. The analysis gave the possibility to find 45 types of three stage schemes which describe auto-oscillations. All of these schemes include one and more three-molecular auto-catalytic stages. These stages play the role of back connection without which the existence of auto-oscillation is impossible. More than 100 schemes describing auto-oscillations were established among four-stage schemes. As a rule, these schemes include linear-and bimolecular stages. The bank of relaxation time and critical phenomena which was worked out is used for the investigation of kinetics and series mecha nisms of concrete catalytic reactions (oxidation of carbon monoxide and hydrogen, interaction carbon monoxide with nitgen monoxide on platinum metals, etc.).

APPLICATION OF ULTRAFINE METAL PARTICLES IN CATALYSIS AND CHEMICAL REACTIONS

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Development of cluster-containing materials with unusual properties is of great interest for physics, chemistry and material science. One type of this materials is the ultrafine metal particles in nonaqueous media. The metal vapour synthesis (MVS) is the rather new method for preparation of such particles. In our work we study the cocondensation of metal vapours with various tertiary amines under cryochemical conditions results in formation of ultrafine metal particles (UFP) (stable giant metal clusters or colloids) in organic media and its investigation as catalysts.

In this work, metal vapour synthesis was used for preparation of UFP of different metals (Na, Pb, Mg, Mn, Cu, Sm) in tertiary amine media. The samples were studied by IR, UV-VIS, ESR at low temperature and photon correlation spectroscopy (PCS) in solution for determination of particle sizes.

We obtained for the first time, the stable colloidal solutions of magnesium, manganese, copper, led, sodium and samarium in triethylamine. Stability of this colloids are linked with the formation of unstable low temperature intermediates. These complexes are precursors for the double electric layer on the surface of the UFP in metal-triethylamine systems. This way allow to obtain the stable metal - colloids in non-aqueous media.

Chemical and catalytic properties of UFP was investigated for soluble and supported form of catalysts.

It was found that:

- UFP of Mg in pyridine provide the isomerisation on n-hexane at room temperature in solution;
- UFP of Mg, Cu, Mn, Sm provide isomerisation of olefins at room temperature in solution;
- UFP of all investigated metals provide rapid addition of carbon tetrachloride to double bonds of olefins in solution.
- UFP of all investigated metals provide isomerisation of halolefines in supported forms on silica and Al_2O_3.

Nature of this phenomena is discussed.

PPC-61

KINETIC AND CATALYTIC STUDIES OF OXIDATIVE COUPLING OF METHANE OVER OXIDES OF ALKALINE-EARTH METALS.

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INTRODUCTION The oxides of the alkaline-earth metals (AEM) are promising catalysts for the oxidative coupling of methane (OCM) and have been extensively studied for the past few years. Differences in selectivity and activity for these catalysts in OCM reaction were interpreted in terms of basicity and acidity of oxides [1], their ability to form stable peroxides [2] or were attributed to the concentration of defects in the lattice [3, 4]. However, the individual reaction steps and the influence of homogeneous and heterogeneous reactions on the oxide structure remain relatively unknown.

The purpose of this paper was twofold:

the role of the gas phase and surface reactions in the formation of steady defect structure of AEM oxides and influence of defects on OCM process;

kinetic peculiarities of the OCM over SrO as a basis for reaction modelling and simulation using N_2O as oxidant.

EXPERIMENTAL To prepare catalysts the high purity materials were used. M/CaO (M=Li or Na) catalysts were prepared by impregnation of the original CaO with lithium or sodium hydroxide followed by drying and calcination at the air for 3 hours at 1273 K. $SrCO_3$ was calcinated at the oxygen for 2 hours at T=1523 K to remove the carbonates. Catalytic activity was examined at 1023 K in microcatalytic quartz fixed bed reactor. The method of radiation probe which consists in γ-irradiation of samples followed by registration of EPR spectra was used to study the composition of defects of catalysts.

RESULTS AND DISCUSSIONS The obtained SrO and the solid solutions of CaO with oxides of alkaline metals were examined in OCM reaction. The following results are presented.

i) It was shown that the concentration and nature of defects in the bulk of M/CaO (M=Li or

Na) catalysts were depended on the composition of gas phase. O_3^{2-}, CO_2^{2-}, $M^+CO_3^{2-}$ ($M=Li^+$ or Na^+) defects are formed in M/CaO lattice after the contact with CH_4-O_2 reaction mixture. These defects are not observed when CH_4-N_2O mixture was used. It was established that the increase of the portion of $M^+CO_3^{2-}$ defects resulted in increasing C_2- selectivity. It was proposed that CO_2^{2-} defects may be served as the intermediate sites for CO_2 formation.

ii) The nature of defects in SrO lattice is the same after the treatment of catalyst by both reaction mixtures. $H_2CO_2^-$ and V_{OH} are main defects in the bulk of SrO after catalytic reaction.

The difference between two catalytic systems (SrO and M/CaO) may be caused by distinctive steps of N_2O decomposition over studied catalysts.

iii) The kinetics of OCM process over SrO was studied. The rate of CO_2 formation has a first order with respect to N_2O. However, this rate does not depend on methane pressure. This observation confirmed the limited availability of oxidant on the surface because the slow step of N_2O activation is followed by the rapid reaction of the active oxygen species with hydrocarbons or by slow desorption of carbon dioxide, releasing the active sites.

The rate of C_2H_6 formation increases with increasing concentration of N_2O up to 2 vol.% but for higher partial pressure of N_2O the rate of reaction approaches to almost zero order with respect to N_2O pressure. The poisoning effect of CO_2 produced during the reaction was investigated to obtain the correct order of ethane formation with respect to N_2O. The experiment was carried out with CO_2 addition to the gas stream and dramatic decrease of the rate of ethane formation was found. SrO seems to react with CO_2 to form $SrCO_3$ under catalytic conditions and then decrease the concentration of active oxygen species. These observations allow to conclude that N_2O decomposition is the rate-limiting step and CO_2 is a poison for the ethane formation.

Acknowledgements The research described in this publication was made possible in part by Grant NRKM300 from the international Science Foundation and Russian Government.

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PPC-62

Radical Formation in the Reaction of CCl_4 with CaO.

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In the last time some works appeared suggesting the possibility of chlorinated organic interactions with surfaces of certain metal oxides (CaO, MgO) under a rather mild conditions [1]. It was shown that in some cases the deep conversion of ultrafine (nanoscale) CaO into $CaCl_2$ by the interaction with CCl_4 may take place according to reaction:

$$CaO + CCl_4 \rightarrow CaCl_2 + CO_2 \qquad (1)$$

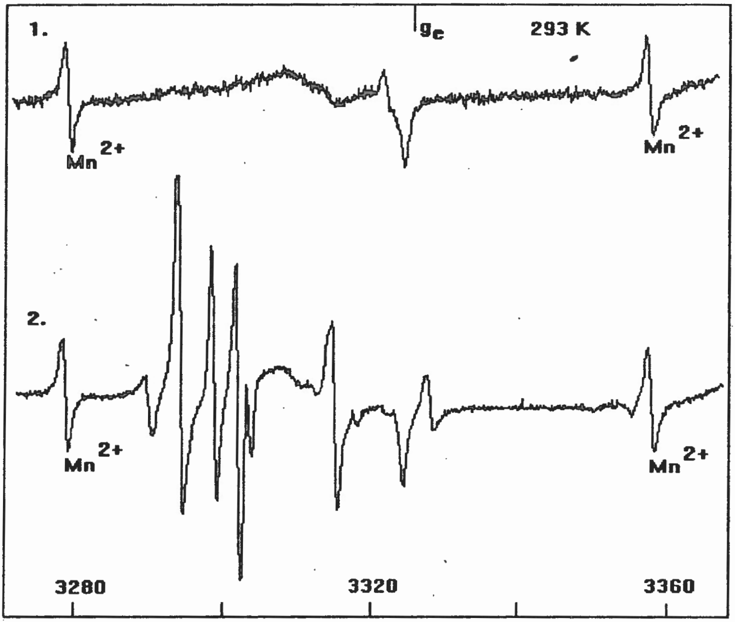
Such reactions are energetically quite favourable, however their mechanism remains unclear. In this work we have investigated the possibility of radical intermediates formation by the CCl_4 interaction with the active surface sites of thermally activated CaO samples.

Fig. shows the EPR spectrum of initial CaO sample recorded after its activation in vacuum at 873 K (spectrum 1) and the spectrum of radicals obtained after CCl_4 adsorption on this CaO sample at 293 K (spectrum 2).

It should be noted that for the formation of such radical particles the CaO activation in vacuum was necessary. The CCl_4 adsorption on CaO heated in oxygen at 773 K was not accompanied by the radical formation. We may suppose that the electron type centres (**e**) resulting from the removing of surface oxygen are active in such processes.

The dissociation of γ-irradiated CCl_4 in homogeneous systems is well known [2]:

$$CCl_4 + e \rightarrow {}^{\bullet}CCl_3 + Cl^- \qquad (2)$$



One can predict that in our case the first step of reaction is described as in eq.(2) and the spectrum 2 is due to more stable secondary radicals.

We have shown that oxidised CaO samples were able to form the same radicals as under illumination. In this case the CCl_4 dissociation (reaction 2) could occur on photoinduced electron centres.

This investigation was supported in part by the Russian Foundation for Basic Research (Gr. *N* 94-03-08690) and the ISF (Gr. *N* NPL000).

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PPC-63

LIQUID CRYSTAL AND METAL CONTAINING POLYMER FILMS PRODUCED BY CONDENSATION ON COLD SURFACE IN VACUUM

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Polymer films containing stabilized metal clusters and polar organic associates are of great interest due to their unique physical and chemical properties.

Poly-para-xylylene films containing polar organic substances with mesogenic properties and Ag-clusters have been obtained by low-temperature polymerization of layer or codeposited condensates.

P-xylylene monomer was produced by heating of para-cyclophane up to 600°C and then condensed on cold (77K) copper or glass surface in vacuum. After heating up to 130K the system was polymerized.

The mesogenic substances we used were: 4-amyl-4\`-cyanobiphenyle (5CB) with mesophase existance temperature range from 21 to 36°C, 4-methoxy-benzylydene-4\`-butyl-aniline (MBBA) (from 21 to 47°C), 4-hexoxyphenyl-4\`-butyl-benzoate (N-21) (from 19 to 40°C). Some films were obtained by deposition of liquid crystalline and metal silver vapour on the surphase.

To identify phase transitions produced polymer films were analised by optical-polarized microscopy method. Optical and electrophysical properties of produced films were considered. Influence of low-temperature matrix anisotropy was discussed.

Acknowledgements.

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KINETICS OF CATALYTIC HYDROLYSIS OF ALKALINE SOLUTIONS OF KBH_4 IN PRESENCE OF INTERMETALLIC La-Ni_5 COMPOUNDS

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In temperature interval 298-318 K it was investigated behaviour of intermetallic compounds $LaNi_{4.5}T_{0.5}$ (T - Mn, Cr, Co, Al, Fe, Cu) in alkaline (0.1; 1.0; 4.0 mol/l KOH) solutions of KBH_4.

By gasevolumometric method it was studied kinetics of catalytic hydrolysis of KBH_4 in 0.1, 1.0 and 4.0 mol/l KOH solutions with presence of $LaNi_{4.5}T_{0.5}$ (T - Mn, Cr, Co, Al, Fe, Cu). For all investigated intermetallic compounds reaction of catalytic hydrolysis KBH_4 has zero order with respect to KBH_4 and first order with respect to $LaNi_{4.5}T_{0.5}$.

It was found out that partial substitution of Ni in $LaNi_5$ for Mn, Cr, Co, Al, Fe, Cu exerted essential influence on speed of KBH_4 hydrolysis. It was discovered enormous increase of KBH_4 hydrolysis speed with increasing of concentration of alkali with presence of $LaNi_{4.5}T_{0.5}$.

Activation energies of catalytic hydrolysis KBH_4 with presence of intermetallic compounds $LaNi_{4.5}T_{0.5}$ are in interval 60-65 kJ/mol.

It was found out that hydriding of intermetallic compounds $LaNi_{4.5}T_{0.5}$ (T - Mn, Al) took place with forming hydride phases $LaNi_{4.5}T_{0.5}H_{4.5}$.

The work was carried out under financial support of The Russian Foundation of Basic Research (grant No. 95-03-09615a).

PPC-65

PHOTOSENSITIZED REDUCTION OF CENTRAL ION OF Mn(III)-PORPHYRINS IN HOMOGENEOUS AND MICROHETEROGENEOUS SYSTEMS

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It is known that manganese(II) porphyrins (Mn(II)P) are effective catalysts of selective oxidation reactions of unsaturated hydrocarbons. Usually, they are produced in situ from Mn(III)P in the presence of powerful chemical reducing agents(sodium borohydride, hydrogen/Pt-colloid, ascorbic acid). However it is difficult to avoid a side reactions of substrate. In this work the photosensitized reduction of central ion of Mn(III)P in homogeneous and microheterogeneous systems have been investigated. Dye acridine orange and CdS were used as photosensitizers. The homogeneous systems were the solutions of Mn(III)P, photosensitizer and electron donor in various solvents. A heterogeneous system was CdS suspension in Mn(III)P solution in MeOH or acetonitrile, the film of perfluorated ionexchanging membrane MF-4SK with Q-particles CdS and Mn(III)P immobilized in it or the glass plate with the layers of CdS and Mn(III)P deposited by continuous vacuum evaporation, which was plunged in solution of electron donor. In heterogeneous system the reduction of central ion Mn(III)P is by electron transfer from conduction band of CdS to Mn(III)P. The exposing to light of photosensitizer absorption band always results in the formation of product whose absorption band coincides with those of corresponding Mn(II)P formed by chemical reduction.

The work is executed at financial support of russian fund of fundamental researches (Code 93-03-18346).

STRUCTURE OF HYDROGEN ACTIVATED Cu-CONTAINING OXIDE CATALYSTS USING HT XRD IN SITU

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Complex oxides, in particular copper containing oxides Cu-Cr, Cu-Zn, Cu-Al,Cu-Mg - are widely used in a catalytic prosesses realized in reducing media.

It was shown that for 180-350 °C temperature range under hydrogen treatment the system of flat copper particles bonded epitaxially with the oxide surface as well as oxide is formed. This state is characterised by reversibility in different media. These phenomena are associated with structural features of oxide-precursors.

In the present work the hydrogen interaction with copper chromite, copper aluminate and zinc oxide containing clasters of copper ions was studied by the method of high temperature X-Ray powder diffraction (HT XRD) in situ. Precision of in situ XRD provides information about structures of all available phases. The distribution of cations in structures of reduced spinels was performed with Rietveld's method. The measurement of parameters of zinc oxide crystal lattice is conducted in the process of the dynamic changes under the action of the temperature and medium in situ.

Copper chromite was shown to transform in a defect cubic spinel at 320 °C in hydrogen. The part of copper ions (8a-crystallographic position) participates in exchange interaction: $Cu^{2+} + 2H^0 = Cu^0 + 2H^+$, that leads to the formation of copper atoms at the surface of copper chromite microcrystalls. The other part of copper ions participates in the following exchange interaction: $Cu^{2+} + H^0 = Cu^{1+} + H^+$. As a result, forming copper ions diffuse in nearest octahedrel site (16c).Hydrogen is shown to possess two states in the . structure of copper chromite, namely, specific hydrogen species H* which occupies octahedral interstate sites being forbidden in the spinel structure (16c), and protons (32e), wich form as a result of the exchange interaction between hydrogen and copper ions. An analysis of the interatomic distances indicates that the protons interact with the lattice oxygen and form of hydroxide bond.

Similar to copper chromite, metall copper from copper aluminate spinel (degree of inversion 0.5) is formed on the spinel surface in hydrogen. Again, only tetrahedrally coordinated copper ions are reduced whereas octahedrally coordinated ones still occupy their sites. In contrast to copper chromite the redistribution of three valent aluminium ions, which occupy free from copper tetrahedrons, occurs in the reduced aluminate. A certain part of octahedral sites become vacant,in which protons stabilizing the structure are located. However, the changed distribution of Al^{3+} ions prevents copper ions from coming back to the spinel structure and, thus, the latter - from its reversible transformation to the initial aluminate.

Phenomenon of reversibility was observed also for the solid solution of copper ions in anion-modified zinc oxide. A complex system which is composed of solid solution of copper ions in zinc oxide saturated with hydrogen and metallic copper epitaxially bounded to the spinel surface forms as in the previous cases. The feature of this system is that after effect by hydrogen and the replasement its on flow He more the favourable conditions are created to formation of true solid solution of copper ions in oxide zinc. Such solid solution is different from initial solid solution of where the copper ions are distributed as clasters. The changes of zinc oxide structure under influence of medium is confirmed by high resolution electronic microscopy (HREM).

Thus, new data about structure of the hydrogen activated Cu-containing catalysts were received. All investigated systems under the condition of the reduction in given area of temperatures demonstrate formation of the complex systems of phases - copper metal epitaxially bounded with surfase of . defect oxide stabilized by hydrogen. Observed of correlations between phase compositions and structure of catalysts (Cu-containing oxides) and their catalytic behaviours for hydrogenation of aceton to isopropylic alcohol and synthesis of methanol showed that only those structural states that are observed at 180 - 370 °C have high activities. The knowledge on structures of active states and conditions for their formation makes it possible to give conclusions about mechanism of their catalytic action.

The work was funded by the Russian Foundation of Basic Reseach, Grant N 94-03-08260.

NEW PHENOMENA OF LIQUID METAL-CARBON INTERMEDIATE COMPOUNDS FORMATION AT LOW-TEMPERATURE (600-700°C) CATALYTIC GRAPHITIZATION OF AMORPHOUS CARBON BY METALS OF IRON SUB-GROUP

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We have discovered and studied experimentally a previously unknown phenomena of liquid metal-carbon intermediates forming in the process of solid-phase interactions of iron, cobalt or nickel particles with amorphous carbon under heating in vacuum to the temperatures which are 500-900 °C lower than the melting points of pure metals or their eutectics. The experiments have been carried out in situ in column of electron microscope JEM-100 CX under residual pressure of 10^{-4}-10^{-5} torr with use of a heating device and video recording of processes dynamics. The thickness of amorphous carbon support was 20-30 nm. Fe, Co, Ni or their hydroxide, oxide, salt particles have been deposited on this support. When using hydroxides FeO(OH), $Co(OH)_2$, $Ni(OH)_2$ as initial compounds their interaction with carbon support under heating in the electron microscope column proceeds in the following way. At first dehydration of hydroxide particles occurs and Fe_2O_3, CoO and NiO oxides form. At 600°C and above the oxide crystals react with carbon support and are reduced to metals. The particles remain solid and do not move over the support up to their transition to metallic state. The liquid particles Fe-C, Co-C and Ni-C form as a result of solid-phase reaction of metal and amorphous carbon under specific conditions of heating in vacuum to some critical temperatures. The critical temperatures at which Fe, Co and Ni particles turn into the liquid state are 640, 600 and 670°C respectively. Under conditions mentioned above in the system "metal particle - amorphous carbon surface" some efficient interaction mechanism takes place. This mechanism leads to a detachment of carbon atoms (or clusters) from the support and their dissolving "at the moment of forming" in metal. We have established the limit concentration (50 atom %) of dissolved carbon, when stability of metal particles structure is lost. As a result, these particles turn into the liquid state forming anomalously supersaturated solutions of carbon in metal. 10-100 nm particles turn into the liquid-like state totally, then they begin to move chaotically onto the carbon support remaking it to the graphite tracks. When moving these liquid-like particles are dipped into support, their thickness is equal to that of carbon support (in our case it is 20-30 nm). The thickness of graphite tracks is also 20-30 nm, their width corresponds to the determinant sizes of liquid particles. When moving such particles change their form and geometric contour all the time, and there is no diffraction contrast observing them in situ. The liquid particles movement velocity depends on metal chosen and temperature but almost does not depend on the particle size in the interval noted above. So, at 700°C the initial velocities of liquid Fe-C, Co-C and Ni-C particles movement are 1000, 30 and 10 nm/s respectively. The liquid-like state takes place only under dynamic conditions at a fast movement of metal-carbon particles on the carbon support. The particles which lost their mobility turn into the solid state by phase composition corresponding to carbides and/or metals.

This work was supported by the Russian Foundation of Fundamental Researches (grant number 94-03-08698).

Partial Oxidation of Ethane by Dioxygen, Activated at Carbon Gas-Diffusion Cathode

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Cathodic activation of dioxygen on a porous carbon membrane (gas-diffusion electrode) is proposed in the present work as an approach to selective oxidation of ethane.

It has been shown [1] that ethane can be oxidized to acetaldehyde (65%) and ethanol (35%) in a gas or gas-liquid electrochemical cell on a Nafion-H promoted carbon gas-diffusion electrode under the atmospheric pressure at 80-100°C. Effective removal of the oxigenates through the gas-diffusion electrode out of the reaction zone provides high selectivity of the partial oxidation, the amount of carbon dioxide formed due to the deep ethane oxidation not exceeding 2%.

The reaction has been proved to proceed via an intermediate formation of hydrogen peroxide on the carbon electrode due to cathodic reduction of dioxygen. The effects of current density and partial pressure of dioxygen on the rate of hydrogen peroxide production are studied. A correlation between H_2O_2 generation rate and ethane partial oxidation has been shown.

The presence of Nafion-H film on the electrode has proved to be of crutial importance for the promotion of ethane partial oxidation not effecting the rate of hydrogen peroxide formation.

Evaluation of the effects of the reagents concentrations, pH and temperature on the reaction rate and selectivity has proved the radical mechanism of the reaction. The nature of the active oxygen and mechanism of ethane activation are discussed.

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Financial support from INTAS (grant N. 93-2402) is gratefully acknowledged.

PPC-70

M-containing heteropolytungstates as catalysts of H_2O_2 participated reactions. Mechanistic study of oxidation of unsaturated hydrocarbons.

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Oxidation of organic substances under the action of H_2O_2 arouses the permanent interest. At the present time, a part of interest is given to a new type of redox catalysts which represent M-containing heteropolytungstates $PW_{11}M$. Enthusiasm in researches about this field could promise a rapid remarkable advance in catalytic oxidation, if H_2O_2 participated reactions were not as complex as attractive. Realizing this complexity, we decided to approach the problem in the way of combined study of $PW_{11}M$ in two reactions: the oxidation of cyclohexene and benzene with H_2O_2 and accompanying process of H_2O_2 decomposition.

Providing stability for original ions PW_{11}, M-containing heteropolytungstates of a general formula $PW_{11}M(L)O_{39}^{n-}$ were synthesized and isolated as organic solvent soluble $[(n\text{-}C_4H_9)_4N]^+$ salts; M- transition metal, L may be H_2O, OH^-, O^{2-}. The catalytic experiments were performed in CH_3CN solution using aqueous H_2O_2. The rate of H_2O_2 decomposition varied within wide range from the highest for Co and Cu to small for Ni and V (as for original PW_{11}) and negligible for Ti. Possessing a moderate activity in H_2O_2 decomposition, only Fe- and Cr-containing heteropolytungstates showed a capacity to catalyze cyclohexene oxidation with H_2O_2.

For some metals, the catalytic properties of MPW_{11} were extremely sensitive to experimental conditions of their synthesis. To investigate in detail the effect of precursor and procedure of synthesis (increasing temperature, prolonged keeping solution, varying molar ratio of starting reagents and acidity), a number of Cr-containing heteropolytungstates $PW_{11}Cr$ were prepared and characterized by elemental analysis, UV-VIS and IR spectroscopy. Tetrabutylammonium salts of $PW_{11}Cr$ were examined in catalysis of H_2O_2 decomposition and oxygen transfer from H_2O_2 to hydrocarbon substrates cyclohexene and benzene. At the other identical conditions of synthesis, increasing pH value gave samples more active in H_2O_2 decomposition. In the system $H_2O_2/PW_{11}Cr$, benzene formed phenol and cyclohexene formed a mixture of cyclohexenone, cyclohexenole and cyclohexene oxide. Activity of $PW_{11}Cr$ in hydrocarbon oxidation depends on the procedure of sample synthesis.

Variable spectral characteristics and catalytic properties of $PW_{11}Cr$ samples were suggested to depend on the nature of bond between Cr(III) ion and $PW_{11}O_{39}^{7-}$ anion. As distinguished from typical M-substituted polyoxometalates, the samples obtained contain Cr(III) ions which are, probably, connected with surface oxygen atoms of $PW_{11}O_{39}^{7-}$ heteropolyanion near the vacancy of Keggin structure.

Surface location of Cr(III) ions is supposed to favor oxygen transfer from H_2O_2 to hydrocarbon. In the presence of H_2O_2, $PW_{11}Cr$ solutions showed the increase of visible absorption and a shift of its maximum from 15200-16300 to 15500-18000 cm^{-1}, that arose from reaction of $PW_{11}Cr$ with intermediate products of H_2O_2 decomposition. Resulting oxidized species $PW_{11}Cr[O]$ are active oxidants in reaction with unsaturated hydrocarbons.

We are grateful for support from ISF grant No RP-5300.

NEW SPHERES OF CATALYSIS APPLICATION IN TRANSFORMATION OF NATURAL ORGANIC POLYMERS AND KINETIC STUDY OF CATALYTIC REACTIONS OF MODEL-TYPE ORGANIC COMPOUNDS

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The problem of natural organic polymers conversion to fine chemicals and carbonaceous materials with high rate and selectivity throws the challenge to the modern chemistry.. Taking into account the great role of catalysis in oil chemistry it seems reasonable to expect that the development of catalytic chemistry of natural organic polymers will promote the extensive drawing of alternative materials to organic synthesis.

The research design was connected with the elaboration of approaches to effective catalytic promotion of chemical bonds in solid organic matrix. Two different principles: the direct action of catalyst on chemical bonds and the indirect route, based on the translation of catalyst action through the reaction medium, were used. Reaction of thermocatalytic transformation of wood hexasanes into levoglucosenone, levulinic acid, hydroxymethyl furfural and wood lignin into aromatic aldehydes and hydrocarbon mixtures were studied in flow and static reactors. Kinetic data on model compounds catalytic reactions made possible to describe the routes of chemical bonds transformation in studied polymeric materials.

The phenomenon of indirect catalysis was investigated in the two processes of different type: oxidative pyrolysis of natural organic polymers (wood lignin and coals) in a fluidized catalytic bad and in high-temperature coking in the presence of catalytic additives. Systematic study of catalyst action on the yield and composition of liquid, gaseous, solid products, on the structure and properties of obtained carbon materials was accomplished. Obtained data made possible to understand the main peculiarities of natural organic polymers thermocatalytic transformations. Different physical (IR, NMR, chromato-mass, ESR spectroscopy, X-ray, SEM, HRTEM, TGA, adsorption techniques) and chemical methods of analysis were used for the study of catalytic reactions of natural polymers and model-type compounds.

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PPC-72

STRUCTURAL ASPECTS AND DYNAMIC BEHAVIOR OF V_2O_5-$Cs_2S_2O_7$ SYSTEM WITHIN 25-550°C ACCORDING TO NMR DATA

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The chemistry of $V_2O_5-M_2S_2O_7$ (M= K, Na, Cs) systems has been thoroughly investigated by a number of chemical and physical methods due to their importance as an active component of the catalysts for sulfuric acid production and for cleaning of flue gases from SO_2. Nevertheless, some structural aspects and dynamic behavior of the systems remain unclear due to their complexity which exibit the tendency for the glass formation. Modern solid–state and high–temperature NMR is well suited for the structural analysis of highly disordered and complex systems, as well as the dynamic aspects of glass structure due to its high sensitivity to the local environment of the nuclei under study. NMR studies of V_2O_5–$M_2S_2O_7$ are hindered by high conductivity and high viscosity of these systems in molten state that is why these systems have still not been studied thoroughly by this method.

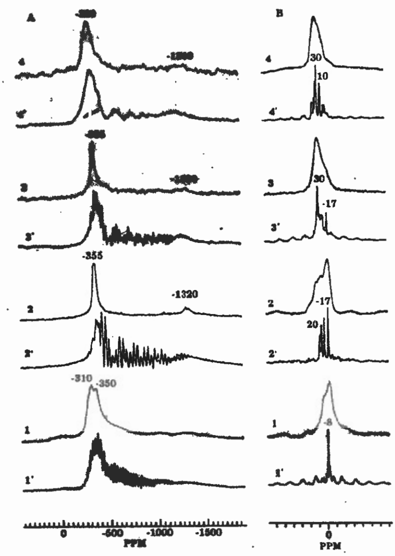

Figure 1. Static (1–4) and MAS (1'–4') NMR spectra of $V_2O_5-Cs_2S_2O_7$ mixtures measured at ambient temperature and different Cs/V ratios. The samples were prepared at 500°C. A: ^{51}V spectra. B: ^{133}Cs spectra.

Here we present the first results of ^{51}V and ^{133}Cs NMR studies of the $V_2O_5-Cs_2S_2O_7$ system of different compositions in a temperature range from 20 to 550°C that includes both solid and molten state of these samples with the use of a specially constructed probe head for the measurements of NMR spectra at high–temperature.

^{51}V and ^{133}Cs NMR indicate that three different states of V(V) are formed dependent on molar ratio Cs/V at 20°C. In samples very dilute with respect to vanadium (Cs/V = 50) an distorted octahedral complex is formed. At higher concentration of vanadium (Cs/V=4) another octahedral complex (probably $Cs_4(VO)_2O(SO_4)_4$) is observed. ^{133}Cs NMR spectrum of this sample has four different lines, it is in very good agreement with the unit cell of the complex. For the Cs/V = 1 sample also a distorted octahedral vanadium complex is formed. The ^{133}Cs MAS spectrum of this sample exhibits only one line which belongs presumably to the compound $CsVO_2SO_4$.

The ^{51}V NMR spectra of V_2O_5-$Cs_2S_2O_7$ samples with Cs/V=1; 2 and 4 and different temperature demonstrate different dynamic behaviour of these samples under temperature. The types of mobility seem to be different for crystalline and glassy samples. Some kind of phase transition probably takes place for crystalline Cs/V = 1 and Cs/V = 2 samples followed by averaging of the local environment of V due to thermal mobility of atoms in these compounds. For glassy Cs/V = 4 sample at temperature between 100 and 200°C (below the melting) effective averaging of the chemical shift anisotropy takes place most probably due to rotation of the polymeric network of glass structure (fig 2, spectra 3 and 4). The further increase of temperature probably breaks the polymeric chains with the rearrangement of the structure with formation of different V structures that include long and relatively short networks with V in different environments.

^{133}Cs data for $Cs_2S_2O_7$ demonstrate different types of Cs mobility in this material, including the migration between different Cs positions in the crystal structure, a kind of anisotropic diffusion of Cs inside the crystal, and the rapid isotropic diffusion near the melting point.

This work has been supported by the INTAS (Grant 93-3244) and the Russian Foundation for Fundamental Investigations (Grant 95-03-08365a).

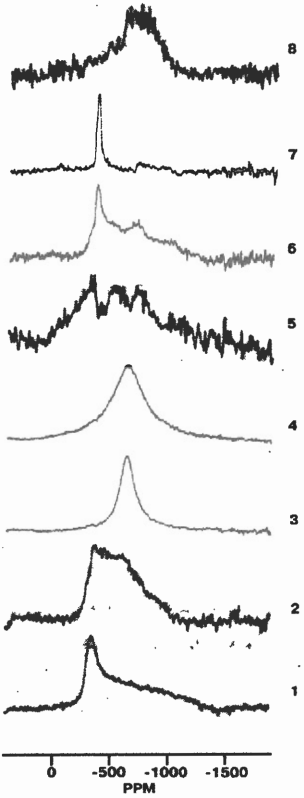

Figure.2. ^{51}V NMR spectra of V_2O_5-$Cs_2S_2O_7$ sample (Cs/V = 4) measured at different temperatures: 1-120° C; 2-170°C; 3-220°C; 4-240°C; 5-260°C; 6-280°C; 7-320°C; 8-400°C.

PPC-73

PROPERTIES OF PD-CU BIMETALIC CATALYSTS PREPARED FROM MIXED ACETYLACETONATES

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Bimetallic Pd-Cu catalysts supported on silica have been prepared from the acetylacetonates of the two metals. A mixed crystalline complex is identified on the support by its X -ray diffraction spectrum. By elimination under argon at 670 K of the organic ligands, an alloy is formed. It has a fcc structure in the whole composition range, except at the vicinity of the 50/50 composition, where it is cc. This agrees with the phase diagram of the bulk alloys.The mean diameter of the particles is 2.5 nm and they have an homogeneous composition.

It is shown by LEEIS (ion scattering), that the surface contains more Cu than the bulk, specially for the low Cu content.

The reactivity of these catalysts in the hydrogenation of butadiene is lower than that of pure Pd; but if the reaction temperature is raised to reach a high conversion, their selectivity for the formation of butenes is always 100 %, at the difference of the pure Pd catalysts. This is explained on the basis of CO adsorption studied by infrared. Indeed the modification of selectivity is attributed to an increase of the ratio of the adsorption constants of butadiene and butenes; this phenomenon is probably due to the coverage by cu atoms of « hot » adsorption sites, where both molecules are strongly bonded: edges and (100) facets of the surface.

PPC-74

Design of surface nanostructures chemically bonded on silicon dioxide.

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New tendency arising in modern heterogeneous catalysis and surface chemistry can be defined as "design of surface-bonded nanostructures". This means the controlled preparation of supramolecular structures that are formed from molecules covalently binded with surface of support and possibly with each other.

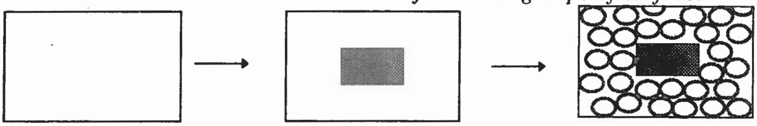
In the present paper we propose the methods for preparations of surface nanostructures on chemically modified surfaces.

Islands of bonded molecules. The method of molecular templates (imprints)

The molecular imprinting methods has been successfully used in adsorption and catalysis [1-4].

The use of chemical modification for the "fixation" of imprints is proposed. The idea is clear from Figure 1. In the first stage, template molecules are adsorbed in small concentration on the surface of SiO_2. Water

I. Adsorption of a template. *II. Blocking of accessible functional groups of surface:*



III. Desorption of a template. *IV. Modification of islands formed.*

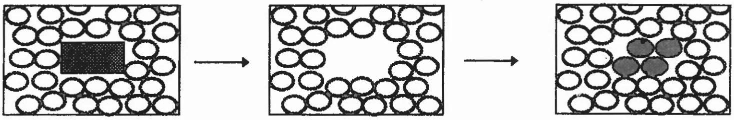


Figure 1. Method of molecular templates in chemical modification of surface.

soluble cyclodextrines and organic dyes were used. Surface distribution of the templates adsorbed belongs to the random or uniform way. This leads to the presence of predominantly isolated adsorbed molecules. The second stage involves the blockage with trimethylchlorosilane of surface silanols, which are not covered with adsorbed templates. At the third stage, the templates adsorbed are removed under the mild acid conditions. Size and distribution of the islands formed were studied by means of ESR-spectroscopy and nitroxide paramagnetic labels.

Finally, the islands of nonmodified surface can be modified by the desired modifier.

"Mosaic structures." Bonded molecules are situated in the sets of a regular lattice

In order to obtain the mosaic bonded structures the following approach is suggested. First, the surface is covered with a dense monolayer of large flat molecules covalently bonded to the surface along the axial anchor group (Fig.2). This idea was realized for phthalocyanine of silicon on the surface of SiO$_2$. Surface organization of adsorbed phthalocyanine molecules was studied with scanning tunnelling microscopy.

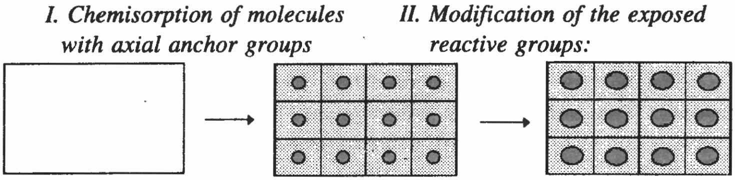


Figure 2. Scheme for preparation of a regular lattice from bonded molecules.

The objects obtained were studied in oxidizing catalysis.

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PPC-75

Relative Reactivity of Alkanes and Alkylarenes in the Reaction with Peroxynitrous Acid (Peroxynitrite).

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For last few years nitric oxide, NO, was recognized to play many important physiological roles. It's formed *in vivo* by enzymatic oxidation of L-arginine by dioxygen. Superoxide anion is one of the major intermediate in the process of biological dioxygen reduction and was shown to react quickly with NO to form peroxynitrite:

$$NO + O_2^{\cdot -} \rightarrow ONOO^-$$

Peroxynitrite is believed to be one of species responsible for NO toxicity. Its protonated form (pK = 6.8) shows radical like reactivity, which is often attributed to a formation of free hydroxyl radical by homolytic O-O bond cleavage in peroxynitrous acid:

$$HOONO \rightarrow HO\cdot + NO_2$$

For a long time we were involved in the study of alkane and alkylarene oxidation by various oxidants, numerous data on their reactivity being obtained[1]. In this study we used our kinetic approaches to look at the reaction of peroxynitrous acid with alkanes and alkylarenes to answer the question, whether hydroxyl radical is formed from peroxynitrous acid.

To overcome the problem of very low hydrocarbon solubility in water we have developed a so-called "kinetic distributing technique[1]." In its most useful version the competitive oxidation of two substrates, R_aH and R_bH, is studied in closed reaction flask with known volumes of a gas- and liquid-phases under vigorous agitation. Following the kinetics of substrate consumption in the gas phase one can find their relative observed rate constants of oxidation:

$$\lg[R_aH]_g = (k^a_{ob}/k^b_{ob})\lg[R_bH]_g \ ,$$

which are related to the actual bimolecular reaction rate constants by the expression:

$$(k^a_{ob}/k^b_{ob}) = [(k^a(1 + \alpha^b\lambda)]/[k^b(1 + \alpha^a\lambda)],$$

where λ is the ratio of volumes of gas and liquid phases, an $\alpha = [RH]_g/[RH]_l$ is the solubility of substrate.

PPC-75

Peroxynitrous acid itself decomposes too quickly at pH < 8, $k = 1.3\ s^{-1}$ (25°C), therefore a mixture of hydrogen peroxide and nitrite under weakly acidic conditions being used to generate slowly peroxynitrous acid *in situ*. This mixture was found to oxidize alkanes and alkylarenes at pH = 4-5, the reaction follows first orders on the respect of the alkane/alkylarene concentrations. Relative reactivity of various normal-, branched- and cycloalkanes, as well as alkylarene has been measured.

The reaction exhibits low substrate selectivity, resembling qualitatively that of hydroxyl radical. However, in our case hydroxyl radical can be definitely ruled out: i) hydroxyl radical is expected to react faster with an excess of buffer components (acetic acid/acetate) or with nitrite anion, than with substrates; ii) the observed order of reactivity, *n*-alkanes ≥ *iso*-alkanes > *cyclo*-alkanes > alkylarenes, is quite unusual and different from that of for hydroxyl radical; iii) the obtained value of kinetic isotopic effect (KIE), $k^{cyclohexane}/k^{cyclohexane\text{-}d\text{-}12} = 1.5$, as well as the ratio $k^{cyclopentane}/k^{cyclohexane} = 2.5$, also differ from that of for hydroxyl radical, 1.05 and 1.13, respectively.

Careful examination of all data led us to the conclusion, that the reaction partly proceeds in a gas phase. A new kinetic model, as well as a new experimental approach, have been developed to the case, when the reaction proceeds in both phases. Relative reactivities of hexane/toluene, cyclohexane/cyclopentane and KIE were measured for the reaction in each, gas and liquid, phases.

The nature of reactive species are discussed. In a liquid phase the reactive species might be some form of peroxynitrous acid itself, while in a gas phase it is believed to be one of the uncharged radical product of peroxynitrite decomposition. Nitrogen dioxide was showen to be non reactive under our experimental conditions.

We are gratefully acknowledge the financial support by INTAS (grant 93-1060).

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ELECTROSTATIC FIELD EFFECT ON THE CATALYTIC ACTIVITY OF SURFACE OF SOLIDS

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On theoretical description of adsorption processes on the surface of polar sorbent the approaches, based on the approximations of so-called "hard zones" and cluster model of solid are especially fruitful. In the framework of the first approach it is considered that on the surface of adsorbent the uniformly distributed charge is accumulated; this charge creates in the near-surface region the electrostatic field, which defines the physical adsorption of molecules. The alternative cluster approach assumes the quantum-chemical analysis of electronic structure (and if it is necessary, the geometric structure) of the chosen fragment of adsorbent surface layer or adsorption complex, calculation of energetics of the interaction adsorbent-adsorbat, and also charge distribution on the atoms of the studied cluster, etc.

Therefore for elucidating the role of electrostatic field in adsorption processes we propose the approach,combining to some extent the peculiarities of approximations, described above.At first two types of electrically neutral clusters are chosen,one of which models the part of the crystal's surface and the other -the bulk phase of the crystal. At the next stage the electronic structure of these basic clusters is calculated by the quantum-chemical method,being suitable for this work (MNDO, MINDO/3,etc.).The obtained wave functions of clusters are used for calculation of the electrostatic potential in the near-surface region. Later of the contributions from basic clusters with account of crystal's symmetry are summarized.This approach of electrostatic potential calculation and field calculation has a series of advantages in comparison with direct summarizing of contributions from ions forming the crystal's lattice.

When an admolecule gets into EFS the shifting of admolecule's one electron energy levels takes place. As a consequence, the conditions can be created when Fermi level of a crystal depending on admolecule's nature may coincide with the energy level of one of the lowest vacant or the highest occupied molecular orbitals, that is the condition of "orbital resonance" is realized.

The high values of adsorption heat and substantial reactivity of some electrodonor molecules may be reffered to the orbital resonance.

The series of field mass-spectrometric experiments (the ionization of molecules by external electric field of high strength) is supposed to carry out for revealing the cases of orbital resonance. In addition, there is reason to think, that the electric field can remote or impose restrictions, affecting the running of chemical reactions by the rules of orbital symmetry.

PPC-77

ELECTROPHILIC CATALYSIS BY PROTONS AND ACYL CATIONS IN ALTERNATIVE ACTIVATION OF CARBONYL COMPOUNDS OR NITRILES

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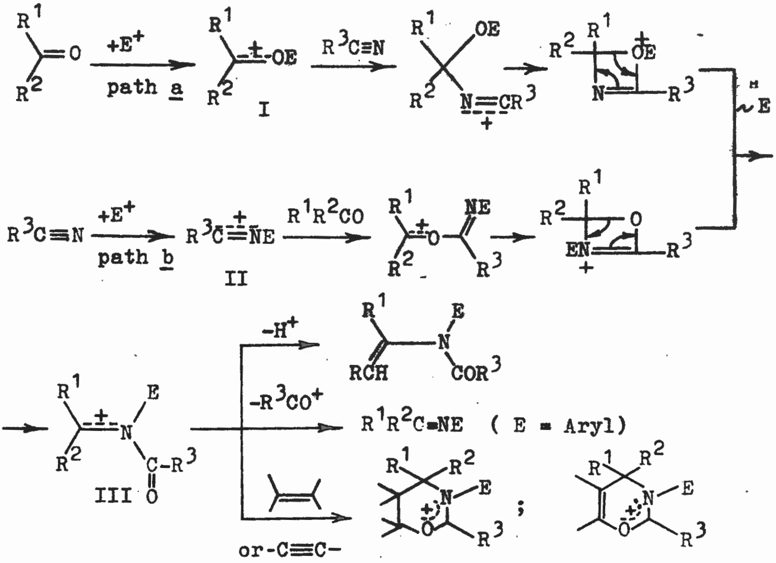
Recently we found a new approach to the electrophilic activation of carbonyl compounds for their reactions with weak nucleophiles. This approach involves the conversion of aldehydes and ketones into highly active acyloxycarbocations $R^1R^2C^+\text{-}OCOR^3$ by the action of acylium ions regardless of the origin of the latter. It has been shown that the electrophilic catalysis by acyl cations in carbonyl reactions takes place which was used in the reaction of both aldehydes and ketones with nitriles.

It should be noted that few examples of the intermolecular reactions of carbonyl compounds with nitriles are known. These reactions proton acid catalyzed are considered in all publications as nucleophilic addition of the nitriles to carboxonium intermediates I, i.e.a Ritter-type reaction (path a, if E=H). However, we have shown that such path a is realizable only when the activating electrophile E is acyl cation. On the contrary, the proton acid catalyzed (E = H) interaction of carbonyl compounds with nitriles occurs via a mechanism involving the electrophilic addition of nitrilium ions II to the carbonyl group (path b). The nitrilium ions II behave as a heteroanaloga of acylium ions. The both paths a and b lead to the same N-acyliminium ions III which are precursors of the valuable compounds such as N-acylated enamines, various 1,3-oxazine derivatives, etc.

In that way, two independent paths for the reaction of carbonyl compounds with nitriles under alternative electrophilic activation of either components have been found experimentally as well as by theoretical calculations. This interaction includes two variants of rearrangement which proceeds with the participation of the internal nucleophile (O or N heteroatoms) but the latter was formerly the electrophilic particle.



Therefore, in contrast to earlier proposals, this interaction cannot be considered to be a variant of the Ritter reaction because it differs from the latter by two types of electrophilic activation of reagents and by two types of rearrangement. Besides, this interaction occurs at oxidation level two, while the Ritter reaction occurs at oxidation level one. In that way, we consider that the acid catalyzed reaction of carbonyl compounds with nitriles in question is an independent reaction, little investigated until now.

Authors are grateful to International Science Foundation (grant NRV000) as well as ISF and Russian Government (grant NRV300) for financial support of this research work.

PPC-78

INVESTIGATION OF ELEMENTARY ACTS OF HETEROGENEOUS-CATALYTIC REACTIONS BY MICRO CALORIMETRY

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The calorimetric method is widely used in research of the mechanism of the heterogeneous-catalytic reactions, to define the limiting stages, to define the velocity constants of the elementary reactions. We have developed a modified calorimetric method, which allows us to study the temperature characteristics of the catalytic reactions in time. A small semiconductor thermoresister was coated with a layer of catalyst and was placed in a gas reaction media. When an eczo- or endothermic reaction takes place on the surface of the catalyst, the temperature of the semiconductor sensor changes and duc to that the conductivity of it changes. By monitoring the changing conductivity, it is possible to monitor the temperature of the catalyst during the course of the chemical reaction.

This method was used by us to study the mechanism of the heterogeneous-catalytic decomposition of ozone. When the catalytic sensor was placed in the ozone flow it got wormed up to a maximum value, then the temperature dropped and later reached a certain stationary level. By looking at the character of the temperature change of the catalyst in time, we can suggest the following mechanism of ozone decomposition: adsorbtion of ozone on the active centres of the catalyst, decomposition of the adsorbed molecules and desorbtion of the decomposed product - oxygen and freeing the active centres. This calorimetric research showed us that the limiting stage in the ozone decomposition is the stage of decomposed product desorbtion. During this research work the mathematical modelling of this heterogeneous-catalytic decomposition of ozone was carried out. The solution of the appropriate system of the differential equations allowed us to calculate the constants of the elementary stages of the reactions and allowed us define the life time of ozone on the surface of the catalyst.

The Mechanism of Acetone Hydrogenation

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This work is devoted to studies of acetone hydrogenation on copper chromite catalyst using kinetic and in situ HT XRD methods..

We have observed [1] that at 180-370°C the reversible hydrogen absorption by copper chromite takes place resulting to the formation of copper flat particles bonded epitaxially to the defect spinel surface. Release hydrogen from spinel bulk results to catalyst transformation to the initial copper chromite. The reversible separation to two phases is the consequence of substitution of a portion of copper ions by protons. Catalyst exhibits activity in acetone hydrogenation to isopropanol only in the region of reversible hydrogen absorption.

The interaction of acetone with hydrogen-containing copper chromite was studied in this work. Catalytic testing of the samples was made in a pulse flow reactor with chromatographic analysis of products. X-ray spectra were obtained with a D 500 Siemens diffractometer with CuK$_\alpha$ radiation. An HTK-10 Anton PAAR cell was used for in situ high temperature registration of the spectra in a reagent flow.

It was shown that formation of the alcohol takes place in absence gaseous hydrogen. Feeding acetone to pre-reduced copper chromite resulted in formation of the αisopropanol and bringing the structure back to its initial state. Hydrogenation rates depend on hydrogen amounts in the spinel bulk. The hydrogen content is a function of pre-reduction temperature.

The observed reversibility of the system and the bulk uptake of hydrogen, a portion of which is in the form of protons, make it possible to treat the mechanism of the reaction under investigation in terms of the approach developed for the reduction of ketones to alcohols by the metals dissolved in a “protonic medium” [2]. According to the approach the hydrogenation proceeds as follows: the attachment of the electrons from the metal and a proton from a “protonic medium” to a ketone molecule which becomes negatively charged is followed by bonding another proton from the “protonic medium”. If the hydrogen-containing spinel with the copper deficiency of ca.50% is considered as the “protonic medium”, the hydrogenation of acetone over copper chromite can be suggested to follow the same mechanism. Acetone is adsorbed as a π-complex on copper atoms [3], the metal electrons being localized at the antibinding π-orbitals of the carbonyl group. At the same time a proton from the “protonic medium” is bonded to the adsorbed acetone molecule. The organic molecule gets a negative charge, and the metallic copper is oxidized and occupies the spinel positions it has left during the reduction; the bonding of the second proton is followed by the desorption of the alcohol molecule. The catalyst being in the reduced state under the reaction conditions, the second stage is thought to be the rate limiting one. There are both acetone and hydrogen in the reaction medium under the conditions of the catalytic hydrogenation of acetone to isopropanol, therefore it is most likely that the protons of only subsurface layers participate in the transformations, and hence, the reversible transition of the metallic copper to the ionic state occurs only within the subsurface layers too.

Thus, the present work shows carbonyl groups in vapour- phase reaction over solid catalysts to be hydrogenated via the same mechanism as in solutions they are.

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New nonstandard method of phase analysis of heterogeneous catalysts

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Up a today a problem of phase analysis of solids is resolved essentially by physical methods, in the main by X-ray diffraction, determining structural parameters of any individual phase. However these methods provide no precise information regarding the elemental composition and stoichiometry of the phase. In turn the possibilities of methods for the phase composition determining are also bounded by two factors. Firstly, there is an abundance of unknown phases and especially as their various mixtures. Secondly, there is a need to have references close to each phase of the sample. The selection of matched pairs of reference and sample still seem to involve considerable difficulties for all standard methods.

New nonstandard stoichiographical method of differential dissolving (DD) for phase analysis has been developed in the Institute of Catalysis in 1986. It has a great advantage over the other methods as a new analytical technique for determining the dissolving kinetics processes. The method is based on stoichiography regularities which determine the stoichiometry unsteady-state processes of mass-transport [1]. Runs and results of the processes may be conceived as a set of functions of the molar relationships of dissolving rates for elements component the given sample. In this case there is no need to describe the process rates using some kinetic equations, and unique possibility is appeared for molecular analysis by the nonstandard analytical technique.

The DD method has been developed in exchange for the classical technique of selective dissolving which is little promising one [2]. The DD method consists in the following:

- dissolving a given sample under dynamic conditions provided in time increasing the chemical potential of the solvent;

- recording the kinetic dependencies for all or portion of elements consistent the sample;
- calculating and analyzing the stoichiograms to deduce empirical formulae and determine amounts each of the phases of the sample.

There are two factors that have been most influential in the success of DD: working out the theory and instrumentation extensively and solving some practical analytical problems. It gives us a assurance that novel universal nonstandard technique will be widely used for analyzing the complex solid mixtures.

DD-method permits validly to perform the separation and collection of phases with following identification by the other fitting methods. The DD- method together with X-ray one were very usefull in study of the complicated processes of forming the catalysts including interection between active components and supports. In this case the quantitative information about contents of the crystalline or amorphous phases of the same composition could be obtained. DD is rather rapid method and in most cases it has already been possible to determine an unknown phase composition of any catalyst from the first experiments.

Now there are about 50 papers devoted DD-method and appliedtion of its to the phase analysis of the various matters such as the starting and intermediate products, heterogeneous catalysts with various types and structures. As a rule they all were characterized by the complicated phase compositions, high or low content of active components [3]. Results obtained by DD-method provided insight into the nature of heterogeneous catalysts.

This work was supported by the Russian Foundation of Fundamental Researches (Grant 93-03-05112) and by the International Science Fundation (Grant RA9000).

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"Dynamic activation of C-H and C-C bonds. Theoretical study."

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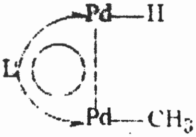
The development of methods for selective transformations of alkanes to their functional derivatives through C-H and C-C bond activation under mild conditions is an important and challenging problem of modern catalysis. Oxidative addition of alkanes to the surfaces of bare transition metals, to metal atoms and their clusters in gas phase are the key steps of such catalytic transformations [1,2]. The study is aimed at the development of dynamic quantum chemical models for oxidative addition reactions (OARs):

$$Pd + CH_4 \longrightarrow [PC] \longrightarrow [TS] \longrightarrow CH_3\text{-}Pd\text{-}H \qquad (I)$$

$$Pd + CH_3\text{-}CH_3 \longrightarrow [PC] \longrightarrow [TS] \longrightarrow CH_3\text{-}Pd\text{-}CH_3 \qquad (II)$$

$$Pd_2 + CH_4 \longrightarrow [PC] \longrightarrow [TS] \longrightarrow CH_3\text{-}Pd\text{-}Pd\text{-}H \qquad (III)$$

$$\mathbf{Pd_2L + CH_4 \longrightarrow PC \longrightarrow TS \longrightarrow}$$



(IV)

(IVa: $L = -(PH_2)\text{-}(CH_2)_2\text{-}(PH_2)-$
IVb: $L = -(PH_2)\text{-}(CH_2)_2\text{-}(NH_2)-$)

where PC, TS introduce pre-reaction complex, and transition state, respectively.

The Reaction Path Hamiltonian formalism [3] has been involved into the study. Potential energy surfaces (PES) have been computed by the CNDO/S^2 [4] semiempirical LCAO MO SCF technique. Structures corresponding to the PES stationary points were corrected with those obtained by *ab initio* calculations. Thermal rate constants *k(T)* have been estimated in terms of quasiclassical approximation through reaction probabilities *P(E)* which depend on translational energy. In order to find out the tunnel contribution into the rate constant we have evaluated a transmission coefficient $\chi(T)$. $\chi(T)$ is the ratio of the cumulative rate constant to the activation (i.e., over-the-barrier) [5] fraction.

Our investigations show that:

—quantum tunnelling brings an important contribution into the cumulative rate constants for oxidative addition of methane to bare Pd atom, and mono- and binuclear complexes. Tunnel mechanism dominates under low temperature conditions (for reactions I, IV while $T<200K$).

—Pd_2 clusters and their complexes are of more efficiency for CH_4, C_2H_6 oxidative addition than their mononuclear analogues owing to composition of a four-particle transition state.

—Variation of the Pd-Pd distance in the course of reactions II, IV proves the main factor allowing one to affect reaction probabilities and thermal rate constants.

Our research became possible owing to Grant No. **MFC300** from the International Science Foundation and the Russian Government as well as Grant No. 94-03-0.9863 from the Russian Fundamental Investigation Foundation.

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CONVERSION OF SOLID INORGANIC COMPOUNDS UNDER THE EFFECT OF GAS PHASE CHAIN REACTIONS

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The chemical reactions of gaseous molecular reagents with solid inorganic compounds require as a rule high activation energy and therefore, proceed at high temperatures.

This report represents a new approach to the realization of heterogeneous conversion in a gas-solid phase system. The essence is that atoms and free radicals interact with different compounds rather faster than molecules, because they need lower activation energy. As a source of free radicals the gas phase chain reaction can be used.

If active species, generated from gas phase reaction, interacting with solid substance lead to the formation of new active centres, which are able to propagate the reaction chains, then an effective conversion of solid phase would take place. In spite of relatively low (in comparison with molecular reagents) concentration of free radicals, formed during chain reaction, the rates of radical-chain conversion in gas-solid phase system may be higher under certain conditions. It becomes possible to realize the conversion at significantly lower temperatures.

Experimental data confirm the correctness of this approach and show new possibilities for realization of heterogeneous chemical processes.

The reactions of reduction of metal oxides and sulphides, transformation of metal oxides into chlorides, extraction of iron and other metals out of metallurgical slags and natural mineral raw materials, etc. have been studied. The process was carried out in a flow reactor. Definite amount of solid inorganic compound was located within the reactor. Then a reaction mixture (hydrocarbon-oxygen or hydrocarbon-chlor) was passed through the reactor at certain residence time. To detect free radicals a part of reacting gases was taken out and frozen at liquid nitrogen temperature. Then EPR spectra of frozen radicals were registered and concentration measured.

It has been shown that the effective reduction of iron and copper oxides under the effect of chain reactions of hydrogen and hydrocarbons oxidation takes place at T=600-800 and 400°C respectively. The copper powder, obtained in this way is more resistant against further oxidation than that obtained using conventional methods. For molybdenum sulphide and chalcopyrite the kinetics of the process was studied. Free radicals were detected in these processes. Alkylperoxy radicals RO_2 are formed in the course of the process of hydrocarbon oxidation. Under the condition of gas phase reaction interaction with sulphides of metals the significant increase of free radicals concentration and rate of gas phase reagents consumption is observed. In this case EPR spectra belong to a more complex mixture of frozen radicals and are an evidence of sulphur-containing radicals formation. These radicals are formed in the course of complex radical-chain interaction of gas phase reaction with solid sulphides of metals.

Developed approach shows new ways for raw materials processing. It can be illustrated by following examples.

Iron is extracted out of metallurgical slags, natural quartzites and pearlites as a water-less chloride at T=600-700°C and removed from reaction zone by gas flow. Under the same conditions chalcopyrite is transformed into copper and iron chlorides and elemental sulphur. Titanium oxides are transformed into titaniun tetra-chloride without any additional reductant.

Titanium-containing slags and concentrates can be purified up to pure rutyl by removing iron admixtures under the effect of gas phase hydrocarbon chlorination reaction. Further contact of solid compound with gas phase reaction will lead to chlorination of rutyl.

So, a new field for gas phase chain reactions application has been revealed, which is the scientific base for working out the new high-effective chemical and metallurgical processes.

PPC-83

ACID-BASE CATALYSTS IN 4-METHYLTHIAZOLE SYNTHESIS

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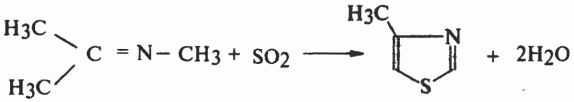
4-Methylthiazole (4-MT) is used for obtaining a highly efficient fungicide thiabendazol. Presently, the interaction of methylisopropylidenimine (imine) with SO_2 at 400-440°C in the presence of some oxide catalysts produces 4-MT:



Yet, the catalyst properties accelerating this reaction are not studied. In the present work we try to elucidate the effect of acid-base catalysts on the rate of 4-MT formation from imine and SO_2.

We used CaO, MgO, SiO_2, γ-Al_2O_3 as well as SiO_2, γ-Al_2O_3 treated by KOH, H_2SO_4, or H_2BO_3 as catalysts. Supported catalysts were prepared by the incipient wetness impregnation. All catalysts were calcined in air for 5 h at 500°C. Prior to the reaction CaO and MgO were exposed to He for 2 h at 500°C to remove carbonates and hydroxides.

4-MT was synthesized in a flow setup at $P = 0.1$ MPa, $T = 400$°C, imine concentration = 4.5 vol.%; SO_2 : imine = 1.3-3 and $\tau = 0.2$-3 s. 4-MT, SO_2 and imine were analyzed by chromatography.

Since the unreacted imine decomposes completely in the presence of SO_2 and H_2O, we have determined the catalyst activity from the rate of 4-MT formation normalized to a surface unit at a certain T and at the same yield of 4-MT. Table 1 accumulates the data for $X_{4\text{-}MT} = 20$ mass.% and $T = 400$°C.

The activity of CaO and SiO_2 (the most and the least active catalysts) differs by more than 2 orders of magnitude. SiO_2 and 5% H_2SO_4/SiO_2, which have only proton centers (PC), are of low activity in the 4-MT formation. Al_2O_3 has few PC but it comprises strong the Lewis acid sites (LAS) and moderate basic sites (BS). Thus, the activity of the latter slightly exceeds that of catalysts with the proton acidity. The treatment of Al_2O_3 by H_2BO_3 increases the strength of LAS and decreases their concentration. We think that the decrease of acid sites concentration, but not their strength increase, causes the higher activity of this catalyst as compared to Al_2O_3.

Table 1.

Catalyst	$S(m^2/g)$	$W \cdot 10^3$ $(g/m^2\ h)$
CaO	5.9	48
MgO	34	19.3
7.4% KOH/SiO_2	45	18.5
1.4% KOH/Al_2O_3	185	8
0.7% KOH/Al_2O_3	190	5.8
3.5% B_2O_3/Al_2O_3	193	2.2
Al_2O_3	268	1.3
5% H_2SO_4/SiO_2	178	0.5
SiO_2	259	0.3

Al_2O_3 doping with alkali produces strong BS on the surface and decreases the LAS strength. These affect the catalyst activity in the 4-MT synthesis. If SiO_2 is doped with alkali strong BS appear and PC disappear. The catalyst activity increases by 60-fold as compared to SiO_2.

CaO and MgO have correspondingly the strong and moderate base sites and the weak Lewis acid sites. These catalysts are the most active for the 4-MT production.

Thus, the acid-base properties of catalysts govern the 4-MT production from imine and SO_2. The most active catalysts contain a weak LAS and a strong BS where the latter dominates.

CHIRAL INDUCTION AND CHIRAL SELECTION BY METAL COMPLEXES OF A D_2-SYMMETRIC "CHIROPORPHYRIN"

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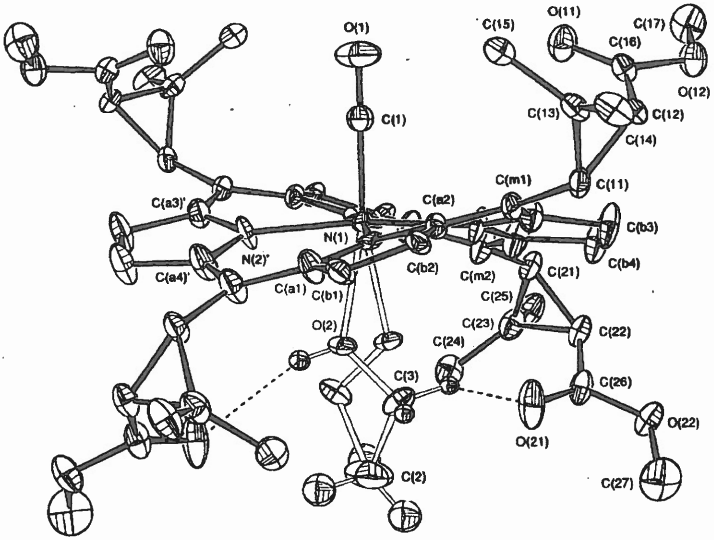
Tetramethyl-"chiroporphyrin" is obtained by condensation of pyrrole with (1R)-*cis*-caronaldehydic acid methyl ester under Lindsey conditions which affords the D_2-symmetric αβαβ atropisomer as the sole porphyrin product. Its manganese complex is an efficient catalyst in the asymmetric epoxidation of aromatic olefins by iodosylbenzene. [1]. The crystal structure of its *trans*-(ethanol)-carbonyl-ruthenium(II) complex 1 shows a C_2-symmetric molecule in which both the hydroxyl and methylene groups of the coordinated ethanol are equally distributed over two sites related by the C_2 axis. Distinct ^{1}H NMR resonances are observed at -70 °C for the diastereotopic protons of the methylene group. Complex 1 behaves as an enantioselective receptor of chiral secondary alcohols which recognizes quite strongly, for example, R(-)-2-octanol over its S enantiomer.



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ANODIC ALUMINA - NEW GENERATION OF INORGANIC MEMBRANES WITH WIDE RANGE OF PROPERTIES

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The minimum pore diameter which can be created by electrochemical oxidation of aluminium is limited by the hydrodynamics of the electrolyte in the pore during the anodization. This is of the order of 13 nm. The crystallisation of the initial amorphou anodic alumina (AA) membrane is accompanied by the chemical stability growing and the creation of a number of cracks or micropores. It has been established, that these micropores, secondary porosity, have a narrow size distribution with a radius in the range 1.5-4 nm. Such secondary porosity has been created in the initially impermeable barrier layer of the AA. Using specialized conditions of anodization and crystallisation of the AA, the membrane with a porous barrier layer (radius pores in the range 1.5-1.8 nm) has been prepared. The thickness of the active ('barrier') layer has been varied, predictably and reproducibly, from 20 to 300 nm. The dimensions of the effective pores of the polycrystalline AA (PCAA) membranes has been proved by as permeability experiments. The pores walls have been modified by the creation of a monolayer of alkyl phosphonic acid. This technique of modification of PCAA surfaces hasallowed predictable decrease of the pore diameter. For example, modification by n-butanephosphonic acid should decrease the radius by 0.5 nm. Comparison of the fluxes, which are controlled by the Knudsen diffusion mechanism and proportional to the diameter of the pores, fordifferent gases through these membranes before and after modifications has proved that film-type PCAA membranes with uniform nanoporous active layers have been developed. Polycrystalline anodic alumina (PCAA) membranes with nanoporous active layers (pore radius in the range 1.5-1.8 nm), and local roughnes on this side not greater 15 nm, have been used as a support for the creation of high temperature catalytic membranes with a dense palladium layer. The adhesion properties, stability under hydrogen and thermal cycling, up to 400 C, have been investigted. Based on these data, composition and thickness of the intermediate layer has been optimised. A Palladium/Ruthenium target has been used to create a dense layer of Pd alloy on PCAA by a sputtering technique. The thickness of the dense layer has been varied from 500 nm down to 50 nm. The hydrogen, nitrogen, argon and helium permeabilities, and separation factors for these gases, of the prepared membranes has been estimated over a range of temperatures up to 400 C. The optimal parameters and conditions for the preparation of high temperature PCAA membranes with Pd alloy dense layers have been established.

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The interaction of noble metals with gases at different condition.

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The nature of the gas-metal interaction on the noble metals has been the subject of extensive study. The data presented here may be very useful in use of noble metals as catalyst in petrochemical, chemical processes and in thin film sensor technology. The effect of different atmospheres (argon, oxygen, hydrogen) and vacuo on the sintering of palladium (Pd) electrode-catalyst was studied in the temperature range 100-600°C. The samples were obtained by electrodeposition onto platinum plates. The catalyst was heated in flowing gas inside a quartz tube. The surface area of Pd was used as a parameter for the study of sintering problems. The surface of the catalysts was evaluated by the amount of adsorbed hydrogen measured by galvanostatic desorption of hydrogen from Pd in acidic solution. The surface area decreased rapidly with time of sintering at each studied temperature and the stationary values of surface area were found to decrease with increasing the temperature. The maximum decreasing of surface area was revealed on Pd samples after heat treatment in vacuo and minimum decreasing - in oxygen. The process of sintering in oxygen was limited by oxidation of Pd. The different hydrogen species on Pd was studied using the cyclic voltammetry. The treatment of Pd in hydrogen, argon atmospheres and in vacuo led to disappearance adsorbed hydrogen that is tightly bound to the surface. On the other hand, the quantity of tightly bound hydrogen did not change after sintering in oxygen. The influence of heat treatment on structure of Pd was fixed by X-ray diffraction method. The heat treatment was accompanied with a marked increase in crystal size of Pd especially in oxygen atmosphere and in vacuo. Morphologies of worked Pd samples were examined by high-resolution scanning transmission electron microscopy. It was determined that the treatment of Pd samples can be lead to the activation of Pd in the hydrogenation reactions.

The data given in this paper were related to results of similar investigations of rodium, iridium and platinum.

PPC-87

VITAMINS OF K–GROUP: NEW CATALYSTS AND CATALYTIC REACTIONS

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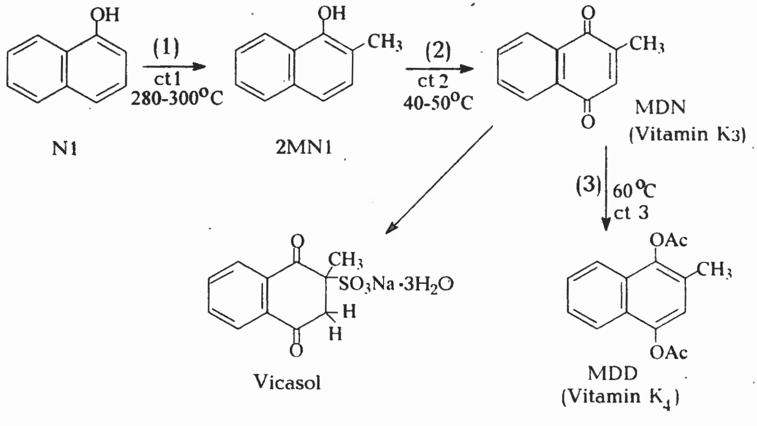
The manufacture of K–vitamins is a significant branch of fine organic synthesis. The conventional technologies of K–vitamins synthesis base on non–catalytic reactions. For these reasons they are harmful to environment and not feasible. The contemporary deficit of K–vitamins and the defects of conventional technologies of their synthesis is possible to overcome by developing of new methods and technologies of K–vitamins synthesis.

As a base of new technology we proposed a series of novel catalysts and catalytic reactions for K–vitamins production from 1–naphthol (N1) as a available raw material. These reactions involve (1) methylation of N1, (2) oxidation of resulting 2–methyl–1–naphthol (2MN1) to 2–methyl–1,4–naphthoquinone (menadione, MDN, or vitamin K_3) and (3) hydroacetylation of MDN to 2–methyl–1,4–diacetoxynaphthalene (menadioldiacetate, MDD, or vitamin K_4). Interaction of MDN with $NaHSO_3$ leads to vicasol that is a soluble form of vitamin K_3 posessing the highest biological activity. All new catalysts and reactions compose the backgrounds of VIKASIB technology of K–vitamins preparation.



1. For methylation of N1 to 2MN1 by methanol the heterogeneous catalyst (ct1) is developed. The active component of such catalyst is a mixture of Fe_2O_3, V_2O_4 and some other oxides of transition metals. Selectivity of this reaction is more than 85%. By–product is 2,4–dimethyl–1–naphthol, but it also can be

oxidated to MDN in the next stage (2). This catalyst can be used also for preparation of methylated phenols which are a raw material for E–vitamins synthesis.

2. For oxidation of 2MN1 and 2,4–dimethyl–1–naphthol to MDN we developed new homogeneous catalysts (ct2). They are aqueous solutions of Mo–V–phosphoric heteropoly acids $H_{3+n}PV_nMo_{12-n}O_{40}$ (HPA) or their acidic salts. These compounds are rather strong oxidants and their reduced forms can be easily reoxidated by dioxygen. The oxidation of 2MN1 is carried out in a system of two immiscible phases. The aqueous phase contains the catalyst, the organic phase contains the starting compound and reaction products. Selectivity of oxidation on the stage (2) is 75–80%. Reoxidation of reduced forms of HPA is to be carried out in a separate reactor. These catalysts can be also used for oxidation of methylated phenols of benzene series.

3. We developed a new polyfunctional catalysts (ct3) for hydroacetylation of MDN to MDD by dihydrogen and acetic anhydride. This reaction consists of three steps: (a) hydrogenation of MDN, (b) isomerization of resulting 2–methyl–2,3–dihydro–1,4–naphthalenedione to 2–methyl–1,4–dihydroxynaphthalene (menadiol, MDL) and (c) two–step acetylation of MDL to MDD. The catalyst for this complex reaction (3) is Pd supported on active carrier that is stable to mixture of acetic anhydride and acetic acid. The active carriers are TiO_2, ZrO_2 or Zr phosphates. The yield of MDD is more than 90%. These catalysts can be used also for hydroacetylation of other quinones.

The technology VIKASIB is friendly to environment and it was successfully used in its separate parts on pilot plants. The prepared vicasol was successfully tested in two poultry farms of Novosibisk region.

PPC-88

STRUCTURE OF STANDARD CATALYSTS EVROPt-1 AND INCATPt

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The composition of model platinum catalysts was studied by X-Ray Radial Electron Distribution (RED) technique and EXAFS spectroscopy. Oxidized platinum catalysts, supported on SiO_2, comprise highly disperse phases of platinum oxide PtO and of metallic phase Pt^o. For catalysts supported on γ-Al_2O_3, the active component appears to interact with a support: platinum ions locate in octahedral positions of an alumina protospinel structure.

Two platinum particle models are used for relating the experimental and calculated EXAFS spectra. (1) The traditional model, which is characterized by the one average shortest distance Pt-Pt similar both in the particle bulk and on its surface, with Gauss distribution around of this distance. (2) The model, which has two different shortest Pt-Pt distances for the particle bulk and its surface. Model 1 give underestimated coordination numbers for the platinum particle structure, which do not fit the data of the electron spectroscopy and RED. Model 2 provides coordination numbers corresponding to the dispersity and part of a Pt^o phase in samples. Pt-Pt distances on the platinum surface particles appear to be shortened.

During reduction, the structure of platinum particles conserves, while Pt-Pt distances slightly increase both in the bulk and on the surface. However, the samples evacuation causes a decrease of these distances.

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PPC-89

INVESTIGATIONS OF ALKYLCYCLOPENTADIENYL TITANIUM AND ZIRCONIUM COMPOUNDS (AS CATALYSTS OF ALKENE POLYMERIZATION) UNDER ELECTRON IMPACT

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At present, high-activity catalytic systems based on titanocene and zirconocene derivatives are studied widely for in organic synthesis [1] and olefin polymerization processes [2,3]. The high activity of these compounds is observed in the presence of specific cocatalysts (MAO), which is accounted for the formation of ionic polar complexes [3,4]. The concept of mechanisms and the nature of active centers of such systems is an important problem to design new metallocene precursors. We used the electron impact method of gene-ration of cation metallocene complexes to investigate the rearrangement ways of metallocenes cation. Studies carried out in gaseous phase under electron impact showed that the reactions of cation complexes formed are useful for discussion of some separate stages of catalytic process [5]. Regarded in that light, knowledge of metallocene properties appearing under electron impact is of interest.

In the present work, the rearrangement processes of $(C_5H_4R)_2MC_{12}$ (M=Ti, Zr; R=H, Me, Et, n-Pr, i-Pr, n-Bu, t-Bu, $SiMe_3$, c-C_6H_{11}) and $(C_5Me_5)_2MC_{12}$ under electron impact are considered and impor-tant role of alkyl substitutents in the fragmentation character of these compounds is shown.

The structure of an alkyl substituent in a cyclopentadienyl ligand has been shown to determine the dissociative ionization direction. The availability of hydrogen atom at a substituent alpha-carbon atom alone gives the possibility of proceeding the rearrangement process with the elimination of an HCl molecule from a molecular ion. The role of the process above increase with the increasing carbon atom number in alkyl sustituent of the normal structure. The complete substituent of hydrogen atoms by methyl groups in cyclopentadienyl ring reduces the probability of the rearrangement process with HCl elimination occurring due to steric hindrances. The HCl elimination is the main process for compounds with R = i-Pr and c-C_6H_{11} substituents.

On basis of the decomposition of the compounds $[C_5H_4C(D)Me_2]_2MC_{12}$ direct evidence of the participation of the hydrogen atoms at the substituent alpha-carbon atoms in the rearrangement processes has been obtained. The elimination of DCl molecule has been demonstrated to be one of the direction of molecular ion decomposition. The subsequent abstraction of an HCl molecule is suggested to result from deutero-hydrogen exchange or the participation of methyl groups in the substituent.

A straightforward analogy between catalytic processes and decomposition processes under electron impact cannot always be observed. Nevertheless, in the study of ethylene and propylene polymerization with the system of bis(alkylcyclopentadienyl)zirconium dichloride- methylalumoxane, it was established that compounds with an isopropyl and cyclohexyl substitutent in ring show the largest catalytic activity.

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PPC-90 NUMBER OF ACTIVE SITES ON MANY-COMPONENT POLYMERIZATION CATALYSTS DETERMINED BY SELECTIVE AND NON-SELECTIVE METHODS

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The complexity and even ambiguousness of a problem of determination of active sites in polymerization is largely created, as it seems to us, due to existing various polymerization regimes both with qualitatively dissimilar kinetic regularities and with various relationships of living and dormant sites [1]. The problem is also complicated by the fact that the passing from one characteristic area to the other occurs often on changing concentration of uncontrollable active catalyst components, whereas the concentrations of living centers, attached to polymer chains, may essentially depend on the duration of a polymerization process.

Not touching on peculiarities of experimental technique and details of a mechanism of stoppers and markers acting to catalyst components (these aspects are extensively discussed in a number of works [2-4]) we will adhere to classification of methods of active sites determination under selective and unselective ones, which is commonly accepted [4, 5] and somewhat idealizated.

As it is visible from Table, for various areas it is possible to receive strongly distinguished results of measuring the number of active sites (and relevant constants of a chain propagation) not only by various methods, but by the same method for the same system. Such distinction could on the first sight seem paradoxical, as the transition from one area into other could take place due to uncontrollable variation in amount of a coactivator.

We have addressed to literary data and analysed, using Table, experimental results with active sites determinations as with homogeneous as with heterogeneous catalysts.

The views developing in this paper, can be useful on interpreting results of active sites determinations for olefin polymerization.

Expected results of measuring concentration of active centers and relevant constants of rate of polymer chain propagation for various polymerization regimes

Polymerization regime	Unselective methods at long-time polymerization $t/\tau >> 1$	Unselective methods at short-time polymerization $t/\tau < 1$	Selective methods
Arbitrary regime	$[C]$, $k_{ef}=k_p[C^*]/[C]$	$[C^*]$,	k_p
Area of a transition metal $\frac{[Z]}{W}\cdot\frac{dW}{d[Z]} = n \simeq 1$ $[C^*]=[C]=[Z]$	$[Z]$, k_p	$[Z]$,	k_p
Area of a cocatalyst $\lvert n \rvert << 1$ $[C] = [Z]$ $[C^*] = [P]$	$[Z]$, $k_{ef}=k_p[P]/[Z]$	$[P]$,	k_p
Inverse area $n \cong -1$ $[C] = [Z]$ $[C^*] \sim \frac{[P_1]^{\alpha_1}[P_2]^{\alpha_2}}{[Z]^{\alpha_3}} < [Z]$	$[Z]_0$, $k_{ef}=k_p[C^*]/[Z]$	$[C^*]$,	k_p

Note: t - characteristic polymerization time, τ - a period of chain growth on a living site, k_P - a true constant of rate of chain propagation , k_{ef} - an effective constant of rate of chain propagation , $[Z]$ - concentration of a transition metal, C^* - active ("living") centres, $[C]$ - a sum of "dormant" and "living" centres. $P = P_2$ - cocatalyst, single or being in deficiency in relation to other cocatalysts. In case of the system Zr + MAO it is a "defect" of MAO structure or H_2O. P_1 - cocatalyst, for the system Zr + MAO, this is trimethylaluminum.

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METHOD FOR QUANTITATIVE DESCRIPTION OF PORE SPACE WITHIN "REALISTIC" MODELS OF CATALYSTS.

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The structure of support pore space has a substantial effect on catalyst efficiency. The computer simulation of support structure have been intensively developed for studying pores, specific surface, and percolation characteristics. The simplest models are represented by the dense noncrystaline packings of hard (or soft) equal spheres. A method is available for describing the void space inside such systems. It is based on the well-known geometric Voronoi-Delaunay theorems and can be used to quantitatively determine all pores of the system, to calculate the radii of bottle-necks and the complete network of channels (see e.g. /1/).
The more realistic support models are the systems of spheres of different size. Creating computer models for such polydisperse systems is not more difficult as compared to obtaining monodisperse packings. However, the known method to analyse pore space needs fundamental improvement. Recently, it has been demonstrated /2/ how the ideology of the Voronoi-Delaunay method can be applied to polydisperse systems. The present contribution gives the realization of the generalized method and the results of the analysis of the structure of loose ($\varepsilon \sim 0.7$), dense ($\varepsilon \sim 0.4$) and superdense ($\varepsilon \sim 0.15$) packings of polydisperse spheres. The distribution radii of the interstitial spheres, bottle-necks, critical radii of testing sphere penetrating along the system have been determined.

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PPC-92

EFFECT OF ETHYLENE POLYMERIZATION ACTIVATION BY α-OLEFIN OVER DIFFERENT SUPPORTED ZIEGLER-NATTA CATALYSTS

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It's known that the copolymerization of ethylene with α-olefins (propylene, butene, hexene-1, 4-methylpentene-1) by heterogeneous [1, 2] and homogeneous [3] complex catalysts are accompanied by the effect of increased polymerization rate for ethylene. The activation of ethylene and α-olefin copolymerization was explained by the change in the value of propagation constant due to modification of active sites [3] or the increasing in the amount of active sites [2].

To clear the nature of the phenomena of ethylene polymerization activation by α-olefin besides the copolymerization two steps process of sequential homo- and copolymerization of ethylene and propylene in the presence of supported catalysts distinguishing by structure and composition were investigated. There were used catalysts on the basis of the surface vanadium compounds manufactured by the interaction of vanadium haloid with functional OH-groups of aluminiumhydroxide (AH) and marked by the covalent bond of vanadium with supporter (I); vanadiumaluminoxane catalysts in which vanadium is constituent of donor-acceptor complex with supported aluminoxane (the product of partial hydrolysis of aluminiumalkyls by the supporter surface water) (II); catalysts with dispersed phase vanadium compound in reduced state on the supporter surface (III) and TMC - $MgCl_2/DIBP/TiCl_4$-$AlEt_3$.

The effect of increased polymerization rate of ethylene in the presence of comonomers was tentatively explained by the data on relative reactivity of monomers (constant values r_1 and r_2) and by specific activity of catalyst in sequential polymerization, and from the determination of the number of active sites (Cp) for polymerization process of ethylene after preliminary propylene polymerization.

It was shown, that the ethylene polymerization was activated not only in the presence of propylene comonomer, but as well upon preliminary polymerization of propylene (or copolymerization ethylene with propylene), complete removal of the residual propylene (or C_2H_4+C_3H_6) from the reaction zone, and its substitution by ethylene. The nature of ethylene Cp by the action of propylene and the nature of the propylene Cp in presence of ethylene are not changed. In two steps process the number of active centres after preliminary propylene polymerization rather more than the number of active centres in the ethylene homopolymerization.

A peculiarity of immobilized catalysts action in the processes of the ethylene and propylene copolymerization and sequential ethylene and propylene co- and homopolymerization depends on the catalyst structure and character of catalytic complex and supporter interaction. The activation effect of the ethylene polymerization by propylene, takes place only in the case of supported catalysts containing dispersed phase of transition metal compound.

To explain the experimental results obtained in studies of two-step process of ethylene and propylene co- and homopolymerization with supported vanadium catalysts and TMC the concept of catalyst matrix fragmentation by the resulting polymer was used [4]. It was concluded that the effect of ethylene polymerization activation by comonomer is related to the change in the number of active centres, involved in polymer chain propagation, and depends upon the structure of catalyst matrix and its capacity for fragmentation by nascent polymer.

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PPC-93

Formation of catalytically active element-containing centres on silica surface modified by organoelemental compounds of boron and aluminium

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The modification of silica surface by organoelemental compounds (OEC) followed by their partial thermodestruction in vacuum is one of the most efficient and promising methods of controlled forming of centres with definite properties and structure. Besides, the study of the decomposition mechanism of OEC adsorbed on SiO_2 surface is a separate scientific problem.

This paper investigates the structure and mechanisms of formation of catalytically active element-containing centres on silica surface modified by OEC of group IIIB (alkyl, haloidalkyl and alkyloxide compounds of boron and aluminium), used to produce heterogeneous metal-complex catalysts.

It has been shown for the first time by IR spectroscopy methods that silanon (>Si=O) groups are formed on the surface of SiO_2 thermoactivated at 800 °C as the silicon-oxygen skeleton is depolymerized simultaneously with radical defective active centres. Their reactions with H_2O, D_2O, CH_3OD, H_2, D_2 and OEC of boron and aluminium are studied. The fact of deactivation of terminal silanol groups relative to organo-aluminium compounds as the temperature of SiO_2 preliminary activation is raised to 800 °C [1].

The coordination of the above-mentioned OEC on structural defects of the surface is shown to be thermodynamically efficient. The structure and the ways of decomposition of the surface element-containing intermediates, including the behaviour of carbene, saturated and unsaturated hydrocarbons, haloidalkyls formed during their decomposition are investigated. Activation parameters of these reactions are estimated.

The structure and properties of active surface hydride E-H centres (where E = B, Al, Si), Si-R and Si-Hal groups (where R = Me, Et; Hal = Br, Cl) and reactive boronon (-B=O) groups formed when silica, OEC-modified by boron and aluminium are thermally treated in a vacuum are investigated [2]. On the basis of IR-spectra and results of mass-spectrometric analysis of thermodestruction products several ways of forming of such active centres are revealed. The causes of structural inhomogenity of these centres and their reactivity in a number of catalytic reactions are discussed. Using the IR-spectra of adsorbed pyridine and CO the acidity of the surface of silica modified by boron and aluminium-organic compounds is determined.

It is shown that the mechanism of formation of surface active element-containing centres with definite structure and properties on silica is affected in a decisive manner not only by the structure of the OEC but also and especially by the temperature of the preliminary activation of silica.

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PPC-94

SURFACE PHASE TRANSITION AND COMPLEX CATALYTIC MECHANISM: A MUTUAL INTERACTION

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Now, it is well known, that open catalytic systems may display the complicated kinetic behaviour such as multiplisity of steady states (m.s.s.), oscillations of reaction rate, and so on [1]. Mathematically, critical phenomena are connected with nonlinear features of kinetic equations for physicochemical rate processes. Usually, it is assumed that adsorbed overlayer is ideal. This means that critical phenomena are directly connected with nonlinear steps in detailed mechanism.

We have studied two models of heterogeneous catalytic processes taking into account the surface phase transitions. At the first, this is the process described by Temkin - Boudart mechanism. We will assume that it is harnessed in C.S.T.R. taking into account the surface phase transitions into adsorbed overlayer. We have choosed a lattice gas model (LGM) as a model of surface. It is well known, that phase transitions take place for LGM at low temperatures. Thus, the adsorbed overlayer becomes essentially non-ideal and rate constants begin to depend on the surface coverage. We used the most general expressions for these constants obtained by Zhdanov within the framework of theLGM and transition state theory [2].

The parametric analysis allows to obtaine the general criteria of m.s.s. for system under consideration at arbitrary set of lateral interactions. This criteria has following sense: the sum of coverage and its derivative with respect to dimensionless chemical potential is more than unit in the some points [3]. Such points always exist for systems with phase transitions. For system under consideration it was shown that an arbitrary non-even number of steady states can exist as a result of mutual interactions between the mechanism structure and the structure of lateral interactions. Using the transfer matrix method the numerical analysis for some sets of lateral interactions have been carried out. The regions of parameters with three and five steady states were found. It was shown that m.s.s. may be observed at temperatures three times as much as critical temperature of phase transition. This is the one of the most important results. Usually, the energies of lateral interactions are into region 1 - 3 kcal/mol. This means that m.s.s. may be observed into temperature region 400 - 1200 K. Such temperatures are usual for real catalysis. Thus, the role of phase transitions into adsorbed overlayer may be considerable for real catalytic processes. It was also obtained new results for Langmuir - Hinshelwood model taking into account the surface phase transitions. Particulary, it was shown that the region of m.s.s. is very sensitive to lateral interactions.

We can conclude: in the some cases the critical phenomena are the outcome of mutual interaction between reaction mechanism structure and structure of adsorbed overlayer.

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