Russian-Korean Seminar on Catalysis

Novosibirsk, May 16-19, 1995

ABSTRACTS

PART I

Russian Academy of Sciences

Korea Science and Engineering Foundation

BORESKOV INSTITUTE OF CATALYSIS
RUSSIA

Russian Academy of Sciences
Korea Science and Engineering Foundation
Scientific Council on Catalysis and its Industrial Use
of RAS and the Ministry of Science

RUSSIAN-KOREAN SEMINAR ON CATALYSIS

Novosibirsk, May 16-19, 1995

ABSTRACTS

(Part I)

Novosibirsk 1995
Russia

УДК 541.128

It is generally recognized that catalysis is one of the top research frontiers in chemistry. There is always a pressing need to develop new catalytic technologies and to improve the available ones. One may expect that, as going to the future, the solution of specific problems, currently made by local research teams, companies, and countries will require joint efforts in order to promote the fastest accomplishing of the problems.

The international cooperation in science plays the important (and in the future may appear to play the dominant) role in the information exchange that is fundamental to the success in handling the emerging problems. International congresses, symposia, conferences, and seminars are habitual to familiarize scientists with innovations outside their own research and to disseminate the information about the results achieved to a wider audience. However conferences and seminars, owing to their non pompous and non immense characters and to more confined scopes, seem most productive to treat specific tasks.

We have no long history of the Russian-Korean Seminar on Catalysis. The urgency of such a periodic event was realized no long ago, and since 1991 we have made two attempts to hold the meeting of Korean and Russian chemists; our efforts happened to be unsuccessful for a number of uncontrollable reasons (in commercial practice they would be referred to as the "force majeure circumstances").

The 1995 Russian-Korean Seminar will focus on four basic problems of catalysis and catalytic technologies. They are:

- Zeolite catalysis
- Catalysis for fine synthesis. Development of catalysts and catalytic processes for production of vitamins, medicines, biologically active substances
- Catalysis for environmental protection: DENOX processes, treatment of wastes and soil containing organic chlorides and pesticides
- Catalysis for oil refining and petrochemistry

These topics reflect the most pressing demands in catalysis and catalytic technologies of today. Whatever research institution or company is engaged in at least one of these areas that, evidently, makes it important for a scientist to become acquainted with the relevant "catalytic schools".

The Seminar encompasses a wide range of research activities: from studies of the nature of catalyst's active sites and the mechanisms of their actions on atomic and molecular levels through the molecular design of catalysts towards the descriptions and presentations of commercial catalysts and catalytic technologies.

The Program of the Seminar involves not only the contributions by Russian and Korean scientists. The topics appeared attractive to the scientists from foreign countries, first of all the republics of the former USSR. We are waiting for visitors from Belorussia, Georgia, Kazakhstan, Ukraine.

The Organizing Committee do hopes that the Seminar will encourage the actual scientific cooperation in understanding the mechanisms of catalytic acts and processes of fine "tailoring" the pathways for chemical processes, in development of fundamentals for prognosis of catalytic action, in promotion of solutions for sustainable progress of human society.

I wish you a good seminar. Enjoy the meeting and your stay in Akademgorodok.

ORAL PRESENTATIONS

Location of Tb(III) Ions in Na-Y Zeolite Determined by Luminescence Spectroscopy

Suk Bong Hong
Korea Institute of Science and Technology
P.O. Box 131, Cheongryang, Seoul 130-650, Korea

The thermal stability and catalytic activity of zeolites can be considerably improved by ion exchange with rare-earth ions. The extent of improvement is controlled by the degree of exchange and thus the location of trivalent cations.[1] Since thermal treatments of rare-earth-exchanged zeolites at elevated temperatures give rise to the migration of rare-earth-ions to internal sites of zeolites, the cation distribution in these zeolites has been extensively investigated by a number of techniques including X-ray and neutron diffraction, infrared and NMR. However, little attention has been directed toward the study on the intrazeolite migration pathway of rare-earth ions. This may be due to the lack of proper analytical methods for this study.

The purpose of this work is to evaluate the applicability of luminescence spectroscopy in monitoring the thermal effects on the distribution of rare-earth-ions in zeolites. Luminescence methods have been employed to investigate the physicochemical properties such as oxidation states or coordination environment of rare-earth ions in zeolites.[2] Here we present the results from the luminescence spectra of TbNa-Y zeolites treated in the temperature region of 300-773 K. The luminescence measurements demonstrate that the band intensity and position of the ^7F - ^7D transition between 4f and 5d shells for the Tb(III) ion are sensitive to the treatment temperature. . Such spectral changes can be qualitatively correlated with variations in the site symmetry around the Tb(III) ions. Our luminescence data on TbNa-Y reveal that most of the Tb(III) ions exchanged into the supercages of Na-Y migrate to sodalite cages at temperature lower than 473K and then migrate to hexagonal prisms at the tamperature-region of 473 - 523 K[3]. It can be concluded that luminescence spectroscopy can be useful for monitoring the intrazeolite migration of rare-earth ions, which is difficult to be ascertained by other analytical methods.

References

1. Jocobs, P.A. Carboniogenic Activity of Zeolites; Elsvier: Amsterdam, 1977.
2. Tanguay, J. F.; Suib, S. L. *Catal. Rev. -Sci. Eng.* **1987**, *29*, 1.
3. Hong, S. B.; Seo, J.S.; Pyun, C. -H.; Kim, C. -H.; Kim, C. -H; Uh, Y. S. *Catal. Lett.* **1995**, *30*, 87.

Selective Oxidation using Catalytic Electrode Supported by Solid Electrolyte

Seung-Doo Park, Ji-Hoon Jung*, Suk-In Hong
Department of Chemical Engineering, Korea University
*Department of Chemical Engineering, Hanseo University,
Seosan 352-820, Korea

Most of catalysts in the important industrial processes have played a role in raising the reaction rate. A lot of studies in catalysts have been carried out to increase the selectivity and the yield of any reactions at the lower temperature. In particular, the selective oxidation reaction requires the high activity as well as the high selectivity of the catalysts. But the high selectivity can result low conversion in many cases, and so these catalysts may not be used in practical processes. Therefore it is essential to improve the total yield considering both the conversion and the selectivity through comparing the performance of the catalysts. Some electrochemical reactions were reported for accomplising this purpose. The catalytic electrode with solid electrolyte is essential to the electrochemical reaction. Recently, it is found that the oxygen ions for selective oxidation are pumped from the electrolyte to the catalytic electrode surface. These ions induce the dramatic change of the activity and the selectivity of the catalysts by modifying the work function of the catalytic electrode. On this theoretical base, the butene oxidation as the probe reaction is examined, and the results are compared to the other published results. YSZ(yttria stabilized zirconia) which has been applied to the solid electrolyte for the fuel cell is used as electrolyte in this study. This material has been used to some electrochemical reactions because of its good property for conducting ions. The possibility of YSZ as the support of the catalytic electrode, and also the electrolyte for pumping oxygen ions is examined.

Butene and O_2 gases were used for reactant with the O_2/butene ratio of 5 by pressure. The partial pressure of butene and O_2 was made in the range 0.02-0.04 and 0.1-0.2 atm by diluting with helium gas, respectively. The reactants and products were analyzed using a gas chromatography featuring a Tenax-GC column. The electrochemical reactor was composed of an one-end-closed YSZ disk in a furnace. Silver porous counter and reference electrodes were deposited on one or both sides of the YSZ disk surface. The catalytic activities of V_2O_5 and MoO_3-Ag were examined, and V_2O_5 and Ag were used as electrodes, too. Preliminary experimental results show that the V_2O_5 was one of the most favorable catalysts for the selective oxidation of butene to maleic anhydride(MA). A MoO_3-Ag catalyst was composed of three layers, YSZ, silver and MoO_3.

The measurements of steady state kinetics were carried out by in-situ monitering of the chemical potential of the oxygen adsorbed on the catalytic electrode. The potentiometric results were consistent with the theoretical value by the Nernst equation. When the butene was added to the reactant, the value of open circuit potential was gradually decreased, and so the steady state value was obtained. This means that the mixed potential exists between the butene and the oxygen. The selectivity of MA was increased with providing the moderate negative potential for the V_2O_5 catalytic electrode. It could be explained that the electrocatalytic enhancement of the selectivity in the oxidation resulted from the reduction of the V_2O_5 surface, and strengthening of the attractive force between the V_2O_5 electrode and oxygen ions. For MoO_3-Ag catalytic electrode, the conversion of the butene to the butadiene was reversibly changed with the current density.

IONIC CLUSTERS OF ALKALI METALS WITHIN ZEOLITES

Kyung-Byung Yoon

Department of Chemistry, Sogang University, Seoul 121-742, Korea

The ionic clusters of alkali metals generated within zeolites have received increased attention owing to their potential use as basic heterogeneous catalysts and owing to their interesting magnetic and optical properties. However, extensive investigations of their utility have been hampered since most of the techniques involved in the generation of the species have required high temperatures, high vacuum techniques, or required the equipments that are not readily available in most laboratories. In this regard, we have developed several new methods that are particularly amenable to a large-scale synthetic preparations. The results are summarized in the followings.

I. Organolithium Compounds as Reducing Agents

The addition of a hexane solution of n-butyllithium (n-BuLi) to NaX in an inert atmosphere at room temperature immediately led to the formation of Na_4^{3+}. The method is amenable to large-scale preparations. However, when the less reactive phenyllithium (PhLi) was employed as the reducing agent, irradiation with $\lambda > 350$ nm in diethylether was necessary. The tetrasodium ionic cluster was similarly produced within NaY and NaA by applying the same method. However the ESR spectra revealed the presence of a strong central component, that arose presumably due to the presence of metallic clusters, in the middle of the 13-line spectra.

II. Alkali Metals as Reducing Agents

A. Direct Stirring

Formation of Na_4^{3+} was achieved by stirring a rigorously dried NaY with metallic Na or K in tetrahydrofuran or diethylether under an inert atmosphere. The formation of K_4^{3+} in KY was similarly achieved by treating with K. The ESR spectra of the samples prepared by this method showed a broad singlet as well as the 13-line spectra. Interestingly, the above processes tended to be facilitated by the addition of small amounts of crown ethers such as 15-crown-5 and 18-crown-6. The addition of crown ethers also resulted in the disappearance of the central singlets in the ESR spectra. Na_4^{3+} was similarly generated in NaX by stirring the zeolite with K (but not with Na) in organic solvents.

Most interestingly, direct stirring of zeolites with alkali metals *in the solid state* was even more efficient in terms of alkali metal uptake into zeolites. However, the solid-state method was very much dependent upon the stirring methods and the amounts of alkali metals initially added. The solid-state method was also highly distinguished from the solution analog in terms of the variety of the generated ionic clusters. Thus Na_6^{5+} was produced within NaX, while Na_4^{3+} was generated within NaY. Interestingly, K_3^{2+} was generated within KX, while a mixture of K_4^{3+} and an unidentified ionic cluster was formed within KY.

B. Sonication

A remarkable acceleration of the cluster formation was noticed when the ethereal slurries of zeolites and alkali metals were irradiated with ultrasound (28 kHz) by dipping the Schlenk container in a sonicator bath. In this method, 10~30 min is usually enough to complete the reaction. The addition of samll amounts of appropriate crown ethers not only accelerated the reaction but also gave rise to the formation of highly pure ionic clusters. This method was particularly useful for the generation of pure Na_4^{3+} in NaX from a diethylether slurry using K as the reductant in the presence of 18-crown-6 (> 20 mole %). The corresponding potassium analogue K_4^{3+} was similarly generated in KY from a THF slurry. In the case of NaY, however, the formation of pure Na_4^{3+} is best achieved by employing Na and 15-crown-5 from a diethylether slurry.

III. Electron Sparks as Reducing Agents

The tetrasodium ionic cluster could be generated within NaY upon mere exposure to a stream of sparks generated from a Tesla spark coil under a static vaccum ($<10^{-5}$ Torr), at ambient temperatures. Interestingly, however, only the top surface layer of the zeolite powder was active. Therefore it is necessary to bring up the rest of the powder to the surface during the exposure by frequently shaking the flask to generate the clusters within the whole zeolite powder. The ionic clusters generated by this method was unstable and slowly disappeared at ambient temperatures. The ionic cluster could also be generated in NaX by this method but only at 77 K. The formation of the corresponding potassium ionic clusters was not observed within KY or KX even at 77 K.

ISOMERIZATION OF C_5/C_6 PARAFFINS OVER PLATINUM LOADED ZEOLITES

Jeong-Kyu Lee, Ho-Taek Lee and Hyun-Ku Rhee
Department of Chemical Engineering, Seoul National University
Kwanak-ku, Seoul 151-742, Korea

INTRODUCTION

Isomerization of *n*-paraffins is an industrially important octane-upgrading process. Thermodynamic consideration of isomerization reactions reveals that the lower the reaction temperature the greater the increase in the octane number[1] and thus chlorinated alumina base catalysts, which can be operated at low temperatures(383-453K), are regarded as the best bifunctional catalysts. These catalysts, however, present corrosion problems and are sensitive to impurities, and hence their usage requires severe pretreatment of feedstocks. The noble metal loaded zeolite catalysts are free from these drawbacks. Zeolites with high thermal stability and acidity have gained increasing importance in the preparation of highly dispersed supported metals[2,3,4].

EXPERIMENTAL

Platinum loaded zeolite catalysts, Pt-HZSM-5(Si/Al=26.0), Pt-HM(Si/Al=5.0, 12.5, 22.5) and Pt-HY(Si/Al=2.8), were prepared by ion-exchange method [5] with $Pt(NH_3)_4Cl_2$ in competition with NH_4NO_3. The calcination and reduction of the samples were carried out under various conditions. The acidic properties of the samples were examined by TPD of ammonia and FT-IR spectroscopy of pyridine-adsorbed catalysts whereas TEM, TPR, H_2-TPD and H_2 chemisorption were employed to characterize the metal site. The reaction experiments were conducted in a fixed-bed flow reactor.

RESULTS AND DISCUSSION

The pretreatment conditions appeared to have a significant influence upon the metal cluster distribution on the zeolites as well as the dispersion level and thereby upon the activities of bifunctional catalysts for the isomerization of C_5/C_6 paraffins. The catalyst calcined at 300℃ and reduced at 500℃ showed the greatest activity. When the sample was calcined at 300℃, most of platinum particles were found located in the channels of mordenite. Calcination at temperatures above 300℃ induced sintering of platinum particles which apparently reduced the catalytic activity. TPR profiles of the samples calcined at different temperatures showed different patterns. Three TPR peaks appeared at temperatures above 100℃ and each of these may be regarded to correspond to the Pt^{+2} ions located in the main channel(12-membered ring), the Pt^{+2} ions located in the smaller channel(8-membered ring connecting the main channels) and the platinum oxide on the external surface, respectively. As the calcination temperature increased, the amount of H_2 consumed decreased substantially and three peaks appearing at temperatures above 100℃ were merged into two peaks.

The temperature giving maximum yield of isomers decreased in the order of HY > HM > HZSM-5. This sequence turned out to be the same as the order of the strength of the acid site, which was determined by TPD of ammonia and FT-IR spectroscopy of pyridine-adsorbed catalysts. Among three different platinum loaded zeolites, Pt-HM gave rise to the largest yield of isomers and the highest selectivity to dimethylbutanes(DMB's). Over the Pt-HZSM-5 catalyst, formation of DMB's was sterically hindered by the medium sized pore although the conversion of n-hexane was the largest. Due to the low acidity, the conversion of C_5/C_6 paraffins to isomers over the Pt-HY catalyst was limited by the thermodynamic equilibria. Both the Pt-HZSM-5 and the Pt-HM catalysts were found stable within the range of experimental conditions of this study whereas rapid deactivation by coking was observed at high reaction temperatures over the Pt-HY catalyst. In case of the Pt-HM catalyst, the acidity increased with the Si/Al ratio and there existed an optimum value of the Si/Al ratio with respect to the stability and activity of the catalyst as well as the product selectivities.

On the basis of the experimental results it was found that while methylpentanes(MP's) were the primary products formed directly from n-hexane, 2,3-DMB was the secondary product formed from MP's and 2,2-DMB was the tertiary product formed from 2,3-DMB. Therefore, the reaction pathways for the isomerization of n-hexane could be represented as n-C_6 $\rightleftarrows$ MP's $\rightleftarrows$ 2,3-DMB $\rightleftarrows$ 2,2-DMB.

CONCLUSIONS

Pretreatment conditions of platinum loaded bifunctional catalysts appeared to play an important role for the isomerization of C_5/C_6 paraffins and should be carefully selected. Consideration of both the catalyst stability and the yield of DMB's revealed that zeolites with unidimensional 12 or more membered oxygen ring would be favored and that the strength of the acid sites should be taken into account. The isomerization of n-hexane may be regarded to proceed by a three-step sequence of reversible reactions.

REFFERENCES

1. A. P. Bolton, in *Zeolite Chemistry and Catalysis* edited by J. A. Rabo, ACS Monograph 171, Washington, D. C., 714(1976).
2. S. T. Homeyer and W. M. H. Sachtler, *J. Catal.*, **117**, 91(1989).
3. Gabriel N. Folefoc and John Dwyer, *J. Catal.*, **136**, 43(1992).
4. B. T. Carvill, B. A. Lerner, B. J. Adelman, D. C. Tomczak, and W. M. H. Sachtler, *J. Catal.*, **144**, 1(1993).
5. G. E. Giannettoe, G. R. Perot and M. R. Guisnet, *Ind. Eng. Chem. Prod. Res. Dev.*, **25**, 481(1986).

Electron Spin Resonance Analysis of Paramagnetic Pd(I) Species in Pd(II)-Exchanged H-Rho Zeolite

Jong-Sung Yu[a] and Larry Kevan[b]

[a]Department of Chemistry, Han Nam University, Taejon, Chungnam, 300-791, Korea

[b]Department of Chemistry, University of Houston, Houston, Texas 77204-5641, USA

Zeolite rho was synthesized and Pd(II) exchanged into it. Pd(II) was reduced to paramagnetic P(I) by a thermal activation process. Zeolite rho has a body-centered cubic arrangement of α-cages joined through double eight-rings. Structurally, zeolite rho is similar to zeolite A, but zeolite A consists of smaller β-cages connected by double four-rings to form α-cages. There are no β-cages. in zeolite rho. The location of Pd(I) in zeolite H-rho and its interactions with oxygen, water, methanol, ethanol, ammonia, carbon monoxide, hydrogen, ethylene and benzene have been studied by electron spin resonance (ESR) and electron spin echo modulation (ESEM) spectroscopies. The ESR spectrum of an activated sample shows the formation of one Pd(I) species which is suggested to be located at the center of double eight-rings of the zeolite rho framework. Pd(I) interacts with water vapor or molecular oxygen to form Pd(II)-O_2^-, indicating decomposition of water. Equilibration with methanol or ethanol results in a broad isotropic ESR signal which is attributed to the formation of small charged palladium clusters. ESEM shows that the Pd clusters coordinate to one molecule of methanol or ethanol. Adsorption of ammonia produces a Pd(I) complex containing four molecules of ammonia based upon resolved nitrogen superhyperfine coupling. Adsorpition of carbon monoxide results in a Pd(I) complex containing two molecules of carbon monoxide based upon resolved ^{13}C superhyperfine coupling. Upon adsorption of hydrogen, a new Pd(I) species occurs which disappears upon

exposure to oxygen. ESR and ESEM results indicate that exposure to ethylene leads to two new Pd(I) species each of which coordinates to one molecule of ethylene.

XAFS Characterization of Supported $PdCl_2$-$CuCl_2$ Catalysts for CO Oxidation

Sun Hee Choi and Jae Sung Lee
Research Center for Catalytic Technology and Department of Chemical Engineering
Pohang University of Science and Technology, San 31, Hyoja-dong, Pohang, Korea

Introduction

Carbon monoxide is a common air pollutant present in exhausts of many combustion systems or oxidation reactors. Its removal using heterogeneous noble metal catalysts usually requires high reaction temperatures above 300°C. It is known that $PdCl_2$-$CuCl_2$, a well-known Wacker-type homogeneous catalyst, can oxidize CO at ambient conditions [1,2]. It has also been shown that this catalyst could be heterogenized by loading it on a support without sacrificing its activity [3-5]. We performed X-ray absorption fine structure(XAFS) study of alumina-supported $PdCl_2$-$CuCl_2$ during CO oxidation in order to elucidate the structure and chemical nature of the catalyst under the reaction conditions.

Experimental

The sample was prepared by co-impregnation of γ-alumina with aqueous solutions of $PdCl_2$ and $CuCl_2$ to incipient wetness. The oxidation of CO was performed in a flow reaction system. Feed gases of 0.1 % CO in He and air were supplied through a water vapor saturator enclosed in a constant-temperature bath. The reactor was a 1/4-inch Pyrex U-tube. Products were analyzed by an on-line gas chromatograph.

For XAFS, sample discs were sealed in a cell with a Kapton window under the same gas atmosphere as for their pretreatment. The spectra were taken for K-edges of Pd and Cu at beamline 7C or 10B of Photon Factory in Tsukuba, Japan. They were analyzed by a standard EXAFS program.

Results and Discussion

The catalyst showed stable activity of CO conversion even at room temperature as far as water was fed together with reactants. XANES at Pd edge showed features similar to those of $PdCl_2$ for both used and unused catalysts. But catalyst which did not contain Cu showed that $PdCl_2$ had been reduced to metallic Pd. The result supports the conventional view on $PdCl_2$-$CuCl_2$ catalyst that the role of Cu is to maintain Pd in its active Pd(II) state. XANES at Cu edge showed that $CuCl_2$ had lost some of its chlorine ligand and picked up hydroxyl ligand. However, it still remained in Cu(II) state.

The species of Pd and Cu present in the catalyst used for the reaction were modeled by theoretical EXAFS. For Pd, $PdCl_2$ gave adequate fit. The quality of the fit improved slightly when the presence of carbonyl ligand was assumed together with chlorine. However, the difference in the goodness of the two fittings was not large enough to conclude that the latter was the real active species. For Cu, either $CuCl_2$ or $Cu(OH)_2$ alone gave poor fits. A good fit was obtained only when it was assumed that both Cl and OH were present in the ligand sphere of Cu.

References

1. Yu L. Sheludyakov and V.A. Golodov, *J. Mol. Catal.*, **7**, 383 (1980).
2. E.G. Zhizhina, L.I. Kuznetsova, and K.I. Mateev, *Kinet. Katal.*, **29**, 130 (1988).
3. M.N. Desai, J.B. Butt, and J.S. Dranoff, *J. Catal.*, **79**, 95 (1983).
4. K.I. Choi and M.A. Vannice, *J. Catal.*, **127**, 489 (1991).
5. K.D. Kim, I. Nam, J.S. Chung, J.S. Lee, S.G. Ryu and Y.S. Yang, *Appl. Catal. B.* in press.

Characteristics of Metallic Iron in Y-Zeolite Catalyst Reduced by Hydrogen Atom Beams

Son-Ki Ihm[1] and Jin-Ho Lee[2]
[1] Dept. of Chem. Eng., Korea Advanced Institute of Science and Technology
373-1 Kusong-dong, Yusong-gu, Taejon 305-701, Korea
[2] Dept. of Chem. Eng., Chungbuk National University
Gaesindong, Cheongju, 360-763, Korea

Introduction

Zeolite matrix has been known to be especially well suited for the preparation of highly dispersed phase of catalytically active metals(1). Pretreatment procedures, however, often cause the migration of some metal particles to form large metal aggregates outside zeolite crystal. Besides, ionic species of some metals like iron are notorious for poor reducibility in Y-zeolite(2,3). The hydrogen atom beams prepared by microwave power generator were used to reduce the ionic species of iron(Fe(II) and Fe(III) in Y-zeolite, which are known very difficult to be reduced to zero-valent metal without matrix destruction. The reduced iron metal in Y-zeolite was characterized by electron ferromagnetic resonance (FMR) and O_2 consumption. Hydrogenation of carbon monoxide was also carried out to observe the catalytic properties of reduced iron metal in Y-zeolite.

Experimental

The Fe(II)-Y and Fe(III)-Y samples were prepared by a conventional ion exchange method under nitrogen atmosphere from oxygen free 0.01 M ferrous sulfate(Aldrich) solution(pH 4.2) and 0.01 M ferric chloride(Aldrich) solution(pH 4.5) respectively. After drying, the sample were stored in a dry nitrogen box. The zeolite-supported iron catalysts were reduced through two different methods; one by conventional reduction with molecular hydrogen at 500 ℃ for several hours and the other by hydrogen atom beams activated by a microwave power generator (Hitachi, 600W) at room temperature. The CO hydrogenation reaction was carried out in a differential reactor operating at atmospheric pressure, 230 - 350 ℃, and H_2/CO ratio of 2.

Results and Discussion

Fig. 1 shows that the reduction by hydrogen atom beam at room temperature resulted in a FMR spectrum similar to those from hydrogen molecule at high temperature or carbonyl ($Fe(CO)_5$) impregnation. This indicates the possibility of the reduction of the ferrous ion into the metallic iron having the characteristics of ferromagnetic and superparamagnetic species.

Table 1 shows that the steady state activity for CO hydrogenation varied with different reduction methods. This also suggests that the hydrogen atom beams can reduce the iron ions in Y-zeolite to the metallic state.

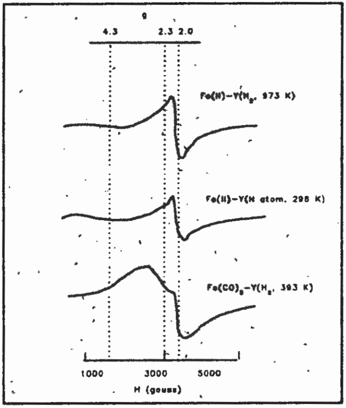


Fig. 1 FMR spectra of catalysts reduced by hydrogen atom and hydrogen molecule

Table 1. Steady state activity on CO hydrogenation (270℃, $H_2/CO = 2$).

Catalyst	Rate at 270 ℃ (μmole of CO/gFe·sec)	
	Reduced with H_2 at 500 ℃ for 10 hr	Reduced with atomic hydrogen at 25 ℃ for 4 hr
Fe(II)-Y	-	34.
Fe(III)-Y	-	21.
Fe_2O_3-Y	21.	-
α-Fe_2O_3	22.	-

The present study reports some FMR evidences that the iron ions were reduced with atomic hydrogen into metallic irons without destruction of zeolite matrix. The oxygen uptakes and catalytic activity in CO hydrogenation were also measured to show the different reduction characteristics between atomic and molecular hydrogen.

References

1. Minachev, K. M. and Isakov, Y. I. in "Zeolite Chemistry and Catalysis" (A.C.S. Monograph 171), p.552, Washington D.C., 1976.
2. Jacobs, P. A., in "Studies in Surface Science and Catalysis". Vol. 12, p. 71, Elsevier Amsterdam, 1982.
3. Minachev, Kh. M., Antoshin, G.V., Shpiro, E. S. and Yusotev, Yu. A., "Application of Zeolite in Catalysis" (eds. Boreskev, G. K. and Minachev Kh. M.), p.153, Budapest, 1979.

Ethylene dimerization and polymerization over transition metal-exchanged montmorillonite catalysts

Jong Rack Sohn and Man Young Park
Department of Industrial Chemistry, Engineerig College, Kyungpook National University, Taegu 702-701, Korea

The natural clays have been widely used in chemical industry as catalysts as well as adsorbents. In particular, montmorillonites have been frequently used as catalysts inorganic reactions involving catalysis by Brönsted or Lewis acids(1,2). The montmorillonite(K 10) was obtained from Aldrich Co. The samples were exchanged by the cations, Ni^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Cr^{3+}, and Al^{3+}, as described in preceding publications(3). The cation-exchanged montmorillonite was washed successively with deionized water until chloride ion was not detected and was molded into 2 mm diameter pellets. The resulting solids were dried at room temperature. The catalytic activity for ethylene dimerization and polymerization was determined at 20℃ by a conventional static system following pressure change from an initial pressure of 300 Torr. A fresh catalyst sample of 0.2 g was used for every run after evacuation to 10^{-4} Torr(1 Torr=133.3 Pa) at different temperatures for 1h. Reaction products were analyzed by gas chromatography with a VZ-7 column at room temperature.

Six catalysts were tested for their effectiveness in ethylene dimerization and polymerization. It was found that over Ni^{2+}-montmorillonite and Cr^{3+}-montmorillonite, ethylene was continuously consumed, where Ni^{2+}-montmorillonite was evacuated at 100℃(optimun temperature) for 1 h and Cr^{3+}-montmorillonite was evacuated at 500℃ for 1 h. Over Fe^{2+}-montmorillonite, Fe^{3+}-montmorillonite, and Al^{3+}-montmorillonite, on the other hand, an adsorption of ethylene was observed only in the initial stage and no gaseous reaction products could be detected under these conditions. However, Co^{2+}-montmorillonite showed weak activity for the dimerization of ethylene. Furthermore, this catalyst did not exhibit any observable activity under many other experimental conditions. Therefore, in this paper the emphasis is placed on the Ni^{2+}-montmorillonite and Cr^{3+}-montmorillonite catalysts only. The catalytic activity was calculated as the amount of ethylene consumed in the initial 5 min.

It was found that over Ni^{2+}-montmorillonite, dimerization of ethylene to n-butenes proceeded selectively. In the composition of n-butenes, analyzed by gas chromatography, 1-butene was found to predominate exclusively at the initial reaction time as compared with cis-2-butene and trans-2-butene. However, it was shown that the amount of 1-butene decreases with reaction time, while the amount of 2-butene increases with time. Therefore it seems that the initial product of ethylene dimerization is 1-butene and the 1-butene produced is also isomerized to 2-butene during the reaction time. Over Cr^{3+}-montmorillonite, high polymerizaiton occured, and the polyethylene produced had a high melting point and density. After the reaction had occurred, the IR spectrum of the product on the catalyst exhibited three doublets at 2920 and 2850 cm^{-1}, 1475 and 1465 cm^{-1}, and 735 and 723 cm^{-1}, which are attributed polyethylene.

The catalytic activities for the ethlene dimerization and polymerization were closely correlated with the acidity of the catalysts. The active sites for the ethylene dimerization consisted of nickel ion and Brönsted acid, while the active site for the polymerizaiton was related to the Lewis acid, chromium ion. Water is a poison for the $Ni-^{2+}$montmorillonite evacuated at lower temperature, while an appropriate amount of water is required to confer catalytic activity on the Ni^{2+}-montmorillonite.

References

1. J.M. Adams, Appl. Clay Sci., 2, 309(1987).

2. P. Laszlo and H. Moison, Chem. Lett., 1031(1989).

3. J.T. Kim. and J.R. Sohn, J. Korean Chem. Soc., 19, 317(1975).

SELECTIVE CATALYTIC REDUCTION OF NO OVER METAL OXIDES INCORPERATED WITH ZEOLITES

Sang-Eon Park

Catalytic Research Division,
Korea Research Institute of Chemical Technology, Taejon, Korea 305-606

Selective catalytic reduction(SCR) of nitric oxide with propylene in oxygen rich condition was investigated over ZSM-5 supported mixed metal oxides catalysts. Among metal oxides which have capabilities of NO adsorption and decomposition, partially strontium substituted La-cobaltate perovskite-type mixed oxide was adopted for supporting on ZSM-5 via modified citrate method. De-NOx activity was measured by flowing the reaction mixture consisted of 1500 ppm NO, 1000 ppm C_3H_6, and 3.0 % O_2(balanced with He) over a 0.1 g of catalyst mounted and the space velocity with 30,000-60,000 hr^{-1}. The reaction temperature range was from 200 to 600°C. A gas chromatograph(Chrompack CP 9001) eqipped with TCD were used to monitor catalytic activity together with the combustion analyser(Dai System 6000).

NO decomposition activities and sorption characteristics of mentioned mixed metal oxides catalyst were observed at the initial reaction step by looking at the completely zero concentration of NO in product stream for certain period of reaction time, and resulted in higher concentration of oxygen in outlet stream than that of in inlet. De-NOx activities were enhanced via making composite with ZSM-5 as a support for all the temperature range.

There was the observation of synergetic effect in SCR activities of NO by loading mixed metal oxides on ZSM-5 which gave greatly enhanced activities on the reduction of NO in oxygen rich atmosphere with propylene as a reductant at such relatively low temperature range. On the other hand, mixed metal oxides gave poor durability in the temperature range of this study, even they had high NO decomposition activities at the initial stage of reaction. These facts indicated evident interactions between mixed metal oxides and ZSM-5, which were seemed to be strongly affected by not only the lability of oxygen of mixed metal oxides but also the oxygen carrier ability and the pore structure of supports, which were typical properties of metal oxides and supports and resulted from the modifcation by the composite formation.

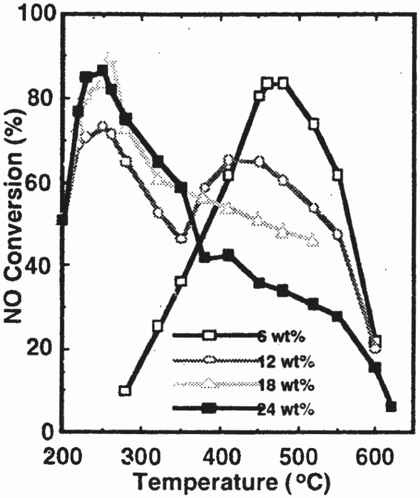


Fig. 1. Twin peaks maxima in de-NOx activities over CoO_x - La_2O_3/ HZSM-5 catalyst.

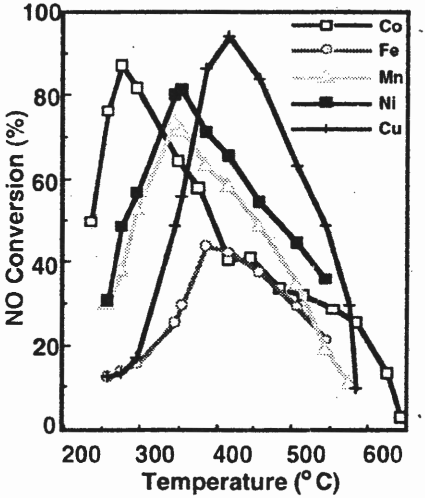


Fig. 2. Effect of transition metal substitution in 24wt%MO_x - La_2O_3 / HZSM-5 catalyst.

XRD pattern showed the quite small intensities of perovskite structure with the reduced intensities of ZSM-5. Interestingly, twin peaks maxima on de-NOx activities were observed at 250°C and 410°C over ZSM-5 supported mixed metal oxides catalyst(Fig. 1). Co-containing mixed metal oxide on ZSM-5 among B metal in ABO_3 type perovskites showed the best activity comparing with other transition metals such as Fe, Mn, Cu and Ni(Fig. 2).

I-V Characteristics of ZnO - ZnO Contact during Oxygen Adsorption

Chong Soo Han

Department of Chemistry, Chonnam National University
Kwangju, Korea

In recent, depths of depletion layers in adsorption of oxygen and oxidation reactions on zinc oxide were measured with monitoring the capacitance of two contacting ZnO faces.[1,2] During the measurements, we observed a non ohmic property in I-V characteristics of the system. Microscopically, the crystal surface is not atomically flat and many atomic contacts give the I-V characteristics. If we assume that the atomic contacts have the same conductivity of the bulk, then the area of contact is estimated to the magnitude of 10^{-4} - 10^{-5} of the apparent surface. It is generally accepted that electron transfers in metal-metal and metal-semiconductor contacts accompany the information of energy states of the solids and the tunneling process of electrons. In this study, we analyzed the non ohmic characteristics of the two contacting ZnO (1010) faces during the adsorption of oxygen at various temperatures.

When two contacted ZnO crystals were degassed at 773 K, the conductivity of the sample assembly k increased and a peak was appeared at 10 mV in $(I-kV)$ vs. V characteristics. When the assembly was exposed to oxygen and was degassed at 298 K - 573 K, peaks in $(I-kV)$ vs. V characteristics were observed in the range 10 - 40 mV while the conductivity k decreased. The variation of the peak in $(I-kV)$ vs. V characteristics was checked in the exposure of the sample previously adsorbed oxygen to CO. At 573 K, the peak about 40 mV was decreased and the conductivity increased.

The observed current of the assembly may originate from thermionic emission and tunneling of electrons between the surfaces. The thermionic emission current of the system can be expressed as $A.\exp(-\frac{\mu+e.Vs}{kT}).[1-\exp(\frac{eV}{kT})]$ under a bias voltage V. The apparent surface barrier Vs can be estimated as $Vs = Vs^0(1-\frac{V}{4Vs+Vg^0})^2$ for the experimental system. Vg^0 is a parameter related to the physical separation of two crystals z and the concentration of the adsorbed surface states Ns as $\frac{x.e.Ns}{\varepsilon_0}$ while Vs^0 is the surface barrier originated from the adsorption, $\frac{e.Ns^2}{2k\varepsilon_0 N_D}$. Since the apparent surface barrier Vs becomes to zero at $V = 4Vs^0+Vg^0$, a distinct change in the current is expected at the bias voltage. It is suggested that the peaks in $(I-kV)$ vs. V characteristics corresponds to the change of the thermionic current around $V = 4Vs^0+Vg^0$. The tunneling probability of electrons with a kinetic energy E (eV) through a work function ϕ (eV) with a width z (0.1 nm) is proportional to $f_1.f_2.\frac{E(\phi-E)}{\phi^2}.\exp[-1.02(\phi-E)^{1/2}.z]$ where f_1 or f_2 is the density of the energy state of a surface. For the case of ϕ > E and given z, the probability is proportional to $f_1.f_2.E$ and it may show the non ohmic property in the wide region of the bias voltage.

Comparing the results of the I-V measurements with the theoretical model, we will discuss the nature of adsorption of oxygen on ZnO.

---

1. Han, C. S.; Jun, J.; Chon, H. Bull. Korean Chem. Soc. **1992**, 13, 30.

2. Jun, J.;Han, C. S.; Chon, H. Bull. Korean Chem. Soc. **1994**, 15, 590.

New Notions of Active Surface Composition of Reforming Catalysts

A.S. BELYI

Omsk Department of Boreskov Institute of Catalysis, Omsk

Development and improvement of catalytic reforming to a large extent were defined by improvement of scientific idea of catalysts' structure and quality. First ideas of bifunctional operation mechanism of Pt-Cl/ Al_2O_3 systems in the catalysis of main reforming reactions promoted the development of effective enough aluminum-platinum catalysts for that time (1960-s). Further improving of the catalysts and processes modification based on them was due to the investigations in the field of structure and composition of superdispersed mono- and polymetallic particles (bimetallic clusters), as well as due to the ideas of strong influence of interaction effects between such particles with the support' surface structure.

To the present time quite extensive experimental base on formation of interaction product of platinum with the support's surface was accumulated in the literature. The platinum state in these compositions are interpreted as different from one in the metal composition (and refered as soluble [1], electron deficient [2], ionic [3], etc.). However, properties and role of such platinum atoms in the adsorption and catalysis remain not clear to the present day.

Our laboratory developed method for quantitative analysis of platinum atoms number in reforming catalysts (Pt^{σ}) the state of which differs greatly, as chemical properties concerns, from metallic platinum (Pt^{o}) in the dispersed particles composition [4]. Quantitative analysis of Pt^{σ} is based on ability of such atoms to form coordination bond with σ-donor molecules of water, which supresses totally oxygen adsorption on these atoms. Water preadsorption on Pt^{o} atoms does not prevent oxygen adsorption and does not change chemisorption stoichiometry [4]. Thus, O_2 adsorption consumption difference before and after water preadsorption allows to carry out quantitative analysis of Pt^{σ}

Investigation cycle fulfilled in combination with adsorption method, physical and catalytic methods made it possible to reveal a number of peculiarities of Pt^{σ} atoms' properties in comparison to Pt^{o} [4-9]. The most important of them are:

- as to their charge state Pt^{σ} atoms approach Pt (II) state in chlorides [4,5];
- CO adsorption frequency in IR spectrum of deep-reduced catalyst corresponds to the one of $[Pt(CO)Cl_2]$ complex [6];
- oxidation treatment of the catalyst at 573K leads to the formation of oxide from Pt^{σ} only, whereas Pt^{o} in the structure of metallic particles is not being oxidated yet [7];
- stoichiometries of oxygen and hydrogen chemisorption are expressed by the equations:

$$Pt^{\sigma} + 0.5O = Pt^{\sigma}O_{0.5};$$
$$Pt^{\sigma} + 2H = Pt^{\sigma}H_2;$$
$$Pt^{\sigma}H_2 + 1.5O = Pt^{\sigma}O_{0.5} + H_2O,$$

Pt^{σ}-H bond fastness being considerably higher than that of Pt^{0}-H.

Investigation of the catalytic properties showed that Pt^{σ} is non active in low-temperature reaction of benzene hydrogenation [8] and possesses activity in all the complex of reforming reactions in the temperature range higher than 673K [4,5,8]. Activity and selectivity of reforming reactions are defined by two parameters : ratio of Pt^{σ} and Pt^{0} centers and the nature of ligand environment of Pt^{σ} centers. The latter parameter is of special importance, and the level of commercial properties of the catalyst is defined by the presence and ratio of the following ligands: Cl^{-}, O^{2-}, S^{2-}, Re^{2+}, Sn^{2+} etc.

On the basis of these data the new generation of reforming catalysts for middle and high pressure reactors, series PR-50, PR-51 was developed. These catalysts are applied in two reforming installations at Ryazan Refinery Factory. Three-year experience of their use showed that they possess a number of advantages over previously used platinum-rhenium catalysts.

The main advantages are.

- 5-6 wt% surplus composite yield because of the supression of hydrogenolysis reaction;
- high coke resistance of the catalysts which makes it possible to obtain high-octane component (93-95 RON at P=2,8 MPa) with the regeneration cycle not less than a year;
- high sulfur resistance makes it possible to apply the catalysts at the reactors not equipped for using modern polimetallic catalysts.

The reforming catalysts are commercially produced at Ryazan Refinery Factory, Russia.

1. K.W. McHenry, R.J. Bertolacini, N.M. Brennan, I.L. Wilson: II Int. Congr. on Catalysis. Paris, 2, 2295 (1961).
2. J. Escard, B. Pontviane, M.T. Chenebaux, I. Cosyns: Bull.Soc.Chim. Frans, 3-4, 349 (1976).
3. N.R. Bursian, S.B. Kogan, Z.A. Davydova: Kinet. i Katal., 8, 1283 (1967);
4. M.D. Smolikov, A.S. Belyi, A.I. Nizovskii: React.Kinet.Catal.Lett:37, 437 (1988);
5. V.K. Duplyakin, A.S. Belyi, N.M. Ostrovskii: Dokl. Akad. Nauk SSSR, 305, 648 (1989).
6. M.D. Smolikov, A.B. Zaichev, A.S. Belyi: Kinet. i Katal., 33, 625 (1992).
7. A.S. Belyi, M.D. Smolikov, V.K. Duplytakin: React.Kinet.Catal.Lett, 34,195 (1987).
8. O.B. Bogomolova, N.M. Ostrovskii, M.D. Smolikov: React.Kinet.Catal.Lett,40, 131 (1989).
9. A.S. Belyi, D.I. Kiryanov, M.D. Smolikov: React.Kinet.Catal.Lett, 53, 185 (1994).

UNSTEADY-STATE TECHNOLOGIES FOR CATALYTIC DETOXICATION OF GAS WASTES

V.A.Chumachenko*, L.N.Bobrova** and A.S.Noskov **

* Katalizator Company, Novosibirsk
** Boreskov Institute of Catalysis (BIC), Novosibirsk

For last 10-15 years, the progress in the development of methods for exhaust gas cleaning from contaminants was associated mostly with technologies, that were based upon process operation under unsteady - state conditions. Unique technological features provided by unsteady - state regimes, as well as novel catalysts developed and adjusted to meet specific requirements of the processes made this technology competitive to conventional ones and rather attractive to a customer.

In a short time, many industrial companies created and commercialized highly effective unsteady-state processes for different gas wastes treatment that have occupied now a substantial space of the market.

Note here only a part of the companies that are "confessing" principles of unsteady-state technology in solving the environment protection problems: BIC & Katalizator Co. (REVERSE-Process), Russia; Monsanto Enviro-Chem Systems (DynaCycle, licensed from BIC), USA; H.Topsoe (REGENOX), Denmark; Laboratory of Applied Catalysis (SWINGTHERM), Poland; Salem-Engelhard, USA; Linde, Germany and others.

REVERSE-Process is widely applied in Russia for abatement of sulfur dioxide, organic compounds, carbon monoxide, nitrogen oxides, ammonia and much other species from industrial waste gases. Unsteady-state regimes in the REVERSE-Process mode of operation are performed by periodic reversal of the gas flow through the catalyst bed. Once the cleaning of cool gases is performed without any energy supply, this mode is called autothermal. The autothermicity of REVERSE-Process is attained at extremely low initial concentrations of the contaminants - VOCs : 0.5 - 0.8 g/cub.m, NO_x:

1.5 - 2 g/cub.m, NH_3 : 2.3 - 3 g/cub.m. The toxic compounds are catalytically converted at that into CO_2 , H_2O, N_2.

Detoxication of VOCs usually requires complete oxidation of multi-component mixtures, the concentrations of individuals being considerably scattered. The sustained operation of REVERSE-Process plants is guaranteed by :

* application of copper-chromium-alumina and other oxide-type catalysts having specific sizes and form;

* optimal design of technological, including thermal, process parameters;

* reliable processing of automatic control system .

The effectiveness of gases cleaning at REVERSE-Process industrial plants reaches 98.5-99.5%.

Selective catalytic reduction of nitrogen oxides by ammonia in REVERSE-Process mode is applied for detoxication of technological gases, power plant exhausts and others. Process was realized over vanadia-alumina catalyst and allowed for using both ammonia gas and ammonia water. No ammonia nitrates (nitrites) in explosive amounts was formed and accumulated. The residual content of NO_x in cleaned gases was less than 70 mg/cub.m, while in the inlet one it was as high as 15 g/cub.m.

Recently, a REVERSE-Process method for ammonia removal by its selective catalytic oxidation to nitrogen and water upon Pd-containing or oxide catalysts was developed and tested in a pilot plant. Low-concentrated gases were cleaned from ammonia, and no remarkable quantities of secondary pollutants, such as NO_x and N_2O were observed.

Presented in this lecture are selected results of more than 30 REVERSE-process plants mastering in a variety of industrial applications for VOCs and NO_x destruction, and pilot trial data on NH_3 abatement as well. Operating experience and economics of the plants has proven high commercial importance of the process.

NEW CATALYSTS FOR ENVIRONMENTALLY FRIENDLY FUELS PRODUCTION

V.K. Duplyakin, ***G.A. Urzhuntsev***

Omsk Branch of Boreskov Institute of Catalysis, SB RAS

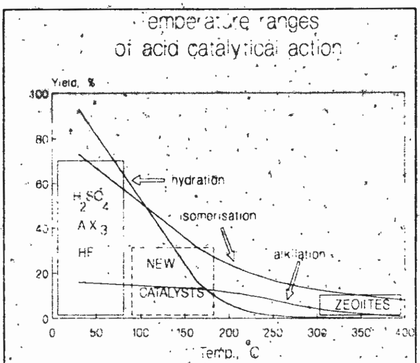


Figure 1.

Numerous existing processes of hydrocarbons conversion require acid catalysts. These catalysts can be classified in two types with regard to the conditions of their most efficient performance (Fig. 1). Strong mineral acids, which catalyze the hydrocarbons conversion at the temperatures below 100 °C, belong to the first type. These catalysts, however, are very harmful to environment. With this regard they become more and more unpopular over the world. Heterogeneous acid catalysts, such as zeolites, amorphous silicates, oxides of various metals, belong to the second type. They are used at oil refining and processing. These catalysts, however, work at essentially higher temperatures ranging from 300 ° C. With regard to thermodynamic restrictions of hydrocarbons conversion, it is mostly reasonable to use catalysts exhibiting the highest activity at 100-250 °C. Moreover, such catalysts should bring no harm to environment. At present an intensive search for such advanced catalysts for alkylation, isomerization, production of antidetonation oxygen-containing additives is in progress. Zeolite and ion-exchange resins seem to be the most popular. A heterogeneous super acid system based on sulfated zirconium oxide attracts a lot of recent research attention. We have designed a new environmentally friendly catalyst, exhibiting a high activity at isobutane alkylation by butenes, isomerization of n-alkanes and olefins hydration. In the present work we present the data on isobutane alkylation by butenes on this new catalyst. The catalyst was tested in a flow reactor (volume 50 ml) with a fixed catalyst bed at 40-120 °C and 1-23 atm. The flow rate of isobutane and butene-2 mixture supply varied from 0.5 to 7 h^{-1}. Molar ratio isobutane:butene-2 ranged from 4 to 12.

Table 1. *Operation conditions and results of alkylation isobutane.*

	New cat.	HF	H_2SO_4
T°C	80	20	7
$iC_4/C_4^=$, mol.	4-6	3-8	4-6
LHSV, h^{-1}	0.35	2.0	0.2
P, atm	7-10	5-10	3-8
Alkylate yield on C_4^-, wt.%	180	170	170
Alkylate yield, $g/l_{cat}*h$	500	3700	400
MON	93	95	92

Table 1 compares the conditions of process performance and results obtained on our new catalyst and on the well known commercial catalysts. The data show, that alkylation parameters on the new catalyst (alkylate yield with respect to olefin, reaction volume efficiency and alkylate quality) are similar to those obtained at the alkylation with sulfuric acid. Note, that alkylation on the new catalyst occurs at higher temperatures. So, no forced cooling is required. This makes alkylation on the new catalyst be more feasible than that with sulfuric acid and HF. The main disadvantage of conventional heterogeneous alkylation catalysts is their poor stability. The best known catalytic systems provide a 10-20 g conversion of olefin per catalyst gram. Then their activity starts to decrease. We have studied the stability of our catalyst at the alkylation of real industrial raw material from the plants of catalytic cracking.

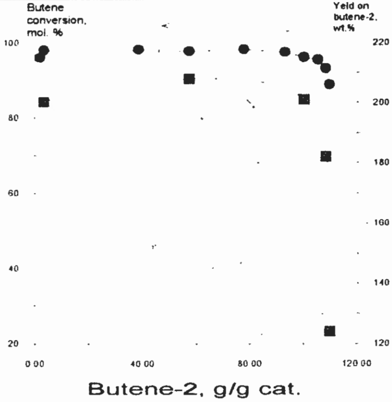


Figure 2.

Fig. 2 shows the data obtained at a long term run. Obviously, our catalyst resists deactivation far better. Only when 108-110 g of olefin are supplied per catalyst gram we observe the decrease of catalyst activity. The oxidative regeneration completely restores the catalyst activity. Thus, our new solid acid catalyst for alkylation opens wide opportunities for designing new technologies, which will produce motor fuels of high quality and comply with the present demands to environment safety.

DESIGN AND INVESTIGATION OF ENVIRONMENTALLY FRIENDLY PROCESSES ON ZEOLITE CATALYSTS

Ione K.G.

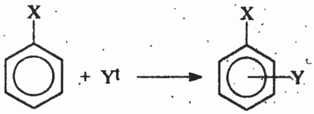
Scientific Engineering Center "Zeosit"
Boreskov Institute of Catalysis, Russia

The particular properties of synthetic zeolites open wide opportunities for designing new solid catalysts exhibiting various acid-base and molecular sieve properties.

At present, the newly designed zeolite-based catalysts of high selectivity are ready for commercialisation and can help to solve various environmental problems of chemical and petrochemical industry.

1. Electrophilic substitution in aromatic rings.

Zeolite catalysts were proved to be active and selective in electrophilic substitution in aromatic rings via reactions:



where X stands for OH, C_nH_{2n-1}, Cl, NH_2; and Y^t stands for C_mH_{2m-1}, NO_2, Cl and others.

A method to synthesize nitroaromatic compounds with high para- and ortho-selectivity has been designed and patented.

We have also studied how the synthesis of alkylphenols, alkylanilines with various substituents in aromatic rings on highly active and selective zeolite catalysts depends on the acidity and structure and catalysts.

All these studies open a way of using solid environmentally friendly catalysts instead of liquid acid catalysts that produce many tons of liquid wastes.

2. Conversion of organic wastes and by-products into aromatic and gasoline high octane fractions.

The Mobil processes MTG and MTO that convert methanol or olefins into the high octane fractions of gasoline are widely known. Chemical and petrochemical plants also produce mixtures of oxygen or olefin-containing organics, which are by-products or wasted to be burnt out. So far we have studied the selectivity of the mixtures conversion into fuel components on various zeolite catalysts. We have shown that simultaneous and consecutive dehydration, oligomerization reactions and hydrogen redistribution allow to synthesize iso-paraffins and aromatic mixtures for motor fuels.

3. Upgrading of low octane gasoline fractions.

This process is very useful for the regions famous for oil and gas-condensate fields with poorly developed transportation service and remote from refineries. The zeolite catalysts help isomerization and aromatization and thus allow to synthesize high octane motor fuels less harmful to environment. In the North of Russia or in Middle Asia the process opens a way to produce fuel in small size sets for near vicinities.

We have found that the acid-base properties as well as [Al] cation coordination and distribution have a decisive influence on the activity, stability and performance of zeolite catalysts in these processes.

4. Bifunctional zeolite catalysts to convert wastes into CO, CO_2 and H_2 mixtures.

At present the reforming of municipal and industrial solid and gaseous wastes is a serious environmental problem. To solve it one can convert the wastes to the mixture of CO, CO_2 and H_2. Many studies and patents show that the selectivity of the latter mixture transformation into alcohols, aromatics and gasoline fraction on zeolite bifunctional catalysts depends on relationship between the acid and hydro-dehydrogenation catalyst functions.

The summarized scientific and design experience in the field allows to conclude that zeolite catalysts can help to create new environmentally friendly processes.

NEW TECHNOLOGY TO PRODUCE ALUMINA SUPPORTS

Z.R.Ismagilov, R.A.Shkrabina, N.A.Koryabkina

Boreskov Institute of Catalysis, Novosibirsk, Russia

γ-Alumina is one of the widely used industrial catalyst supports. Usually gibbsite serves as a starting raw material. There are many technologies for gibbsite processing to pseudoboehmite aluminium hydroxide then conditioned to granules of desired shape, texture and structure.

The conventional industrial production of high purity alumina supports involves gibbsite dissolving and precipitation (reprecipitation) of pseudoboehmite aluminium hydroxide thus disposing the huge amounts of waste waters (~20 t per Al_2O_3 ton).

However, some processes of chemical industry and refinery (e.g., hydrodesulfurization processes) can successfully use catalysts supported on aluminas produced via newly designed technologies. For example, the process of gibbsite amorphization occurring at relatively high temperatures (350-400 °C) under so called «thermoshock» produces a dry powder product that can be directly plasticized to pseudoboehmite. This technology disposes considerably less waste waters and consumes less amounts of reagents.

We suggest the similar technology but modified and more advantageous. The modified technology based on the catalytic heat generator (CHG) uses the fluidized catalyst bed reactor. Its design is compact, it is friendly to environment and reproduces thermal decomposition product (PT) quite well.

Fuel oxidized in the fluidized catalyst bed of CHG produces heat used for the thermal decomposition of gibbsite in the same reactor. The gibbsite powder is continuously fed to CHG by a pneumatic system. Here it consumes heat within a very short residence time (less than 0.1 s) and undergoes amorphization. PT obtained exhibits a high reactivity, its processing to pseudoboehmite is easy and does not involve dissolving, precipitation and reprecipitation.

The product of thermal decomposition can be used to produce supports shaped as extrudates, rings and spherical granules.

In this presentation we shall focus the spherical granules production via hydrocarbon-ammonia moulding (HAM).

We have studied colloidal processes proceeding when the PT powder dissolves in an acid at plasticizing as well as when spherical plasticized droplets fall through the NH_4OH solution and turn to spherical granules. We have thoroughly investigated how the composition and preparation of plactisized mass and the moulding process parameters affect the properties of spherical γ – alumina obtained. Optimizing the HAM parameters we manage to obtain the granules of mechanical strength exceeding 20 MPa.

One of the main advantages of our technology is that it allows us to modify alumina chemically during its granulation.

The chemical modification of alumina produces a new generation of supports exhibiting high mechanical strength and thermal stability. So far we have designed new procedures based on HAM to produce the modified alumina. We have also studied how the introduction method, type and concentration of modifiers, thermal treatment conditions influence the properties of spherical alumina obtained.

For each modifier studied (MgO, CaO, La_2O_3, CeO_2, SiO_2, TiO_2, γ-Fe_2O_3, zeolite, etc.) we have elucidated the optimum concentration and introduction method.

La_2O_3 or CeO_2 serve to increase alumina thermal stability but are efficient only when dry γ --alumina granules are impregnated. Moreover, lanthanium cations (2-4 wt.%) appear to be more efficient than CeO_2.

Mg and Ca cations (2-4 wt.% of oxide) also help to increase the strength of alumina granules but are mostly efficient when we impregnate wet aluminium hydroxide granules in a special way. This increases the crushing strength of alumina granules by 1.5-2 fold at 550 °C and by 4-5 fold at 1200 °C.

SiO_2 is known to increase the thermal stability of oxide supports. We have shown that silica introduction into the plastic mass before HAM increases the thermal stability of the product obtained.

As we introduce more than 5wt.% of SiO_2 or 5-10wt.% of TiO_2, we can obtain spherical alumina with unique properties after calcination at 1300-1400 °C. The granules show a 100-200 MPa mechanical strength and their bulk density is equal to 1.9-2.2 g/cm^3.

We have used this technology to prepare spherical granules containing 50-70 wt.% of various zeolites (strength ~10 MPa) and alumina granules with magnetic properties.

Therefore, our technology of thermal decomposition gives a new generation of granulated supports including unique spherical supports of high mechanical and thermal stability for processes in the fluidized and moving beds.

CATALYST APPLICATION IN PRODUCING OF ORGANIC COMPOUNDS FROM PLANT BIOMASS

B.N.Kuznetsov

Institute of Chemistry of Natural Organic Materials
Siberian Division of Russian Academy of Sciences
Academgorodok, Krasnoyarsk, 660036, Russia

The resources of currently renew wood biomass can be successfully used for the producing all common «petrochemical «products and unique organic compounds. Wood biomass consists of cellulose (40-50%) - linear polysaccharides with $C_6H_{10}O_5$ chains. hemicelluloses (15-30%) - the polysaccharides with $C_5H_8O_4$ chains, lignin (16-33%). constructed from phenyl propane units connected through C-O-C and C-C bonds, extractive compounds and inorganic components. The applied industrial methods of cellulose, ethanol, furfural and other compounds production are mainly based on the acid-base catalysts using. But catalysts and catalytic processes are broader used for complex wasteless processing of wood biomass and for the design of new methods of fine chemicals production from plant raw materials [1]. The study of different catalytic transformations of wood biomass and its components (cellulose, hemicellulose and lignin) was accomplished in the Institute of Chemistry of Natural Organic Materials. The survey of some experimental studies is given in this presentation.

Acid-based Conversions.

It was found [2] that the yield and the composition of aspen-wood and cellulose steam-thermolysis products are significantly changed under the action of acidic and salt catalysts in a flow reactor with the fixed bed of solid substrata precipitated by catalyst. The degree of aspen-wood conversion at 200°C was increased by 4 and 9 times in the presence of $CoSO_4$ and $Al_2(SO_4)_3$ catalysts respectively. Among the reaction products the levoglucosenone is formed with the yield 4.6% at 350°C. Levoglucosenone yield from pure cellulose (8.4% wt. at 300°C in the presence of $CoSO_4$) is higher as compared to its yield from aspen-wood. In autoclave reactor mainly furfural and levulinic acid are formed from wood and cellulose. Cellulose thermolysis by water-steam in autoclave reactor yields up to 34.6% wt. of levulinic acid at 240°C in the presence of H_2SO_4. The comparison of product composition of aspen-wood steam-thermolysis process in flow and static reactors shows that wood hexasanes can be converted to levulinic acid according to the scheme: hexasanes → levoglucosenone → hydroxymethylfurfural → levulinic acid. This scheme was proved using chromatographic, chromato-mass-spectroscopie, NMR methods and kinetic data. The conversions of levoglucosenone to furfural, its derivatives and to levulinic acid ethers was studied in the presence of H_2SO_4, H_3PO_4, CF_3COOH. Schemes of levoglucosenone transformation were suggested based on chromatographic and ^1H, ^{19}F NMR methods.

The short time catalytic hydrolysis under non-isobaric conditions was applied for wasteless processing of wood and wood bark. The effectivity of this activation process depends on two main factors. The action of organic acids weakens some bonds in wood biomass owing to catalytic hydrolysis reactions. At the same time a mechanical loosening of wood matrix is accomplished as a result of fast drop of a pressure during activation procedure. The following components were easily isolated from activated aspen-wood: pure cellulose (yield up to 50 wt.%), sugars from hemicelluloses (up to 14 wt.%) and reactive low-molecular lignin [3]. The activation of coniferous and deciduous wood bark under conditions of non-isobaric steam-hydrolysis accelerates the isolation of some groups of extractive compounds and increases their yields [4]. The optimal operating parameters of bark activation were defined : temperature 240°C, pressure of water-steam 3.4 MPa and time of treatment from 30 sec up to 120 sec. After birch bark activation it was possible to extract betulin with the yield higher than 95% from its initial content in bark. The yield of tannins from activated larch bark was by 2 times higher as compared to non-activated bark. A similar effect was observed for extraction of silver-fir bark by isopropanol and water. An application of fractional extraction technique makes it possible to increase significantly the total yield of extractive compounds from larch-bark and silver-fir bark. Some information about extract composition was obtained by chemical, chromatographic, NMR, IR and UV spectroscopy methods.

Oxidative-Reductive Conversions.

Catalytic reactions of this type were applied for wood lignin processing to fine chemicals and hydrocarbon mixtures. A copper catalyst was used to promote the rate of different lignins oxidation to vanillin and syringaldehyde by O_2 in the presence of alkali [5]. The catalyst using results in a significant increase in the yield of products in comparison with non-catalytic pathway. The influence of catalyst on the lignin oxidation depends significantly on the process operation parameters. The using of suspended $Cu(OH)_2$ in a shaken static reactor results in the increase in of aldehydes yield up to 2 times. But in a flow reactor the similar catalytic effect was observed only for fixed bed of copper catalyst. The absence of catalytic effect of suspended $Cu(OH)_2$ in the flow reactor seems to be connected with an unsufficient mass transfer between liquid phase and suspended catalyst under the flow conditions of the oxidation process. Under the optimal process conditions the total yield of aromatic aldehydes was reached up to 35-40% relative to lignin weight in aspen-wood. These yields of aromatic aldehydes corresponded to 80% selectivity of the most effective reaction lignin oxidation by nitrobenzene. Catalytic oxidation of lignosulfonates yields up to 10 wt.% vanillin in a flow reactor and 14 wt.% in a static reactor. Reaction of vanillin formation was suppressed almost completely at pH below 10.5-10.8. The influence of catalyst on selectivity of vanillin formation and O_2 consumption during lignosulfonate oxidation at 110-160°C has been studied. Oxygen consumption in the process was independent on the catalyst content and pH in the range of pH 10-12, but the vanillin yield changed significantly upon the variation of process parameters. The mechanism of vanillin formation was discussed.

Phenolic fraction of liquid hydrocarbon mixtures can be used as a substitute for phenols and the rest - as liquid fuel. New processes of wood biomass and its components liquefaction were described. The processes of lignin liquefaction by methanol under the action of Fe-Zn-Cr hydroxide catalyst, wood pyrolysis in the presence of Fe (metal)- - Na_2CO_3 system and wood dissolution in the molten mixture NaCOOH-NaOH were studied [6]. In the two of them the non-volatile reducing agents (formate ion and metallic iron) were used. The yield of volatile products of wood pyrolysis was increased up to 14 wt.% and oxygen content in liquid product was decreased to 14% in the presence of the mixture of metallic iron-alkali carbonates at 0.6-1.0 MPa and 500°C. The wood liquefaction by mixture of melting formates and alkali at atmospheric pressure and 320°C yields about 13--14% liquid products (referred to wood weight) with a low oxygen content (8-9%). The possible mechanisms of wood biomass and lignin conversions to liquid products are discussed. Closed technological schemes of studied liquefaction processes were suggested.

REFERENCES

1. B.N.Kuznetsov, Catalysis of Coal and Biomass Chemical Conversions, 1990. Nauka, Novosibirsk, 301 pp.

2. B.N.Kuznetsov, A.A.Efremov, G.A.Slashchinin, E.D.Korniets, L.K.Balakireva. Khimia Drevesiny (Chemistry of Wood), 1990, No5, 51-56.

3. A.A.Efremov, S.A.Kuznetsova, M.T.Balovsyak, V.A.Vink. B.N.Kuznetsov. Sibirskii Khimicheskii Zhurnal (Russia), 1992, No6, 29-33.

4. B.N.Kuznetsov, V.A.Levdanskii, S.M.Repyakh, V.A.Vink, T.A.Shilkina. In: Proc. Int. Organic Substances Solvent Extraction Conf., Voronezh, 1992, P.157-159.

5. V.E.Taraban'ko, A.V.Kudryashev, B.N.Kuznetsov, N.M.Ivantchenko, G.R.Gulbis. In: Proc. 8th Int. Symp. on Wood and Pulping Chem., Helsinki, Finland, June 6-9, 1995.

6. V.E.Taraban'ko, A.V.Kudryashev, G.R.Gulbis, B.N.Kuznetsov. Sibirskii Khimicheskii Zhurnal (Russia), 1992, No6, 14-24.

Design of Carbon-Carbonaceous Composites for Catalytic and Adsorptive Technologies to Abate Environmental Damage

V.A.Likholobov

Boreskov Institute of Catalysis, Prospekt Ak.Lavrentieva 5, Novosibirsk 630090, Russia.
Fax: 7 3832 351453

The intentional design of catalytically active sites and their microenvironments that would be the optimum ones for desired reactions is a new approach to synthesis of efficient catalytic systems for applications to a wide latitude of reactions.

In the case of carbon supports such a microenvironment is governed by the nature (for instance, contributions of basal and edge planes) of pore walls and localization of active components on the surface. The contribution of basal and edge planes to carbon material surfaces may be controlled when the carbon materials are produced from gaseous hydrocarbons by means of catalytic «matrix» synthesis.

This approach was used at Boreskov Institute of Catalysis to synthesize a wide range of carbon materials and carbon-carbonaceous composite materials (CCM) of globular, filamentous, globular-filamentous textures. Among the CCM are: Sibunit produced by supporting pyrocarbon (PC) on carbon black granules (CB) followed by burning-out the CB; carbon filaments (CFC) produced by decomposition of CH_4 over special catalysts allowing the yield of several hundreds gram C per gram catalyst; and the systems such as CFC/Sibunit, CFC/CFC, PC/CFC, etc. The CCM produced are differed by graphite crystallite sizes, their degrees of 3D-ordering, basal and edge contributions to porous surfaces. Specific procedures were used to make the surfaces of hydrophilic or hydrophobic nature.

A number of catalysts and catalytic processes based thereon were studied using physical methods such as HREM, EXAFS, NMR MAS, XPS, XRD techniques. Textural and substructural parameters of the carbon materials were shown to strongly effect the processes of formation and stabilization of catalyst active component particles and, finally, its catalytic behavior. The systems such as $PdCl_2/C$, PdO/C, Pd/C, Ag/C, Ni/C, $LiAlH_4/C$, HPA/C (where HPA is heteropoly anion), as well as bicomponent systems such $LiAlH_4/Pd/C$, Ru/HPA/C, etc. were examined. They were tested for the processes of hydrogenation, oxidation, hydrodechlorination, epoxidation. Some specific adsorptive features of filamentous and globular-filamentous CCM caused by a remarkable amount of slit-like pores built in their textures were revealed. The most spectacular effects of these pores are observed in the systems involving flat or spherical shape molecules, and can be employed to achieve both separation processes and specific catalytic ones.

The data on a number technologies for environmental protection based on the new CCM and CCM-supported catalysts are presented. Among the technologies are purification of power station waste gases from nitrogen and sulfur oxides, soil decontamination from aromatic chlorides, etc.

NEW COMMERCIAL TECHNOLOGIES ON THE BASIS OF FUNDAMENTAL RESEARCHES ON CATALYSIS WORKED OUT AT THE INSTITUTE OF CHEMICAL PHYSICS IN CHERNOGOLOVKA OF RUSSIAN ACADEMY OF SCIENCES

I.A.Makaryan, S.M.Baturin, P.E.Matkovsky, V.I.Savchenko

Institute of Chemical Physics in Chernogolovka, Moscow Region, Russia

Fundamental researches on catalysis, kinetics and mechanism of various chemical reactions are carried out at the Institute of Chemical Physics in Chernogolovka. Also scientific bases of modern technologies and new generation catalysts are worked out in order to promote commercialization of processes developed. The technologies are tested on pilot plants, various products of many applications are manufactured, and preliminary technical and economic appraisals are offered. In consequence a lot of new low investment cost, low energy and resource consumption and ecological pure processes for industrial commercialization were designed. Some of them are presented here.

Catalysts and new technology of metacrylic acid and its esters production by heterogeneous-catalytic oxidation of isobutylene by air oxygen were created. Metacrylic acid esters are produced by acid simultaneous esterification in the presence of aliphatic alcohols. Developed technology has a number of advantages in comparison with the old one: technological simplicity, cheap raw material, possibility of continuous process organization, ecological purity.

Unfiltration technology of liquid-phase hydrogenation of organic compounds under mild conditions was worked out owing to the creation of new catalysts and an original design of reactor for continuous multiphase processes without withdrawal of solid particles with means for effective separation of solid and liquid phases. Catalysts based on platinum group metals are considerably superior to industrial catalysts in activity, selectivity and service life. They can be regenerated many time; net loss of noble metal is about 1-2 g per ton of product. Developed catalysts and reactors are mastered in industrial scale.

Application of developed reactor design is not restricted only to hydrogenation processes. Reactor can be used in any other processes with the participation of suspended solid particles. Examples are the processes of heterogeneous-catalytic esterification, oxidation, polymerization, hydrodechlorination, fractionation of polydispersed systems, etc. Another effective application became the development of unfiltration technology of vegetable oils hydrogenation to ecological pure margarins.

New technology of bifunction oligobutadienediods production by using of original dilithium initiators was created. Products obtained possess unique characteristics:

narrow molecular-weight distribution, high function, containing of cis- and trans-structure links more than 85%. High molecular homogeneity ensures high technology of retreatment of oligobutadienediols to finished products and also ensures high and reproductive technical and exploitation characteristics.

Investigations on controllable polymerization of ethylene to various products of petrochemical and chemical synthesis were carried out. Commercial technologies on their basis are ethylene dimerization in ethers medium, oligomerization of ethylene to high linear alpha olefines, telomerization of ethylene to high alkylaromatic hydrocarbons, ethylene oligomerization to synthetic lubricants, composites production by means of polymer filling of various mineral matrix.Also processes of polymer, metal oxide and ceramic thin film covers production and new original materials on thier basis were created.

An original high-effective and ecological pure technology of optical polymers production was worked out on the basis of frontal polymerization. The technique is based on physical principle of polymer wave self-propagation. Granules for polymer light guides, large-block scintillators and lenses are manufactured on operative installation. The main characteristics of polymers obtained are : $M_w = 40000 - 300000$, M_w / M_n being 2.1-13, transparency about 88-90% (for polysterene) and $M_w = 80000 - 300000$, $M_w/M_n = 2.8-10.8$, $n_d^{20} = 1.480$ (for polymethylmetacrylate).

All processes are characterized by high yield and quality of products obtained, simple technology design, ecological purity, low energy consumption and low investment cost. Some of developed technologies were commercialized in Russia and abroad.

AN AUTOTHERMAL REGIME OF CATALYTIC REACTOR FOR WASTE GAS CLEANING.

V.A.Makhlin, B.N.Okunev.

State Research Centre of Russian Federation.
Karpov Institute of Physical Chemistry
Vorontsovo Pole ul., 10, Moscow, 103064, Russia

The gas wastes cleaning by means of catalytic afterburning of the harmful impurities is the efficient way of environment protection. In the case when the impurities content and/or their specific heats of combustion are high enough, this process may be carried out in the adiabatic - type reactor working in the autothermal regime. Use of such reactors is attractive because of their simple construction and due to the cleaning process operation reliability.

The main problem of such reactor's design and operation is to maintain the stability of the catalyst bed temperature regime while the gas flow inlet parameters are fluctuating continuously. We have investigated this problem by means of reactor modelling and simulation based on the two-phase diffusional model.

Some features intrinsic to the adiabatic reactor dynamics when an exothermic reaction of impurities afterburning is carried out in the fixed bed of the catalyst, have been revealed. Specific area has been shown to exist at the phase plane of gas flow inlet parameters (impurity concentration vs. flow temperature), where the reactor operates in the steady - state autothermal regime, ensuring the required gas flow cleaning degree at any inlet fluctuations within the limits of this area (Fig. 1).

Analytical approach has been obtained which allows to describe these boundaries - namely, the locus of external diffusion regime extinction points (curve 1), the boundary corresponding to allowable values of impurity conversion (curve 2) and the line corresponding to the upper limits of catalyst thermostability (line 3). For the case of dichloroethane manufacture gas waste cleaning from ethylene impurity by its afterburning on the IKT-80 catalyst it has been found that the exact boundaries accounted with the use of complete mathematical model coincide well with the proposed analytical solution.

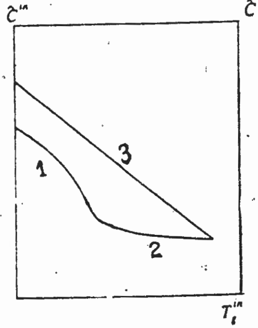


Fig. 1.

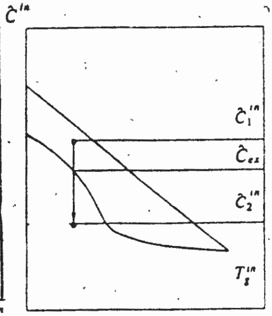


Fig. 2.

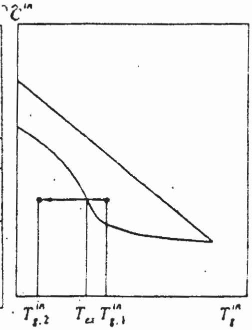


Fig. 3.

The position of curve (1) has been shown to be dependent both on the catalyst activation parameters and on the heat of reaction. The influence of gas flow rate on the curve (1) shifting at various bed geometry (conventional and radial bed) has been investigated. It has been found that the gas flow rate enhancement reduces substantially the area of the steady - state autothermal regime existence and vice versa. For the radial bed an extent of this area depends also on the ratio of the bed external radius to its thickness and on inlet flow direction (from inside or from outside).

To estimate the possibilities of the steady - state autothermal regime stabilization in the case of large inlet fluctuations the dynamic characteristics of the reactor have been investigated. An analytical approach has been obtained, which allows to calculate the critical duration of an inlet concentration stepwise decrease, causing the external diffusion regime extinction, as the function of the ratio of entire concentration decrease, $(\hat{C}_1^{in} - \hat{C}_2^{in})$, to its decrease below the lower boundary of the steady - state autothermal regimes area, $(\hat{C}_{ex}^{in} - \hat{C}_2^{in})$ (Fig. 2). Analogous approach has been obtained for the critical duration of an inlet temperature stepwise decrease (Fig. 3). These approaches allow to determine an admissible time delay of the regulator.

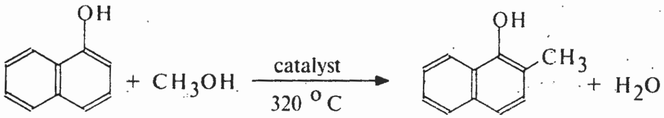
The results obtained allow to establish an advanced approaches to the gas waste catalytic cleaning units design and to the development of their operational algorithms.

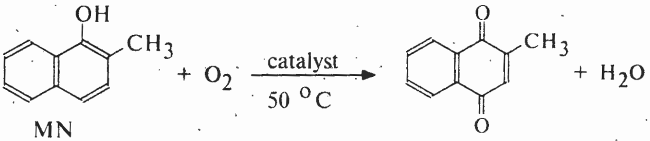
NEW CATALYTIC METHODS FOR SYNTHESIS OF K-VITAMINS: K3, K4 and VIKASOL

K.I. Matveev, E.G. Zhizhina, V.F. Odvakov, N.S. Kotsarenko, V.P. Shmachkova

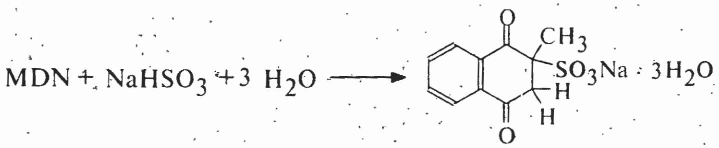
Boreskov Institute of Catalysis, Novosibirsk, Russia

Reactions (1)-(4) form the basis of "Vikasib" technology intended to produce K-vitamins (K3, Vicasol and K4). Here we report on a detailed study of these reactions. All vitamins K are synthesized from menadione (MDN), i.e., 2-methyl-1,4-naphthoquinone, i.e., vitamin K3. Conventional technologies of MDN production require hardly available 2-methylnaphthalene. Moreover, they are harmful to environment, because they do not use catalysts. We have developed a new procedure for the MDN synthesis friendly to environment. It bases on catalytic reactions (1), (2), (4) and uses a common raw, naphthol-1 (N1). For this technology we have also developed three types of catalysts such as alkylation catalysts (for reaction (1)), oxidizing heteropoly acids (for reaction (2)) and multifunction catalysts for hydrogenation and acidic isomerization (for reaction (4)). Biological tests have shown that vitamins obtained via our technology increase the productivity of cattle rising. They are also mostly efficient for rising poultry at industrial production and farming. So, our technology is of great importance for both medicine and cattle rising economics. The catalytic synthesis of MDH, VS and vitamin K4 allows to expand production of K-vitamins and to make it harmless to environment.

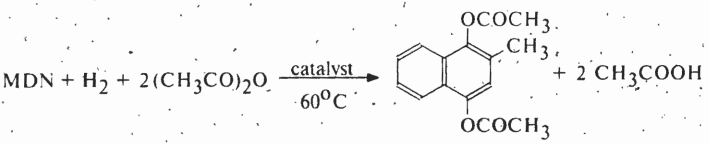

N1 2MN (1)


MN MDN (2)

VS produced via reaction (3) is a commonly used water soluble K-vitamin:


VS (3)

Menadioldiacetate (MDD), i.e., vitamin K4, can be produced from MDN via reaction (4). It can serve as a ready vitamin or as intermediate for the synthesis of vitamin K1, which is mostly important among K-vitamins.


(4)

One can introduce technology "Vikasib" into any working technology of K1 production or use it solely to produce vikasol and vitamin K4 (MDD). The latter tolerates storage better than K-vitamins, but is slightly less active than VS.

The technology suggested includes know-how concerning catalysts composition and preparation as well as reactions performance.

Catalytic reactions accompanied by capillary condensation

N.M.Ostrovskii, N.M.Bukhavtsova

Omsk Department of Boreskov Institute of Catalysis,
Neftezavodskaya 54, Omsk, 644040, Russia

Introduction

It is possible to estimate using Kelvin equation that in some catalytic processes with gas-phase feedstocks and products the capillary condensation of some reagents may occur. Then both gas-phase and liquid-phase reactions take place inside pellet, consequently in large pores (filled with gas) and in small pores (filled with liquid). This leads to the situation in catalyst pellet that is quite different from that in typical three-phase processes [1] and in supported liquid-phase catalysts or in catalysts with melted active component [2]. There are only a few publications on this matter [3,4]. Some problems of catalytic reactions come from capillary condensation will discuss in this report.

Mass transfer limitation

The gas-liquid interfacial area (a_{GL}) at capillary condensation is equal to the total area of meniscus in pores filled with liquid. Therefore a_{GL} is much higher (10^3 - 10^5 times) than that in trickle-bed and one can not limit the mass transfer. The only intra-partical diffusion in gas phase or the reaction rate in liquid phase can be the slowest stage in process accompanied by capillary condensation.

When the reaction rate in liquid (r_L) is less than that in gas (r_G), then pellet effectiveness factor (η) slightly depend on liquid loading (ε_L). In opposite case η is determined mainly by ratio r_L / r_G , else decreases with ε_L ; and reaction is shifted to strong diffusion region.

Intrinsic kinetics

The presence of capillary condensed liquid in pellet can change the "observable" reaction kinetic parameters. In benzene hydrogenation for example it leads to decreasing of the reaction rate order. It changes from 3 to 1-1.5 with respect to hydrogen, and from 1 to 0 with respect to benzene. The observable heat of benzene adsorption decreases with falling temperature and becomes equal to the heat of condensation (8 kcal/mol) at $T \leq 50\ ^{o}C$. Also the slow reaction dynamics occur causes by condensation and evaporation of reagents at low temperature.

Active component distribution

At capillary condensation the micro-distribution of active component in support (among the pores with different size) becomes an important feature of supported catalysts. The influence of micro-distribution parameter depends on only ratio r_L / r_G and does not affected by mass transport phenomena in pellet. When $r_L / r_G > 1$ the localisation of active component in small pores (filled with liquid) has to be prefer. This parameter also affects the catalyst deactivation when more than 40% of active component is loaded in small pores. Additionally the rate constants of deactivation in small and in large pores should differ by more than five times. The variation in micro-distribution parameter allows to increase the catalyst activity and stability, especially in hydrotreating processes.

Example of HDA process

Hydrodesulfurization (HDS) and hydrodearomatization (HDA) of motor fuels are operated in the conditions provided capillary condensation of some reagents. In kerosene HDA process the pores having radius less then 6,0-7,0 nm are filled with the liquid of heavy fraction. It consists about 30% of total pore volume and 50% of specific area [5]. If hydrotreating of diesel feedstocks takes place the condensation can extents up to pores with radius of 100 nm.

The results of modelling of HDA process indicate that capillary condensation decreases the total aromatics conversion because of low reaction rate in small pores occupied by heavy fraction. It comes from extremely low dissolution of hydrogen in liquid. The molar ratio of Aromatics/H_2 = 2-3 mol/mol in vapour phase and $\sim 10^{-3}$ mol/mol in liquid. Therefore mono-aromatics in heavy fraction that being formed from di-aromatics remain practically unconverted.

References:

1. N.O.Lemcoff, A.N.Cukierman, O.M.Martinez: Catal. Rev. - Sci. Eng. 30 (3), 393 (1988).
2. R.Datta, R.Rinker: J. Catal. 95 (1), 181 (1985).
3. D.H.Kim, Y.G.Kim: J. Chem. Eng. Japan, 14 (4), 311 (1981); 14 (4), 318 (1981).
4. D.N.Jaguste, S.K.Bhatia: AIChE Journal, 37 (5), 650 (1991).
5. N.M.Ostrovskii, N.M.Bukhavtsova, V.K.Duplyakin: React. Kinet. Catal. Lett. 53 (2), 253 (1994).

HORIZONS OF CATALYSIS IN ENERGETICS OF THE FUTURE

V.N. Parmon

Boreskov Institute of Catalysis, Novosibirsk 630090, Russia

Traditional way of application of catalytic technologies to energetics is to improve with their use incineration of conventional or available fossil fuels in various large- or small-scale power plants. This allows to increase the heat-producing efficiency of these plants as well as to diminish pollution of the ambient by toxic products of the fuel' combustion. However, there are also some not so evident applications of catalytic technologies which may appear to be of a principal interest for the future. In this presentation, three lines of the modern trends in these fields will be concerned: (i) application of catalytic technologies to use of nuclear and nontraditional sources of energy, (ii) producing the mechanical or electrical energy from the energy of chemical energy carriers and (iii) recovery of middle- or low-potential heat wastes or utilization of some unexpected heat-energy sources (see also [1,2]).

Catalytic Technologies in Nuclear and Nontraditional Energetics. Of the most interest for far future are two non-exhaustible sources of primary energy: nuclear energy released by either fission or fusion processes and solar light. The direct use of both these primary energies is impossible, since they have to be converted into a suitable form. Catalytic processes are capable of converting into energy of chemical bonds any of the above mentioned kinds of energy and to store it in the form of chemical fuels.

As to nuclear fission energetics, the so-called EVA-ADAM catalytic technology is well known for indirect accumulation of released nuclear energy in the form of syngas, its storing and transportation on large distances. Recently, a new much more efficient ICAR (Immediate Catalytic Accumulation of ionized Radiation energy) process was suggested for direct nuclear-to-chemical energy conversion [3]. The peculiarity of ICAR technology is placing the energy-converting catalysts immediately into the active energy-releasing zone of a nuclear reactor or even usage of special multifunctional physico-chemical structures serving simultaneously as a nuclear fuel and a catalyst for the energy-storing chemical reaction. ICAR process has exhibited a high efficiency of nuclear energy conversion combined with ability to maintain the useful specific power loading of the energy conversion up to 100-200 kW/dm^3. These data correspond to those for energy release in the modern fission nuclear power plants. ICAR technology can also be widely used in the fusion thermonuclear energetics, since it seems to be the only technology which allows to utilize the enormous fluxes of ionizing radiation from the future thermonuclear reactors.

In the last two decades serious efforts were made to develop catalytic processes for solar energy conversion. One path in this research deals with ***quantum photocatalytic*** processes which provide production of high quality fuels such as hydrogen upon any type of solar irradiation, including highly scattered. Much more advanced are developments for ***nonquantum thermocatalytic*** processes of conversion of concentrated solar energy. Already in early 80th the prototypes of energy converting installations of a reasonable useful power (more than 2 kW) and of a very high (more than 40%) efficiency of solar-to-chemical energy conversion were tested [4]. Under way is further development of design and other improvemens of such solar energy converting systems [5].

An important contribution to nontraditional energetics will obviously be made by new catalytic technologies for incineration of nontraditional low-caloric fuels like wet biomass, MSW, sludges, etc., as well as for production of high quality liguid fuels from these raws. Of a reasonable importance should be new catalytic technologies of cleaning geothermal steam from hydrogen sulfide without loosing the energetic potential of the steam.

Catalytic technologies in increasing the efficiency of mechanical and electrical energy production. During the last decade, a great interest is paid to application of catalysis for improvement of efficiency of mechanical engines. One approach is based on improvement of fuel combustion in gas turbines or in piston engines. The second one is based on nontraditional ideas of the so-called ***"catalytic heat recuperation"*** providing a great increase in the efficiency of a thermal engine (even over the value given by the Carnot cycle) through using the heat of exhausted gases for catalytic pretreatment of chemical fuels.

The principal improvements of the electricity production are obtained in the field of fuel cells. Most promising are, certainly, high-temperature "molten carbonate" or "solid oxide" fuel cells which allow to use either conventional fuels, such as natural gas, gasoline, etc., or gasified MSW, biomass, etc. An ***"internal catalytic reforming"*** of these fuels is an inevitable element of all these fuel cells.

Of a top interest are recent findings in the field of high-temperature fuel cells, which revealed their ability to operate in a mode of co-generation of both electricity and some valuable chemicals [2]. One of the most promising applications is production of C_2 hydrocarbons (ethane, ethylene) by fuel cells fed with natural gas.

Catalytic technologies for recovery or utilization of middle- and low-potential heat. Catalytic technologies could be efficiently used for utilization of middle- and low-potential heat (200-500°C and even lower than 200°C), yielding by various industrial heat wastes, geothermal water, etc. The main developments in this field are focused on using ***"chemical heat pumps"*** based on middle- and low-temperature reversible catalytic reactions of dehydrogenation-hydrogenation or dehydration/hydration types [2]. Chemical heat pumps reveal some potential advantages as compared to the conventional heat pumps which are based on chemically inactive "working body". The main advantages are a possibility to find suitable substrates for desirable levels of temperature and to store the converted heat for any time in the form of chemical energy.

An ability to accumulate and store the low- and middle-potential heat is given as well by new materials with large absorption capacity. The most attractive materials are zeolites and so-called chemisorbents. When using very simple substrates as adsorbates (say, water, carbon dioxide, oxygen, etc.), these materials are able to accumulate up to 2000 kJ/dm^3 of heat even in the ambient temperature interval [6]. This gives a powerful tool for recovery heat wastes and for efficient utilization of the natural either day-to-night or season temperature gradients.

REFERENCES

1. V.N.Parmon, Chemistry for Sustainable Development, Vol.1, No 1 (1993).
2. V.N.Parmon, Z.R.Ismagilov, M.A.Kerzhentsev, Catalysis for Energy Production. In: Perspectives in Catalysis. Eds. J.A. Thomas and K.I. Zamaraev, Blackwell, New York, p.337-357 (1992).
3. Yu.I.Aristov, Yu.Yu.Tanashev, S.I.Prokopiev, L.G.Gordeeva, V.N.Parmon, Int. J. Hydrogen Energy, Vol.18, p.65-62 (1992).
4. V.I.Anikeev, V.N.Parmon, V.A.Kirillov, K.I.Zamaraev, Intern. J. Hydrogen Energy, Vol.15, p.275-286 (1990).
5. Solar Energy Materials, Vol.24 (1991).
6. E.A.Levitskij, Yu.I.Aristov, M.M.Tokarev, V.N.Parmon. Solar Energy Materials (in press).

INTERACTION OF SO_2 WITH O_2 OVER MIXED Pt, Pd, Pt–Pd AND Pt–Ru CATALYSTS OF OXIDATION AND COMBINED TREATMENT OF AUTOMOBILE EXHAUST GASES

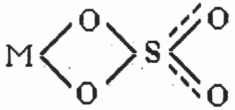
Popova N.M., Umbetkaliev A.K., Dosumov K. and Antonova N.A.

Institute of Organic Catalysis and Electrochemistry, National Academy of Sciences of Republic of Kazakstan, Almaty.

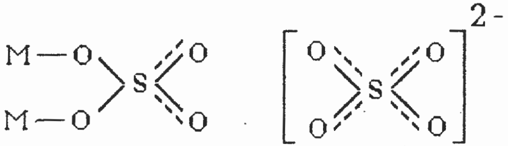
During treatment of exhaust gases, the contacts are affected by poisons, SO_2 in particular. In oxygen–containing mixtures Pt/Al_2O_3 is poisoned more than Pd/Al_2O_3 due to formation of a strong complex with platinum and aluminium sulphate retarding the reaction of CO and CH_x oxidation and changing the pore structure.

The paper presents the results of studying the effect of the composition of mixed Pt and Pd contacts on the nature of adsorbed complexes of SO_2 forming in O_2 presence, by TPD, XPS, mass–spectrometry, IR and electron microscopy methods. Catalyst samples after being cleaned in vacuum ($P = 1 \bullet 10^{-3}$Pa, 3 h, $T = 823$ K), were treated by SO_2 ($P = 1 \bullet 10^2$ Pa, 1 h, $T = 573 - 673$ K), and then O_2 was admitted ($P = 1 \bullet 10^3$ Pa, 5 – 16 h).

Over Pd/Al_2O_3 and mixed catalysts, at $T_{ads.} = 573$ K in TPD regime, there occurs the desorption of SO_2 (in the peak with $T_{max} = 700$ K) and $SO_2 + O_2$ mixture above 900 K as two peaks ($T_{max} = 850 - 950$ and $1000 - 1150$ K). Injection of Ce, Cr and Co into Pd/Al_2O_3 reduces considerably evolution of gases in the peak with $T_{max} = 950$ K, while the peak with $T_{max} = 1000 - 1150$ K remains signification for Pd–Ce, Pd–Cr and is absent for Pd–Co contact. According to IR data, at 800 – 1000 K temperatures there occurs breakdown of complex of adsorbed CO_3-covalent–bound with metal atoms through oxygen (sulphate–1), having 1170 and 1060 sm^{-1} a.b.



At a temperature above 900 K, there occurs decomposition of structure with 1140 – 1150, 1110, and 995 sm^{-1} a.b. typical for the ionic sulphate–2:



According to IR, TPD and XPS data, the formation of surface sulphate – 2 decreases in the sequence of Pd contacts over Al_2O_3:

Pd–Ce, Pd, Pd–Cr, Pd–Co

while the amount of SO_3 bound with metal oxide (sulphate – 1, $T_{max.}$ =900 – 950 K) decreases in the sequence:

Pd–Ce, Pd–Cr, Pd, Pd–Co

From Pt/Al_2O_3, there occurs thermodesorption of SO_2 with O_2 in regions typical for Pd contacts but in higher quantities. From mixed Pt contacts there desorbs less sulphate – 2 and especially sulphate – 1 than from Pt/Al_2O_3 ($T_{max.}$ =935 – 975 K and $T_{max.}$ up to 1050 K), this amount increasing as follows:

Pt, Pt–Pd (1:1), Pt–Ce, Pt–Co, Pt–Cr

Thus by introducing such elements as Co and Cr into Pd and Pt catalysts of deep oxidation of CO and hydrocarbons, one can achieve a significant decrease in the formation of SO_3 complexes with oxidized metals and that of surface sulphates on the support.

The IR study of SO_2 interaction with O_2 over Pt – Ru – Ce catalysts of compex removal of CO, NO and hydrocarbons from gases has shown that on making the catalysts composition more complicated when supporting its elements on alumina, the intensity of some a.b. at 1160, 1080, 1230 cm^{-1} (sulphate – 1) is always low, especially for Pt – Ru – Ce contact. The formation of sulphate – 2 (judging by the relative intensity of 1110 – 1140 sm^{-1} a.b.) decreases in the sequence of contacts over Al_2O_3 :

Pt, Ce, Ru, Ru–Ce, Pt–Ru–Ce

This may be caused by deep interaction of the basic catalyst elements, Pt and Ru forming mixed oxide clusters as well as $CeAlO_3$ containig Ru found by EXAFS, RDA, XPS and TPR methods.

ZEOLITE-ENCAPSULATED METALLOCOMPLEXES AS NANOSCALE MATERIALS

Boris V.Romanovsky and Alexei G.Gabrielov

Chemistry Department, Moscow State University, Moscow

In the last decade, a new class of heterogeneous catalysts which zeolite-entrapped transition metal chelates represent has aroused growing interest. These materials have a variety of potential uses ranging from shape and regio selective catalysis to enzyme mimicing. The unique ability of zeolite structure to host coordinaton complexes with bulky macroligands providing for excellent uniformity of matrix environment creates the possibility of intentional design of nanoscale materials for catalytic applications. It is now appreciated that the catalytic efficacy of these systems is related to tremendous specificity of metallocomplex active centers while the selectivity can be assumed to be a function of the zeolite structure.

This paper aims to review critically different synthetic approaches for the preparation of zeolite-encapsulated transition metal phthalocyanines (MPc) as well as to assess the prospect of using them in molecular catalysis.

In principle, there exist two quite different synthetic strategies in preparing the zeolite-entrapped MPc species: those based upon intrazeolitic assembling of target molecule inside the zeolite void space and those involving the crystallization of zeolite host matrix around a metallocomplex to be included, i.e., in the presence of the complex. The first method developed by us [1] and usually referred to as «ship-in-a-bottle» synthesis consists of reacting a metal-loaded zeolite matrix with a flexible chelating agent such as 1,2-dicyanobenzene which can diffuse freely into the zeolite channels and cavities where the complexation occurs. The resulting complex is too large to escape through the zeolite openings. So, once formed it turns out to be trapped only on the base of molecular size. As starting materials for such an intrazeolitic synthesis, cation-exchanged forms as well as metal-loaded zeolites and those with preadsorbed metal-containing volatile or soluble complexes with loosely attached ligands are used. The second way to prepare the zeolite-included MPc complexes was developed by Balkus et al. [2] and is referred to as «in situ» zeolite synthesis. Given that direct evidences of the formation of true inclusion compounds were available, this method seems to be very attractive since it permits one to overcome some draw backs of the intrazeolitic assemb-ling procedure.

The basic problem facing researchers in the area of intrazeolitic molecular design is the identity of species obtained as a result of all preparative procedures. The assembling of the target species inside the zeolite void space can be ascertained by several physical and chemical methods. Thus, UV reflectance spectra con-sistent with complex formation, X-Ray powder diffraction pattern confirming the crystallinity of the zeolite matrix, XPS showing no detectable surface MPc's in excess and the reduced sorption capacity of the zeolite for water are all in accordance with the formation of the MPc complexes inside the supercages of the zeolites Y. Depending on initial loading of the zeolite with MPc complex precursor and type of metal as well as on the duration and synthesis temperatures, the involving of metal atoms into chelation can be as high as 100%.

The catalysts synthesized by aforementioned «ship-in-a-bottle» me-thod were tested in some 20 reactions in both gas and liquid phases. From the practical standpoint, these catalytic materials have some essential advantages over both homogeneous and heterogeneous systems. So, the zeolite matrix provides a good method of isolating MPc units from one another and thereby prevents bimolecular destruction. As a result, the zeolite-included MPc's exhibit excellent longevity when perform in oxidative atmosphere in contrast to their free analogs.

References

1. Romanovsky B.V., Proc. 5th Internat.Symp.Relat.Homog.Heterog. Catal., VNU Sci.Press, 1986, p.343.

2. Balkus K.J.,Jr., Kowalak S. and Hargis D.C., Stud.Surf.Sci.Ca-tal., 1991, V.69, p.93.

The Problems of Natural Gas Processing into Petrochemicals and Fuel

A.Ya.Rozovskii
Topchiev Institute of Petrochemical Synthesis of the Russian Academy of Sciences
Leninskii Prospect 29, 117912, GSP-1, Moscow, Russia,Fax: (095) 230-2224

The following sequence of stages is being developed or used (Mobil process) as the basic route to process natural gas into petrochemicals and/or liquid fuels: steam-air or steam-oxygen or steam-reforming of natural gas to produce syngas, followed by a reaction sequence: syngas -> methanol -> dimethyl ether (DME) -> petrochemicals and/or liquid fuel. This system of reactions is effected in the form of two consecutive processes: methanol synthesis and methanol transformation into products. Such an approach is historically justified by the fact that the process comprising natural gas conversion into syngas and the transformation of the latter into methanol is well developed industrially. Although at the present time this method is applied to produce more then 20 million tons of methanol annually, the approach has some drawbacks. The most important of these are due to unfavorable thermodynamics of methanol synthesis and high hydrogen consumption in the process. The unfavorable thermodynamics results in significant expenditures for gas circulation and in low space time yield (STY = 0.4 t $m^{-3} h^{-1}$ at 80 atm.).

In the framework of a new approach, the primary processing of natural gas is conducted using dry reforming or steam-carbon-dioxide reforming. The syngas transformation is effected in two stages: the synthesis of DME and its transformation into products. Such kind of processes is proposed by Haldor Topsoe Co, and is developed by our laboratory independently.

In this case, the limitations in methanol synthesis caused by the thermodynamics are eliminated to allow the first of the two syngas treatment processes to be conducted with essentially improved technical and economical indicators, as compared with methanol synthesis. The second process, production of petrochemicals or fuels, also proceeds more readily as DME is next intermediate after methanol in the course of synthesizing hydrocarbons and alike. DME itself can be used as a fuel too.

Highly selective DME can be produced from syngas, the only byproduct, except for methanol admixture, being CO_2. The values of single-pass conversion as high as 80% and STY as high as 2 t per t of the catalyst per h and more can be obtained. CO_2 produced at this stage can be returned back to the first stage of methane reforming. If dry reforming is used, CO_2 utilization may be realized due to the whole process: $3CH_4+CO_2=2(CH_3)_2O$. This process appears to be the preferable one both for natural gas processing and for CO_2 utilization.

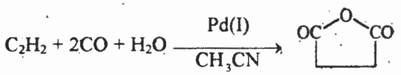
NEW TRENDS AND RESULTS IN CARBONYLATION OF ALKYNES

Oleg N. Temkin, Lev G. Bruk

Moscow State Academy of Fine Chemical Technology, pr. Vernadskogo 86, 117571 Moscow, Russia

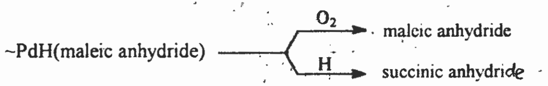
During last 5 years, studies of carbonylation reactions opened a new avenue to the use of acetylene and other alkynes. Especially promising results concern palladium-catalyzed reactions: synthesis of succinic anhydride from acetylene,[1-4] new findings concerning syntheses of maleic anhydride and its derivatives[3,5,6] and diesters of maleic acid derivatives[7] and γ-lactones.[3,7] New catalytic systems were proposed for syntheses of alkynylcarboxylic acid esters.[8,9] This report is devoted to recent findings in syntheses of succinic and maleic anhydrides and alkynylcarboxylic acid esters.

1. Succinic anhydride[1-3] is the product of reaction (1), which occurs in the solution of $PdBr_2$ at 40°C and under pressure of 0.1 MPa. The yield of succinic anhydride is 70% (and that of succinic acid is 15%):



(1)

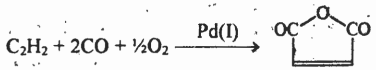
The true catalyst of reaction (1) is a palladium (I) carbonyl complex. A series of experiments (the kinetic study, the IR study [ν_{CO} = 1936 cm^{-1}] and ^1H NMR study of solutions [δ = -1.88 ppm], the study of deuterium exchange [D from D_2O], and the kinetic isotope effect study) validated the intermediacy of maleic anhydride coordinated to palladium hydride complex. The oxidation of palladium hydride complex by oxygen increases the rate of maleic anhydride formation and decreases that of succinic anhydride:[4]



(2)

This process passed tests on a pilot plant.

2. In the presence of oxygen (and other oxidants), the reaction becomes catalytic with respect to maleic anhydride:



(3)

The yield of maleic anhydride based on reacted acetylene reaches 80%. A drastic increase of the rate of reaction (3) with P_{O_2} ($\geq$0.1 atm) is likely associated with the occurrence of a new mechanism of maleic anhydride formation that involves the participation of oxygenated palladium complexes.

The choice of the catalyst of hydride oxidation made it possible to decrease the oxygen concentration in the mixture to 4% when the acetylene concentration is 10%. The possibility of plant-scale syntheses of succinic and maleic anhydrides and their derivatives from natural gas via the stage of methane oxidative pyrolysis is discussed.

3. Depending on conditions, syntheses of alkynylcarboxylic acid esters[8,9] can be conducted by the carbonylation of RC≡CH or RC≡CX (X = I and Br) according to the following reactions:

$$RC{\equiv}CH + CO + \tfrac{1}{2}O_2 + MeOH \xrightarrow[1atm,\ 20^{\circ}C]{PdCl_2\ -\ CuCl} RC{\equiv}CCOOMe + H_2O \qquad (4)$$

$$RC{\equiv}CX + CO + MeOH + Et_3N \xrightarrow[1atm,\ 40^{\circ}C]{PdX_2\ -\ LiX} RC{\equiv}CCOOMe + Et_3NHX \qquad (5)$$

Mechanisms of reactions (4) and (5) are also studied. Possible pathways to key intermediates of these reactions, ~PdC≡CR,[10] are discussed.

References

1. Temkin, O.N.; Bruk, L.G. *9th Soviet-Japanese Seminar on Catalysis*, Novosibirsk, 1990, p. 83.
2. Temkin, O.N.; Bruk, L.G. *Proc. of the First Russia-Japan Joint Symp. on Petroleum, Natural Gas, and Petrochemistry*, 1993, p. 185.
3. Bruk, L.G.; Temkin, O.N. *Khim. Prom-st* **1993**, *5*, 57.
4. Oshanina, I.V.; Bruk, L.G.; Kozlova, A.P.; Odintsov, K.Yu.; Vorontsov, E.V.; Temkin, O.N. *Kinet. Katal.*, in press.
5. Zargarian, D.; Alper, H. *Organometallics* **1991**, *10*, 2914.
6. Bruk, L.G.; Oshanina, I.V.; Kozlova, A.P.; Temkin, O.N.; *Abstracts of 9th JSHC*, Jerusalem, 1994, p. 68.
7. Gabriele, B.; Costa, M.; Salerno G.; Chiusoly, G.P. *J. Chem. Soc. Perkin Trans 1* **1994**, 83.
8. Zung, T.T.; Bruk, L.G.; Temkin, O.N. *Mendeleev Commun.* **1994**, 2.
9. Zung, T.T.; Bruk, L.G.; Temkin, O.N.; Malashkevich, A.V. *Mendeleev Commun.* **1995**, 3.
10. Zung, T.T.; Malashkevich, A.V.; Bruk, L.G.; Temkin, O.N. *Kinet. Katal.*, in press.

Authors wish to acknowledge the financial support from the International Science Foundation and the Russian Fund for Basic Research.

METAL-COMPLEX CATALYSIS IN THE SINTHESIS OF INSECT SEX PHEROMONES AND JUVENOIDS

G.A. Tolstikov

Novosibirsk Institute of Organic Chemistry SB RAS, Novosibirsk

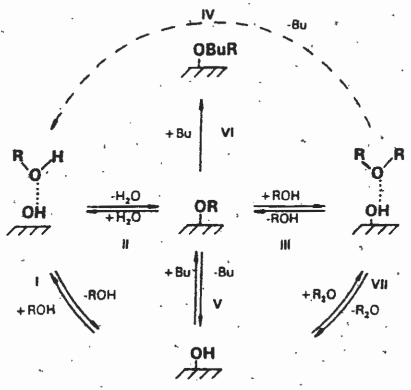
Linear and cyclic oligomerisation of 1,3-dines catalyzed by transition-metal complexes, oxidation of alkenes with molecular oxygen in the presence of Pd-complexes, new reactions of organoaluminium compaunds catalyzed by Cr_2ZrCl_2 were used for synthesis of insect sex pheromones and juvenoids.

REACTION PATHWAYS, KEY INTERMEDIATES AND PORE CONFINEMENT EFFECTS IN DEHYDRATION OF BUTANOLS OVER H-ZSM-5 ZEOLITES AND AMORPHOUS ALUMOSILICATE

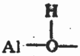
Kirill I.Zamaraev* **and John M.Thomas****
***Boreskov Institute of Catalysis, Novosibirsk, Russia**
****Royal Institution of Great Britain, London, UK**

The kinetics and mechanism of butanols (*n-*, *sec-*, *iso-* and *tert-)* dehydration over well-characterized H-ZSM-5 catalysts and amorphous aluminosilicate (AAS) catalysts have been studied using: (1) - the flow microreactor with the online GC analysis (under steady-state and transient conditions) of the reaction products that escape the catalyst pores, (2) - the «static» microreactors with FTIR and NMR analysis of the products that are formed and trapped inside the pores.

The same overall reaction scheme has been found for all butanols over both H-ZSM-5 and AAS with the $\mathrm{Al{-}\overset{\overset{H}{|}}{O}{-}Si}$ groups as the catalyst active sites and $\overset{OR}{\perp}$ species ($R{=}C_4H_9$) as the key reaction intermediate:



However, for different butanols and catalysts (i.e. H-ZSM-5 or AAS, and if H-ZSM-5 then of what crystallite size), the observed reaction rates and selectivities can be dramatically different even under similar reaction conditions. But all these differences are well understood in terms of the elucidated reaction mechanism. For example, under identical temperature and pressure the density of *n*-butanol inside the zeolite pores is close to that in the liquid *n*-butanol, while pores of AAS are more or less empty. This means that conditions for *n*-BuOH dehydration over the same $\mathrm{Al{-}\overset{\overset{H}{|}}{O}{-}Si}$ active site in the zeolite and AAS are in fact dramatically different. As a result, the two catalysts demonstrate considerable differences in the activation energy (138± 8 kJ/mol for H-ZSM-5 and 96± 12 kJ/mol for AAS) and selectivity of butene formation from *n*-BuOH (e.g. at 378K 6% over H-ZSM-5 and 57% over AAS).

The molecules of butanols have been found to play a two-fold role in catalysis. First, they serve as reagents. Second, via adsorption they protect the active  $\mathrm{Al}-\overset{\mathrm{H}}{\overset{|}{\mathrm{O}}}-\mathrm{Si}$ sites from becoming involved in the undesirable side reaction of butene oligomerization that poisons the catalysts.

The reaction intermediate  $\overset{\mathrm{OR}}{\perp}$ was characterized using solid state ^{13}C CP/MAS NMR, ^{2}H NMR and two dimentional (2D) J-resolved ^{13}C NMR. Butanols selectively labeled with ^{13}C and ^{2}H in various positions were used in these studies.  $\overset{\mathrm{OR}}{\perp}$ was found to exist in two forms, i.e. butyl silyl ether (BSE) and adsorbed butyl carbenium ion (BCI). BCI is a more labile chemical species that seems to be always involved in the main reaction stream. BSE is a more stable species that sometimes is still active enough to participate in the main reaction stream (the case of *iso*-BSE in H-ZSM-5), but sometimes is too stable to be in that stream (the cases of *n*-BSE and *tert*-BSE in H-ZSM-5). Different behaviour of various BSEs can be attributed to their different confinement in the zeolite pores.

References.

1. M.A.Makarova, C.Williams, V.N.Romannikov, K.I.Zamaraev and J.M.Thomas, J.Chem.Soc.Farad.Trans. 86(1990)581.
2. C.Williams, M.A.Makarova, L.V.Malysheva, E.A.Paukshtis, K.I.Zamaraev and J.M.Thomas, J.Chem.Soc.Farad.Trans. 86(1990)3473.
3. M.A.Makarova, C.Williams, J.Thomas and K.I.Zamaraev, Catal. lett. 4(1990)261.
4. C.Williams, M.A.Makarova, L.V.Malysheva, E.A.Paukshtis, E.P.Talsi, J.Thomas and K.I.Zamaraev, J.Catal. 127(1991)377.
5. A.G.Stepanov, V.N.Romannikov and K.I.Zamaraev, Catal.Lett. 13(1992)395.
6. A.G.Stepanov, K.I.Zamaraev and J.M.Thomas, Catal.Lett. 13(1992)407.
7. A.G.Stepanov, A.G.Maryasov, V.N.Romannikov and K.I.Zamaraev, Proc. 10th Intern. Congress. Catal., Budapest, 1992, Eds. L.Guszi, F.Solymosi and P.Tetenyi. Part A, p.621, Akademiai Kiado/Elsevier, Budapest, 1993.
8. A.G.Stepanov, A.G.Maryasov, V.N.Romannikov and K.I.Zamaraev. Magn.Res.Chem. 32(1994)16.
9. A.G.Stepanov and K.I.Zamaraev, Catal.Lett., 19(1993)153.
10. M.A.Makarova, E.A.Paukshtis, J.M.Thomas, C.Williams and K.I.Zamaraev, J.Catal. 149(1994)36.
11. M.A.Makarova, C.Williams, K.I.Zamaraev and J.M.Thomas, J.Chem Soc.Far.Trans. 90(1994)2147.
12. M.A.Makarova, E.A.Paukshtis, J.M.Thomas, C.Williams and K.I.Zamaraev, Catal.Today. 9(1991)61.
13. J.M.Thomas and K.I.Zamaraev. Topics in Catal. 1(1994)1.

Quantum Chemical Consideration of Active Sites in Zeolites

G.M. Zhidomirov, I.V. Yudanov, N.A. Kachurovskaya

Boreskov Institute of Catalysis, Novosibirsk 630090, Russsia

1. Introduction.

Nowdays it is widely recognized that intermediate chemical interaction of reacting molecules with certain groups of atoms of catalyst plays the key role in the mechanisms of chemical catalysis. Such groups of atoms are usually called active sites (AS). The detection of these ASs, the study of their structure and chemical properties are among the main objectives of the fundamental research in catalysis today. Molecular models of the ASs can be proved by quantum chemical calculations of their structure and physical and chemical properties. For these purposes the cluster approach is commonly accepted. This presentation contains a brief review of the cluster models of different ASs in zeolites.

2. Broensted Acid Sites (BAS).

Cluster models of BASs in zeolites were widely discussed in the literature [1,2]. This approach gave the possibilities (i) to understand the nature of Broensted acidity of zeolites; (ii) to investigate the dependence of acid strength on chemical and structural factors and to give reasonable classification of the BASs in zeolites; (iii) to discuss the chemisorption interaction of different reagents with BASs. Beside this the problem of generation of super acid sites in zeolites and their structure was considered.

3. Lewis acid sites (LAS).

The cluster modeling of LASs showed the strong dependence of the hemisorption activity and acidic strength on geometrical structure of LASs. The structure of LAS is really the result of (i) the genesis of the catalyst; (ii) the pretreatment procedure; (iii) the rigidity of the surface. Different possible ways of formation of LASs in zeolites are considered, one of them is associated with the dehydroxylation of non-framework oxide-hydroxide Al-containing species The destroying of zeolite structure and formation of such non-framework species was calculated by quantum chemical methods [3].

4. Transition Metal Ion Species (TMIS).

There are three main types of transition metal ion localizations in the zeolite matrix:

a) In the lattice positions as isomorphous substitutions.

b) In the cationic positions.

c) In the structure of non-framework oxide-hydroxide forms included in zeolites.

The selective oxidation activity of titanium silicalite is considered as an example of the first case. We associate the selective oxidation activity of the FeZSM-5 zeolite with non-framework Fe-containing species, the quantum chemical calculations show that the binuclear Fe-containing species must be the most active [5].

References

[1] G.M. Zhidomirov, V.B. Kazansky, Adv. Catal. 34 (1986) 131.

[2] J. Sauer, P. Ugliengo, E. Garrone, V.R. Saunders, Chem. Rev. 94 (1994) 2095.

[3] A.G.Pelmenschikov, E.A.Paukstis, V.S.Stepanov, K.G.Ione, G.M.Zhidomirov, K.I.Zamaraev, Proc. 9th Intern. Congr. Catal., Calgary, 1 (1988) 404.

[4] I.V. Yudanov, V.I. Avdeev, G.M. Zhidomirov, Phys. Low.-Dim. Struct. 4/5 (1994) 43.

[5] M.J. Filatov, A.G. Pelmenschikov, G.M. Zhidomirov, J. Mol. Catal. 80 (1993) 243.

POSTER PRESENTATIONS

ZEOLITE CATALYSIS

Ultrastable Zeolite-Based Catalysts for Petrochemistry

A.V.Abramova, E.V.Slivinskii, B.K.Nefedov, Yu.Ya.Goldfarb, and E.K.Trusova
The Topchiev Institute of Petrochemical Synthesis, Moscow

Catalytic properties of zeolites can be controlled by varying the acidity through Si/Al ratio, parameters of the crystal structure, by introducing metal additives in order to impart bifunctional properties to the zeolites. This approach seems to have great potentialities in development of new catalysis and improvement of the activities and selectivities of the existing catalysts. From our point of view the treatment of Y zeolites with Si-containing chemicals is the most promising method for synthesis of high modulus zeolites; it allows the dealumination to be followed by filling in the vacancies formed by silicon without destruction of the zeolite.

Ultrastable samples were prepared through the treatment of a zeolite with a solution of $(NH_4)_2SiF_6$ and the decationation by means of the intermediate thermal treatment. The samples produced were studied using IRS, XRD, XPS techniques. The zeolites were found to retain their high degrees of crystallinity (95-100%) during the preparation procedure; the parameter of a unit cell decreased to 24.4-24.3 Å, the dealumination degree reached 80-87%. The induced changes in the Si/Al lattice array expanded from the surface to the bulk, but the lattice was held unchanged in the bulk.

The zeolite samples obtained were examine as components of some industrially important catalyst. Involved in the catalyst for hydrocracking of vacuum gasoil, the ultrastable zeolite was found to enhance considerably the activity for hydrodesulfurization (0.05-0.08% sulfur in the hydrogenate) and separation (up to 80% yields of main gasoline and diesel fractions can be obtained, that is ca.20%

more than those obtained with the known catalysts GKO-1, TK-851 Haldor Topsøe, HYS-642 Teknip).

- Ultrastable Cu-exchanged zeolites can be substituted for the known Pt-containing catalysts for CO-to-CO_2 oxidation. They allow the conversion of CO as high as 90% at 300°C.

High selectivity and activity for isomerization of n-heptane ($iC_5/\Sigma C_5=60\%$, $\Sigma C_5=96\div98\%$) is observed for the ultradispersed Y-zeolites at 300°C; the isomerization is achieved at 60° lower temperature compared to the commercial process involving the catalyst IP-62.

There are some specific features of ultrastable Y-zeolites in benzene alkylation and methanol dehydration: the 100% regioselectivity for isostructure products in the former reaction and the activity for the formation of dimethyl ether at temperature as low as 160-170°C in the latter reaction were observed.

RELATIONSHIP BETWEEN PHYSICO-CHEMICAL AND CATALYTIC PROPERTIES OF ZEOLITES OF DIFFERENT STRUCTURAL TYPES IN THE ETHENE-TO-HIGHER HYDROCARBONS CONVERSION

L.Yu.Dolgikh, N.I.Ilchenko, N.V. Pavlenko

Pisarzhevsky Institute of Physical Chemistry of National Academy of Sciences, Kiev, Ukraine

Summary

The conversion of ethene - an oxidative coupling of methane product - to higher hydrocarbons over zeolites of faujasite and pentasile structural types was investigated. The possibility of regulating the activity and selectivity of zeolite systems by modification of their silicate module and crystallinity was showed.

Results and Discussion

Development of processes involving lower olefines, such as ethene, will permit to obtain valuable chemical products (components of liquid fuels, aromatic hydrocarbons etc.) from feedstocks other than petroleum. The process of making higher hydrocarbons (HHC) by two-step methane conversion may serve as an example: at the 1st step the direct synthesis of ethene from methane by oxidative coupling of methane (OCM) is carried out, at the 2nd step ethene conversion to HHC is accomplished.

In this work the problem of synthesizing HHC from ethene - an OCM product (3-10 vol.% C_2H_4 in helium, T = 573-873 K) - in the presence of zeolites of faujasite and pentasile structural types was attacted. The influence of the silicate module, acid--base properties and structural characteristics (porosity and crystallinity) on the activity (α_{C2H4} ,%) and selectivity to liquid hydrocarbons (S_{C5+},%) of zeolite systems was studied. The dependence of α_{C2H4} and S_{C5+} on the Si/Al ratio of the zeolite framework was shown to be characterized by extremum: the maximum value of α_{C2H4} = 4,5% and S_{C5+}= 73% is obtained for sample with Si/Al=5,5 (T=533 K). Comparison of the physico-chemical and catalytic properties of silicated modifications of faujasite Y indicated that α_{C2H4} and S_{C5+} change proportionally to the number of strong acid centers and unproportionally to the catalyst porosity.

The influence of crystallinity, N, of zeolite (ZSM-5,11) on its activity and selectivity in the ethene-to-higher hydrocarbons conversion was found. The maximum values of α_{C2H4} and S_{C5+}, equal to 32,9 and 31,7%, respectively, was obtained for sample containing 55% of crystal phase (T=573K). Under the same conditions, a high crystallinity sample (N=90%) showed a lower activity, and an amorphous contact (N=0%) was inactive. Comparison of the acid-base properties and texture characteristics of alumosilicate systems permitted to suppose the following. In our opinion, increasing

$\alpha_{C_2H_4}$ and $S_{C_{5+}}$ in the interval N=0-55% is relevant to increase in the number of strong acid centers on the catalysts surface. Further growth of crystal phase content (N>55%) leads to declining $\alpha_{C_2H_4}$ and does not exert essential influence on the process selectivity. The possible cause of the dependence α, S=f(N) observed is the influence of macrokinetic factors (inner diffusion limitations) on the reaction progress at N>55%,which is due to the influence of crystallinity on alumosilicate texture characteristics.

Microporosity of KBaL Zeolite, Pt Localization and Catalytical Properties.

V.P. DORONIN, V.A. DROZDOV, T.P. SOROKINA,
M.D. SMOLIKOV, T.V. KIREEVA

Omsk Department of Boreskov Institute of Catalysis,
Academy of Sciences of Russia Siberian Branch, Omsk.

Catalytic systems of Pt-L zeolite type are of great importance as the base for the catalysts of isomerization, selective cracking and paraffins aromatization [1]. The activity and selectivity of these catalysts are determined to a considerable extent by the metal dispersity and its distribution inside the channels and on the outer surface of the zeolite crystals. In spite of evident importance of the metal localization in the zeolite there is no any reliable method for determinating the metal distribution character between the inner and outer crystal surfaces and for the changing of the zeolite porous structural characteristics with the varios metal localization.

In this work a quantitative evaluation of changing in microporosity - blocking of KBaL zeolite channels by Pt particles and its localization in the porous structure and outer zeolite crystals surface has been carried out.

KBaL zeolite with the cylindrical form crystals was synthesized according to [2]. Barium atoms were introduced by means of ion exchange of prepared zeolite with Ba cations. Series of zeolite samples containing from 0.59 to 2.3 wt% Pt was prepared by means of ion exchange with $[Pt(NH_3)_4]Cl_2$.

The obtained results are found on the measuments of the simpliest gases (N_2, H_2) low- temperature adsorption by zeolites, and of O_2 - H_2 titration of metal surface in the presence of water vapours and without them [3].

The experimental isotherms of N_2 adsorption (77K) were calculated by Comparative method. The addition of Pt (0.6-2.3 %wt) leads to strong reduce of the volume micropores of the samples. This result may be explained by blockage the zeolite channels with supported Pt, because the synthesis conditions of the samples can't cause sharp reduction of zeolite microporosity.

Application of H_2 as a adsorbat at the same condition is of interest for it kinetic diameter (2.89Å) differs essentially from kinetic diameter of N_2 (3.64Å) [4].

The N_2 and H_2 adsorption results were compared and it may be concluded that full blocking of channels (adsorption blockage H_2) exists alongside with partial blocking (blokage N_2). Data of the blockage degree of the microporous Pt-KBaL samples are given in Table 1.

Table 1. Data of the blockage degree of the samples calculated from low-temperature N_2 and H_2 adsorption (77K, P=18kPa)

Pt content, wt %	N_2 ads.; α, %	H_2 ads.; α, %
0	0	0
0.59	29	12
1,23	40	7
2.30	78	39

*- $\alpha = (1-n_i /n_o) \times 100\%$, where n_i, n_o - adsorption value on the Pt-containing sample and on the initial zeolite respectively.

Thus as followed by the experimental data, the main contribution in the blocking effect of the zeolite microporosity is made by Pt located in zeolite channels although the amount of Pt on the outer surface is greater (Table 2).

Table 2. Accessible Pt part on the external surface of zeolite crystals and observed Pt dispersity in the samples according to O_2 - H_2 titration data.

Pt content, wt %	Pt part on the external surface, %	Dispersion D, %
0.59	91	77
1.23	86	88
2.30	49	90

The information may be very important for bifunctional catalysts because active centres of acid character may become unaccessible for reactants while being blocked by metal. Such selectivity of C_6H_{12} aromatization is decreased while the blockage degree of Pt-KBaL samples is increased.

REFERENCES.

1. Gallezot, P., Alarson-Diaz, A., Dalmon, J.A., Renouprez, A.J., and Imelic, B., *J. Catal.* 39, 334 (1975).
2. Europe Patent 0,219,354 (1987).
3. Belyi , A.S., Smolikov, M.D., Fenelonov, V.B., Gavrilov, V.Yu., and Dupliakin, V.K., *Kinet. Katal.* 27, 703 (1986).
4. Breck, D.W., "Zeolite Molecular Sieves." New-York - London, 1974.

PARAFFIN CONVERSION OVER METALCONTAINING PENTASIL ZEOLITES

E.E. Knyazeva, G.M. Telbiz, N.F. Meged

Institute of Physical Chemistry National Academy of Sciences of Ukraine, Kiev, Ukraine

The large scale production of aromatic from paraffin molecules has been of large interest during the last decades. The considerable success of catalysts for this purpose is based on shape selectivity zeolites with reduced acid strength of the Brensted acid centers such as modified ZSM-5. The present investigations have shown that other methods can be also used for the preparation of the catalysts, yielded catalysts with comparable activities and acrostics selectivities.

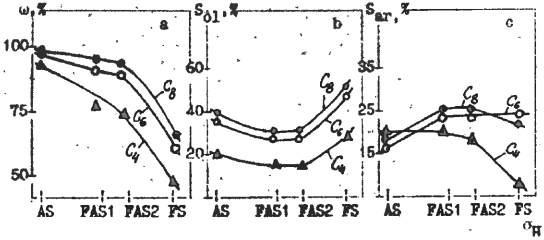
Several pentasil type zeolites were synthesized by procedures reported elsewhere [1]. The synthesis parameters were changed in order to obtain samples with varying characteristics. XRD, IR, AAS were imployed for checking of zeolite samples. The conversion experiments were carried out in a flow-type reactor between 673-873 K [2].

XRD of the crystallization products showed, that a higly crystalline products were obtained. The main characteristics of the synthezied samples are collected in Table.

Composition of the unit cell of pentasils and significances of average partial charge on the hydrogen atom

Sample	Cod	Composition of the unit cell	σ_H
alumosilicate	AS	$H_{2,90}\ Al_{2,90}\ Si_{93,10}\ O_{192}$	0,197
ferrialumosilicate 1	FAS1	$H_{1,90}\ Al_{1,23}\ Fe_{1,35}\ Si_{94,09}\ O_{192}$	0,1984
ferrialumosilicate 2	FAS2	$H_{1,76}\ Al_{0,95}\ Fe_{1,84}\ Si_{94,24}\ O_{192}$	0,1987
ferrisilicate	FS	$H_{1,71}\ Al_{0,06}\ Fe_{2,23}\ Si_{94,29}\ O_{192}$	0,1994

The paraffin conversion, olefine and aromatic selectivity for pentasil catalysts are



Paraffin conversion (873 K) as function of σ_H

a) conversion of paraffins, b) selectivity of olefins c) aromatic selectivity plotted in Figure. We observe, that reactivity of paraffins changes with acidity and decreased with chain length.

The effect on selectivity is more complex. The ferrialumosilicate catalysts show low olefin and high aromatic selectivity with comparison of alumo- and ferrisilicate. A more detail examination of the IR- and TPD-spectra of catalyst samples and changes in product distribution shows, that in order to obtain a high activity in combination with high aromatic selectivity catalysts based on metal containing pentasil zeolites with balanced acidity and dehydrogenation activity are necessary.

Successful reaction, in this case, via protonation of the starting paraffins, hydrogen transfer and aromatization mechanism due to stabilized Fe-O-Fe or Fe-OH-Fe species deposited after temperature treatment on the outer surface of the zeolite crystallities.

Reference:

1. Telbiz G.M., Kalugina E.E., Meged N.F. et al.; In: «Application zeolites in catalysis» (рус.), Moscow, Nauka, 1989, p.59-61

2. Krupina N.F., Meged H.F., Kalugina E.E.; «Neftekhimiya», 1988, v.28, N 4, p.445-451

EFFECT OF ACIDITY ON THE CATALYTIC ACTIVITY OF ACID ZEOLITES FOR THE SYNTHESIS OF ETBE

Yu.N.Kochkin, N.V.Pavlenko

L.V.Pisarzhevskij Institute of Physical Chemistry
National Academy of Sciences of Ukraine,Kiev,(044)2656533

At present alkyl tert-butyl ethers are well known octane enhancers for production of ecologic gasoline, and methyl tert-butyl ether (MTBE) is the fastest growing chemical product.

On the other hand, ethyl tert-butyl ether (ETBE) is attractive in production of gasoline with reduced volatility, and bioethanol from cellulosic biomass may be used in its production.

Acidic ion-exchange resins used for MTBE synthesis are thermally unstable, give acid effluent, and are sensitive to the methanol-isobutylene ratio. Therefore over the last years the increased interest is seen to acid-base catalysts like clays, some oxides, and zeolites. These data, however, are fragmentary that don't give an opportunity to make a notion about optimum set of values for acid strength and acid density of catalysts for alkyl tert-butyl ethers synthesis.

At present work it is studied catalytic activity of acid zeolites, that differ not only structural characteristics but also in acid properties - H-Y, H-mordenite, H-mordenite dealuminated, and H-TsVK.

All of investigated zeolites have weak and strong acid centers and based on its different role in synthesis of hydrocarbons from methanol over zeolites TsVK (1) it is possible to assume that ETBE synthesis proceeds with participation of protonated ethanol on strong acid centers and t-butyl carbenium ion on weak acid centers according to following scheme:

$$C_2H_5OH + HOZ_\alpha \dashrightarrow [C_2H_5OH_2]^+ [OZ_\alpha]^- \qquad (1)$$

$$[C_2H_5OH_2]^+ [OZ_\alpha]^- + (CH_3)_2C{=}CH_2 \dashrightarrow C_2H_5{-}O{-}C(CH_3)_3 + HOZ_\alpha \qquad (2)$$

$$(CH_3)_2C{=}CH_2 + HOZ_\beta \dashrightarrow [(CH_3)_3C]^+ [OZ_\beta]^- \qquad (3)$$

$$[(CH_3)_3C]^+ [OZ_\beta]^- + C_2H_5OH \dashrightarrow (CH_3)_3C{-}O{-}C_2H_5 + HOZ_\beta \qquad (4)$$

HOZ_α - strong acid center, HOZ_β - weak acid center.

With respect to catalytic activity in the synthesis of ETBE (ethanol-isobutylene ratio 1,5; WHSV $1h^{-1}$; gas-carrier - helium; temperature range 80-140°C; pressure 0,9 MPa) the order of investigated zeolites was:

H-Y $\leqslant$ H-mordenite $<$ H-mordenite dealuminated $<$ H-TsVK

and at the same order acid sites densities of zeolites decreases from $18,1.10^{20}$ to $6,8.10^{20}$ centers.g^{-1}.

Dependence of isobutylene conversion and ETBE selectivity on weak and strong acid sites densities and its ratio for studied zeolites has a complicated character. This can be controlled both by the structure of zeolites and differences in its catalytic activity temperature relationship.

Among the catalysts tested, zeolite TsVK appeared to possess the optimum acidity characteristics that makes it possible to achieve maximum activity and selectivity in production of ETBE.

REFERENCES

1. Samchenko, N.P., Alcheev, I.S., and Golodets, G.I., DAN Ukraine B9,57-59(1988).

REDUCTION OF NITROGEN OXIDES BY C_1, C_3-C_4-HYDROCARBONS IN OXIDIZING ATMOSPHERE ON METAL EXCHANGED ZEOLITES

S.N.Orlik, V.L.Struzhko

L.V.Pisarzhevskij Institute of Physical Chemistry
National Academy of Sciences of Ukraine, Kiev, (044)265 62 16

An activity and physico-chemical characteristics (XPA, IR-spectra, surface acidity) of cation exchanged zeolites series type of ZSM with metal ions of 4th period (Fe, Cu, Zn, Co) and lanthanides (La, Ce) in the reaction of NO reduction by methane, propane-butane mixture and propylene were studied in oxidizing atmosphere. It's shown that the catalytic activity is depended upon chemical composition (correlation SiO_2/Al_2O_3, nature of metal exchanged) and surface acidity. The process kinetics and sulphur dioxide influence were studied on Cu- and Ce-contained catalysts.

Highly siliceous zeolites type of ZSM with different correlation SiO_2/Al_2O_3(37-175) were used for preparation of catalysts. Cation exchanged forms with the ions of Fe, Cu, Zn, Co, La, Ce were received by ion-exchanging in liquid and solid phases. Stability and crystal structure of zeolites after ion exchanging were controlled by XPA.

The most activity Cu- and Ce-contained zeolites had shown in NO reduction by propane-butane mixture and for Cu-contained catalysts an increasing of NO conversion was observed at reduction by propylene as compared with reduction by C_3-C_4-hydrocarbons.

NO conversion was achieved 65-70 % (Cu-ЦВН, Ce-ЦВН) at the temperatures by 300-450 ^{0} C and space velocity 6000 h^{-1} for the reaction mixtures: 0,05 % NO + (0,02-0,06)%(C_3H_8-C_4H_{10}) + 6% O_2.

It's shown that NO conversion was increased from 0 to 65 % at increasing the degree of exchanging Na on Cu in ЦВК-zeolite from 0 to 100 %.

It's shown (for Ce-contained catalysts) that activity is depended upon SiO_2/Al_2O_3 correlation in zeolite, which was changed from 37 to 175. The maximum activity was observed on the catalyst Ce-ЦВН with SiO_2/Al_2O_3 = 37.

The acidic properties of starting and ion exchanged forms of zeolites were studied by IR-spectroscopy and was shown that acidic properties are increasing in the next sequence :

ЦВК < Cu-ЦВК < CeЦВК (68) < CeЦВН (37),

that is the most activity catalyst has the most acidity.

Kinetics of the process $NO+(C_3-C_4)+O_2$ was studied on Cu-ЦВК, Ce-ЦВК, Ce-ЦВН.

The influence of sulphur dioxide on Cu-, Ce-contained zeolites activity was studied in SCR process of NO by C_3-C_4-hydrocarbons. And it's shown that sulphur dioxide suppresses reduction of NO by hydrocarbons on Cu-ЦВК completely (partially unreversibly) and on Ce-ЦВН partially (fully reversibly). The influence of SO_2 is proportional to the concentration of sulphur dioxide. The influence of SO_2 on the quantity and strength of acidic centers of the catalysts was investigated by the method of TPD ammonia.

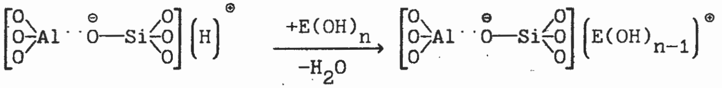
The catalytic activity of Co-contained zeolites in NO reduction by methane was studied. It was shown also that catalytic activity is depended upon method of catalyst preparation. 80 % conversion of NO was achieved on cation-decationizing forms of Co-contained zeolites.

BASE CATALYSIS ON ZEOLITES IN THE FORMALDEHYDE-DIMETHYLAMINE TRANSFORMATIONS

V.N.Romannikov
Boreskov Institute of Catalysis, Novosibirsk 630090, Russia

The using of zeolites of different compositions and structure types as catalysts for the reactions of selective organic and petrochemical syntheses is of significant interest over the past several years. The primary driving forces for this are no longer only markets and process economics, but also the development of new products and processes, and environmental considerations. The most of the reactions studied are typically acid-catalyzed and therefore require zeolites to be applied in decationated H-forms. At the same time, many reactions of selective organic synthesis are base-catalyzed, and application of zeolites as catalysts for these reactions remains to be practically unelaborated problem so far.

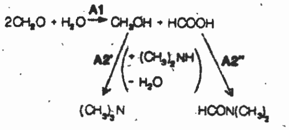
In this work the approach to realize the transformations of such type on zeolites is considered on the example of the simplest and typical base-catalyzed reaction during catalytic transformations in the "dimethylamine-formaldehyde-water" (DMA-F-H_2O) system using ZSM-5 and BETA zeolites as catalysts, in which the concentration of strong protic centers has been varied according to the scheme (1) by the chemical modification and was measured by IRS.



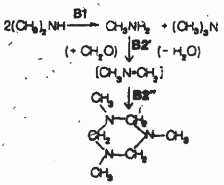
(1)

Under investigated reaction conditions (temperature - 140-320°C, WHSV - 1.3 and 2.8, starting molar ratio (DMA/F) - in the range of 0.7-1.9, molar ratio (H_2O/F) approximately constant and equaled to 9.8-12.5) only three products were found in gas phase at transformations on all catalysts and were identified with NMR as the following: trimethylamine, N,N-di-methylformamide (DMF) and 1,3,5-trimethylhexahydro-1,3,5-triazine (TAZ).

It is found for different catalysts studied that the DMF yield, calculated with respect to formaldehyde passed, increases more than one order of magnitude under decreasing reaction temperature, and the value of the DMF yield at constant temperature is the higher the lower is the concentration of strong centers in both BETA and ZSM-5 zeolites. By contrast, the TAZ yield does not depend or grows with increasing reaction temperature independently of zeolite acidity.



scheme A

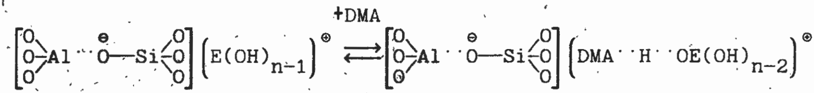


scheme B

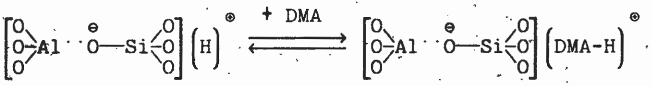
The results obtained allow to describe the observed transformations by the schemes (A) and (B). A disproportionation of aldehyde over Cannizzaro's reaction to produce alcohol and carboxylic acid is the basis of the scheme (A). By contrast, the first stage of the scheme (B) is a disproportionation of dimethylamine to mono- and trimethylamines, from which monomethylamine only is capable to react with aldehyde to produce TAZ.

Unlike the scheme (B), all the reactions of which seem to be not influenced by the catalysts studied, the first stage of the scheme (A) is a base-catalyzed reaction and is known to require the participation of a weak basic site. This type of the sites are supposed to appear in catalysts during the reaction as a result of DMA molecules adsorbtion. Their concentration increases with decreasing both reaction temperature and the concentration of strong protic centers. This leads to the growth of the DMF yield.

Being reversibly adsorbed on weak protic sites in modified zeolite via the scheme (2) unlike ordinary protonation on the strong centers via the scheme (3), DMA molecules keep their basic properties invaried, and the concentration of weakly bound DMA molecules should increase upon decreasing both the reaction temperature and the concentration of strong protic centers.



$$\left[\begin{matrix}O\\O\\O\end{matrix}\!>\!Al\cdots\overset{\ominus}{O}-Si\!<\!\begin{matrix}O\\O\\O\end{matrix}\right]\left(E(OH)_{n-1}\right)^{\oplus}\xrightleftharpoons{+DMA}\left[\begin{matrix}O\\O\\O\end{matrix}\!>\!Al\cdots\overset{\ominus}{O}-Si\!<\!\begin{matrix}O\\O\\O\end{matrix}\right]\left(DMA\cdots H\cdots OE(OH)_{n-2}\right)^{\oplus}\quad(2)$$



$$\left[\begin{matrix}O\\O\\O\end{matrix}\!>\!Al\cdots\overset{\ominus}{O}-Si\!<\!\begin{matrix}O\\O\\O\end{matrix}\right]\left(H\right)^{\oplus}\xrightleftharpoons{+\ DMA}\left[\begin{matrix}O\\O\\O\end{matrix}\!>\!Al\cdots\overset{\ominus}{O}-Si\!<\!\begin{matrix}O\\O\\O\end{matrix}\right]\left(DMA-H\right)^{\oplus}\quad(3)$$

The possibility of a creation of the basic catalytic sites via the weak interaction of dimethylamine molecules with modified low-acidic zeolite during the reaction is supposed to be a key factor, which determines the prevalent transformation route in the system.

ZEOLITE-BASED CATALYSTS FOR SELECTIVE REDUCTION OF NITROGEN OXIDES BY LIGHT HYDROCARBONS UNDER OXYGEN EXCESS .

Vladislav A. Sadykov, Galina M. Alikina, Rimma V. Bunina, Sergei L. Baron,
Svetlana N. Pavlova and Sergei . A. Veniaminov.

Boreskov Institute of Catalysis SB RAN, Novosibirsk.

Alexandr Ya. Rozovskii, Valentin F. Tretyakov

Topchiev Institute of Petrochemical Synthesis RAN, Moscow.

Valerii V. Lunin

Chemical Department of the Moscow State University.

Valerii A. Matyshak

Semenov Institute of Chemical Physics RAN, Moscow.

Introduction.

Selective catalytic reduction of nitrogen oxides by hydrocarbons in excess oxygen is now considered as the most promising process for clean-up of the flue gases of mobile as well as stationary sources. A great number of catalysts have been found, though their performance under real conditions as well as stability has to be steel improved. Copper and cobalt cation- exchanged zeolites with ZSM-5 and mordenite structure are among the most promising systems. To enhance their performance by adding promotors etc ., at least basic stages of the reaction mechanism and the nature of the active centers are needed to be elucidated. Serious problems are connected also with the deactivation of these systems due to sintering of the active components and zeolites dealumination by high-temperature steam action. For practical application, catalysts in the form of rings and honeycomb monoliths are the most suitable. It puts forward the problem to find binders not deteriorating catalytic performance as well as to optimize rheological properties of plastic pastes.

Results and discussion.

1. Basic stages of the reaction mechanism.

The most important question is the route of nitrogen oxides activation. From the chemical point of view, only tightly bound oxidized nitrogen-oxides adspecies might compete with molecular oxygen for hydrocarbons in the real operating conditions.

To verify this hypothesis, for a number of the catalysts based upon zeolites and oxide systems a strength of various NO_x complexes binding with the surface was determined by using TPD methods. Within catalysts of the same structural type (zeolites, oxides) a rather good correlation was found between the operating temperatures in the reaction of selective NO reduction by propane and the temperatures of TPD peaks corresponding to nitrite-nitrates decomposition . This trend is in favor of the nitrite-nitrate participation in the reaction scheme: strongly bound complexes should be thermally activated to desorb or to interact with activated hydrocarbons. To prove this point , a set of in situ spectrokinetic experiments in IR flow cell has been carried out for copper- containing ZSM-5 zeolites. Kinetic parameters of the interaction of propane with nitrites stabilized on copper (2+) centers have been determined and under steady-state conditions the rate of this surface reaction has been found to be practically equal to the rate of catalytic reaction. Hence, for the first time decisive role of strongly bound nitrite-nitrates in the NO selective reduction has been directly demonstrated.

Another important point - the nature of the centers of NO activation and nitrite-nitrate location. Comparison of the NO_x and O_2 TPD parameters for Cu - and Co- containing zeolites with various metal loadings led to the conclusion that NO is primarily activated via oxidative addition on the clusters of transition metal ions where weakly bound oxygen is stabilized. Nitrite-nitrates thus formed are located on the same centers being reoxidized by gas-phase oxygen. The cluster centers are also known to activate easily hydrocarbons via oxidation.

2.Promoters, performance and stability.

From the practical point of view, the results obtained indicate a way to improve catalytic performance under real conditions via addition of the base-type promoters capable to stabilize nitrite -nitrates and thus shift operating range to higher temperatures. In this case increase of the rate of hydrocarbon activation and decrease of the poisoning effects of water and sulfur dioxide are expected to enhance specific catalytic activity. Indeed, by using alkaline-earth promotors we have obtained catalysts having very good performance under real conditions at high space rates. Thus, for mixtures containing 0.1% NO and 0.1-0.3% of $CH_4(C_3H_8)$, up to 5% of H_2O, 10% of CO_2, 700 ppm of SO_2 at GHSV ca 100,000/h , ca 70-90% of NO conversion into nitrogen was achieved in the temperature range 450-700 C. At present these catalysts are among the most active systems reported in the world.

Addition of alkaline-earth promoters has greatly improved stability of zeolite-based catalysts in real operating conditions . Hence ; no catalyst deactivation or even noticeable change in performance was observed after prolonged testing an enhanced (up to 700C) temperatures when unpromoted copper-containing zeolites are known to lose rapidly activity.

3. Binders and shaping.

To shape zeolite catalysts as rings and monoliths, two approaches were used : plastic extrusion and washcoating on the metallic foil . In both cases inorganic binders are required. Such widely used binder as pseudoboehmite was found to cause severe deactivation of zeolite catalysts especially after hydrothermal treatment. So other binders based upon silicasol and amorphous alumosilicates /clays were tested and suitable compositions were found. After optimization of the rheological properties of the pastes by using some surfactants and electrolites, honeycomb monoliths on the bases of synthetic zeolites with high catalytic activity and reasonable crushing strength were obtained.

To form zeolite layer on the metallic support (stainless steel) , an original proprietory binder was used which formed highly catalytically active and strongly bound coatings after drying and calcination. As a result, thin layers of promoted copper-exchanged ZSM-5 zeolite on metallic support were found to ensure ca 75% NO conversion at GHSV ca 30,000/h and propane:NO ratio=1:1 (oxygen excess) in the temperature range 400-500 C , that is sufficient for a number of applications (diesels etc).

Conclusion.

Copper and cobalt-exchanged zeolites promoted by alkaline-earths cations were shown to have good performance for selective reduction of nitrogen oxides by propane and methane in excess oxygen at high GHSV and in the presence of water, carbon dioxide and sulfur dioxide . These promoters were chosen according to idea about the decisive role of the surface nitrite-nitrate complexes in the mechanism of this reaction proved for the first time in these studies. Furthermore, such promoters suppress zeolites dealumination and active components sintering. Binders ensuring manufacturing of honeycomb-type catalysts without loss of activity in the real flue gases were found .

ZEOLITE-CONTAINING CATALYSTS ON THE BASIS OF HIGH SILICA HTsVM ZEOLITE AND LAYER-PILLARED MONTMORILLONITE

E. Stepanova, A. Rat'ko

Institute of General and Inorganic Chemistry, Belarus Academy of sciences, Minsk

One perspective way of improving of sorption properties and thermal stability of clay minerals is the fixing of their structure with the use of inorganic compounds, the latter acting like peculiar pillars. The introduction of oligmer cations into laminated minerals is realized by exchange of inter-layer cations and hydrooxocomplexes of polyvalent metals. Fixing clay layers at the distance 16-17 Å one is able to form three-dimensional zeolite-like structure with high selectivity of sorption.

The use of such layer-pillared montmorillonites as matrix in zeolite-containing catalysts makes it possible to obtain high-selective catalysts for gas-phase synthesis of para-alkyl-aromatics, in particular alkylation of toluene with ethylene and disproportionation of toluene.

Analysis of X-ray data showed that inter-layer space of montmorillonite, modified by Al- and Al+P-hydrooxocomplexes increases up to 16,8-17,2 Å

. In the reaction of toluene disproportionation zeolite containing catalysts with Al- and Al+P-montmorillo-nite matrix (50:50) don't rank below the pure zeolite HTsVM in major properties (xy-lene yield and selectivity of xylene forming).

As for traditional alumina matrix the Figure displays its principal distinction from fixed montmorillonite one. It is seen, the Al_2O_3 matrix doesn't change the character of xylene yield dependence upon temperature but only decrease it highly in comparison with pure HTsVM.

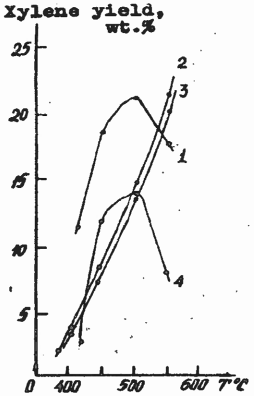


Fig. Xylene yield versus temperature in toluene disproportionaton.
1 - HTsVM, 2 - 50%HTsVM+50%Al-montmorillonite,
3 - 50%HTsVM+50%Al,P-montmorillonite, 4 - 50%HTsVM+50%Al_2O_3.

Since disproportionation takes place with the participation of strong H-sites which are absent on Al_2O_3, the latter ones play only a moulding role in reaction concerned.

At the same time for zeolite-containing catalysts with the Al- and Al+P-matrix the dependence between reaction products yield and temperature is of near-linear character, but not of extremal. One can get interested that the common surface acidity, determind by the pyridine desorption value at 200°C is practically the same for HTsVM and 50%HTsVM + 50%Al-montmorillonite (0,597 and 0,580 mmol/g respectively). But the relative portion of Broensted acid sites in HTsVM, arbitrarily evaluated from the optic density values at 1545 and 1450 cm^{-1} bands (PyH^+ and PyL species) is five times greater than that in 50%HTsVM + 50%Al-montmorillonite sample. It can be accounted for, because fixed pillars consisting of aluminium-oxygen or aluminium-phosphorous-oxygen bridges represent weak Lewis sites: v_{CO} in IR spectra CO absorption is not more than 2185 cm^{-1}. But in contrary to AL_2O_3 small amount of Broensted sites exist on the modified montmorillo-nite surface (PyH^+ band 1545 cm^{-1} is observed in IR spectrum).

Notice that the activity of montmorillonite-zeolite-containing catalysts at 500 °C is lower than that of pure HTsVM. But at 550 °C it increases greatly. At the same time one can observe strong drop down of xylene yield, decreasing of selctivity and increasing of yield of high-boiling xylene destruction products. It witnesses that in case of HTsVM zeolite the force of Broensted sites and their high concentration make the reaction to proceed in a way which followed by a number of by-reactions.

Nothing of the kind happens to montmorillonite -containing samples which possess large portion of more weak sites.

The regular system of matrix channels and their reasonably large sizes favour the unimpeded diffusion of reacting compounds to active zone and back, and high temperature of experiment increases the rate of reaction up to the value which provides the final yield of products and selectivity like in the case of HTsVM at 500 °C.

HETEROPOLY ACIDS AS ZEOLITE-TYPE MODIFIERS OF CATALYSTS SURFACES

N.A.Zakarina, G.V.Artyukhina, L.D.Volkova

Institute of Organic Catalysis and Electrochemistry of NAS
Republic of Kazakhstan, Almaty, FAX (3272) 61-57-22

SUMMARY: The solid-state interactions of Platinum and Palladium with HPA oxide matrix and the forming zeolite-type of metaloxide catalysts have been studied by physico-chemical methods (XPS, UV-, IR-spectroscopy, TPD, BET, electron microscopy for oxidation-reduction reactions.

INTRODUCTION: An important feature of zeolite catalysts is their ability to form isolated active sites on the surface owing to matrix cation stabilization. Proton sites of zeolites are strong energy traps of migrating ions [1]. The addition of transition metals can be considered as an acid-base interaction. According to the NH_3 thermal desorption data [2], the force of HPA acid sites are stronger than the same of HX, HY or amorphous alumina-silicate, and so HPA can be used with success for surface modification, for example of Al_2O_3.

EXPERIMENTAL SECTION: Pt(Pd)+HPA/Al_2O_3 catalysts were prepared by the impregnation method using the aqueous solutions of $PdCl_2$(H_2PtCl_6) and HPA. The specimen were dried (373K) and calcined (623K) followed by reduction (H_2, 623K, 2 hr) or strong oxidative thermal treatment in air (773-973K).

RESULTS AND DISCUSSION: It was shown that this interaction is accompanied by the change of support morphology and the forming of the surface with new characteristics, where the active sites are situated. By the method of low-temperature adsorption of N_2 (BET) the increase of adsorption capacity of modified samples in 2.5-3.0 times in comparison with initial alumina was fixed. The growth of pretreatment temperature from 623K up to 973K leads to the increase of catalysts porous sizes. Besides that, under high temperature a strong interaction between the modifier and Al_2O_3 with the formation of alumina-silicate matrix (in the case of $SiMo_{12}$-HPA) takes place, as it was established by the electron microscopy.

As in the case of zeolites, the injection of transition metal ions extends the number of processes, where the M-HPA catalysts can be put into practice, from oxidation up to reduction of organic compounds. On the XPS-spectra of Pt(Pd)-HPA/Al_2O_3 samples, obtained by impregnation followed by reduction, the peaks of metallic and oxidative (Pt^{2+} - 74 eV; Pd^{+} - 336.1 eV) states are recorded. Depending on pretreatment conditions the proportion of these forms and the state of active sites are changed. Due to the electron microscopy and IR data it was shown that the modification by heteropoly acids followed by temperature treatment ($\geqslant$623K) promotes the dispersity of active metal and the homogeneous distribution of metal particles along the surface. Just these catalysts show the reactivity in 2 times more than that of the traditional Pd/Al_2O_3 in liquid-phase hydrogenation of C=C double bonds of unsaturated organic compounds.

Under the conditions of strong oxidative thermal treatment the solid-state ion exchange processes and replacement of one of the Mo (or W) atoms by Pt (or Pd) take place. The catalysts, which were exposed to this treatment, are not reduced by H_2 and they do not show the activity in hydrogenation reactions. By electron microscopy and IR-spectroscopy methods the absence of metal particles (Pd^0, in particular) on the surface was shown. It should be noted that just these catalysts show a high activity in gas-phase oxidation of carbon monoxide and hydrocarbons to CO_2. So, the lower limit of ignition temperature of modified Pd-HPA/Al_2O_3 catalysts is decreased by 100K and 200K as compared with Pd/Al_2O_3 and HPA/Al_2O_3, accordingly. These systems are distinguished by a high thermostability: under the overheating up to 1100-1200K they maintain their activity.

CONCLUSIONS: Thus, the obtained results reveal that the activating HPA additives can yield zeolity-type structures under certain conditions having a high activity both for oxidative and reductive catalysis.

REFERENCES: [1] A.V.Kucherov, and A.A.Slinkin, Uspekhi khimii 61 (1992) 1687 (in Russian), [2] G.N.Kapustin, T.R.Brueva and A.L.Klyachko, Kinetika i kataliz 31 (1990) 1017 (in Russian)

SELECTIVE REDUCTION OF NITRIC OXIDE BY PROPYLENE ON BLOCK ZEOLITE-, Pt- AND Pd-CONTAINING CATALYSTS

D.V.Sokolsky Institute of Organic Catalysis & Electrochemistry of National Academy of Scienses of the Republic of Kazakhstan, Almaty.

Zakumbaeva G.D., Gilmundinov Sh.A., Toktabaeva N.Ph., Kotova G.N., Nurgalieva D.T., Egizbaeva R.I.

Last time the process of selective reduction of nitric oxide by hydrocarbons in oxidizing medium is studied very intensively besause of environmental problem.

Our work shows results obtained by study of catalytic activity of block zeolite-, Pt-Me- and Pd-Me-containing catalysts in this reaction. The catalysts were prepared from heat-resistant corrugated steel covering uniformly by aluminium oxide. Zeolites were introduced to oxide layer. Active metals were supported on prepared blocks by impregnation according their hydrocapacity. Metals content was varied in ranges 0,05-0,20 % at. The catalysts were dried and reduced by hydrogen.

The reaction was carried out in flow isothermal reactor at 200-500°C, and $25x10^3$ h^{-1} gas volume velocity. The catalyst's block size was 2,5 cm^3. The reaction gas mixture contained NO_x (400 ppm), C_3H_6 (700 ppm), O_2 (0,5 and 3,0 %vol.) and argon. Analysis of gases was carried out by opticacoustic gas-analysers GEAM-15M and GEAM-21. Catalyst activity was determined by NO_x and propylene conversion. Influence of temperature, catalysts nature, concentration of C_3H_6 and O_2 on NO reduction was studied. It was shown that introduction of zeolite to support composition allow to achive a high activity in reaction of interaction of NO with prorylene at 0,5 % content of oxygen. The conversion increases from 15-20 % at 200^0 C to 40-50 % at 500^0C. At the same time C_3H_6 conversion increases. When oxygen content rises from 0,5 to 3,0 %, NO conversion decreases by 1,5 times. Peculiarity of interaction between propylene and nitric oxide over metal catalysts in contrast to zeolite containing catalysts, is incomplete oxidation of propylene to carbon monoxide(0,1%) in reaction products. Monodisperse block Pt-Me catalyst which was prepared by using of metal sols begins to reduce NO by propylene from 200°C and achieves maximum activity (40%) at 400°C. While the temperature is increased NO conversion decreases to 20% and CO content rises (up 0,08%) in reaction products. Negative influence of oxygen is remarkable only at low temperatures. When oxygen concentration rises from 0,5 to 3,0 % vol. NO and C_3H_6 conversion decreases nearly in 4 times at 200-250°C, and only by 1,5 times at optimal temperature 400°C.

Pd-containing block catalyst promoted by YII-YIII groups metals was investigated in NO + C_3H_6 + O_2 reaction in presence of 0,5 and 3,0% oxygen as well. It should be noticed that the promoted Pd-catalyst is more active than Pt-catalyst. High conversion of NO and C_3H_6 (more than 80 %) over Pd-systems was achieved already at 300°C. However NO conversion decreases sharply at temperature high than 400°C and achieves 40 % at 500°C.

This way block zeolite Pt-Me- and Pd-Me-containing catalysts have high activity and selectivity during NO reduction by propylene in presence of oxygen.

POSTER PRESENTATIONS

CATALYSIS FOR ENVIRONMENTAL PROTECTION

UTILIZATION OF ELECTROTHERMOPHOSPHORUS SLAG
AS COMPONENTS OF CATALYSTS

S.N.Bukeikhanova, O.E.Lebedeva
Al-Faraby Kazakh State National University,
Almaty, Republic of Kazakhstan

Industrial wastes often contain valuable components and the necessity of their re-use is obvious. The paper deals with the utilization of the by-products of phosphorus production (phosphorus slags).

Phosphorus slags usually contain calcium and magnesium oxides, silica, alumina, phosphorus oxide. Their structure is presented by silicate or silicophosphate glasses with low content of crystalline phase.

The samples of slags have been characterized by XRD and thermal analysis. Slag glasses have been shown to be thermally stable below 650°C.

Phosphorus slags owing to their composition resemble some traditional oxide catalysts. The slags were supposed to possess catalytic activity in acid-base and oxidative processes.

Catalytic activity of the slag samples have been studied in flow fixed bed reactor. Cyclohexanol conversion and ethanol deep oxidation were chosen as test reactions.

The original slag was shown to have low activity in both processes. However catalytic activity of slag samples can be increased significantly as a result of rather simple modifying procedures. For instance the short-term treatment with the diluted acids solutions was proved to be very effective. Modified slags are thermally stable. Cyclohexanol conversion over modified slag achieves up to 97%.

The dependence of catalytic properties on the modification conditions (nature of acid, acids concentration, time of treatment) has been studied in detail.

Additional physico-chemical investigations were carried out in order to elucidate possible reasons of the growth of catalytic activity after acidic treatment of slags. The treatment was demonstrated to cause a considerable increase of specific surface area and a simultaneous increase of average pore diameter.

The slag samples keep their glass state after acidic treatment. However NMR Si and XRD studies have shown the accumulation of silica to take place.

Surface acidity of original and modified slags was estimated by means of Hammet indicators. The rise of acidity has been noticed after the modification.

Thus electrothermophosphorus slags were proved to be cheap and available materials for catalysts' preparation. The versatile ecological effect can be achieved when industrial wastes are used as components of catalysts applicable for the oxidative clean up processes.

METALCOMPLEX-SUPPORTED CATALYSTS FOR THE CONVERSION OF HYDROCARBONS AND THEIR DERIVATIVES

Chekurovskaya E.D., Zubanova L.G., Kuzmina R.I.,
Tarasova T.M. and Sevostianov V.P.

Saratov State University
Scientific Research Institute of Chemistry
Saratov, Russia

Nowadays the catalysis with metalcomplex-supported catalysts is one of the quickly developed direction in the catalytic chemistry. It has been appeared on the joint between the homogenecus and heterogeneous catalyses. Realizing the ideas of both catalyses, metalcomplex-supported catalysts are obtained both better properties.

In the synthesis of methylpyridines from acetic aldehyde and ammonium 25 samples of catalysts have been studied. A row of catalysts based on Pt, Pd, Fe, Co, Ni, Cu complexes with N-, S- and P-containing ligands have been synthezised. The main product of the reaction is 4-methylpyridine. A correlation between the catalyst activity and the nature of heteroligands has been established. The activity of the Pd-complex catalysts decreases in the row: P-complexes > S-complexes > N-complexes of Pd. The influence of the reaction conditions, the quantity of complex carrier (0,5-5,0*10 Pd/g carrier), the solvent and metal properties on the reaction course has been studied. The activity and selectivity attitude 4-methylpyridine of most catalysts is more then 90%. The testing of the best catalysts in the condition of flowing system using a large load of them shows their high stability and activity. The influence of the solvent nature on the reaction course has been shown: on using dimethylformamide 4-methylpyridine has been synthezised, in the case of acetylaceton - pyridine is the main product, using 1 *n* hydrochloric acid - acetonitryl has been obtained with 100% yield, using dimethylsulphoxide - a mixture of high homologs of pyridine has been obtained.

The transformations of *n*-hexane and cyclohexane have been studied in the catalitic systems, obtained by heterogenization of complex compounds on the surface of carrier. For creating these catalysts the S-containing organic complex compounds of Rd(III) and Pt with different ligands have been used.

It has been synthezised on the basis of rhodium chloride. Using this catalyst the hydrocracking process is suppressed and cyclohexane is selectively dehydrogenated into benzene at 380^{0}C. The catalyst $Rh(L)/Al_2O_3$ (L - ligand - 5-butyl-1-methylthiopyrrolidone-2); Rh(III) is the most active one.

The investigations show that the catalyst $Rh(L)/Al_2O_3$ is more active than the catalyst $Pt(L)/Al_2O_3$ in all of the transformations of *n*-hexane. The difference in the catalytic activity of the named catalysts is explained with a different configuration of the starting complex compounds of Rh(III). It is known that rhodium complex compounds have the octahedral configuration and those of Pt(II) have the configuration of plane square.

In order to confirm the configuration influence of the starting complex compound on the catalyst activity the catalyst $Rh(L')/Al_2O_3$ has been studied. It has been synthezised by putting rhodium from $Rh(PPh_3)_3Cl$ on the surface of carrier and has the configuration of plane square. It is not possessed a high catalytic activity. The yield of the aimed product - benzene - at temperature 500^{0}C is 9.0 mass % against 37.4 mass % in the presence of the catalyst $Rh(L)/Al_2O_3$.

With the hexane conversion as an example the adsorption and activation of hydrogen have been studied at the putting temperature regime of the hydrogen desorption.

It has been estimated that the hydrogen adsorption on the surface of catalyst appears within two temperature intervals: 160-360^{0}C and 425-540^{0}C. The maximal rate of desorption takes place at 200^{0}C. The correlation of the hydrogen adsorption and the metal nature and the structure of complex compound has been found.

CATALYTIC PURIFICATION OF WASTE GASES FROM HYDROCARBONS AND THEIR O-, N-, AND Cl-DERIVATIVES

R.I.Kuzmina, L.G.Zubanova, E.D.Chekurovskaya,
T.M.Tarasova, and V.P.Sevostianov

Institute of Chemistry, Saratov State University,
Saratov

The development of engineering and industry, the invention of new techological processes, especially in the period of scientific techological revolution, lead to enhancing pollution of the environment, this pollution has got the total character. The search for effective ways of the puritication of waste gases was and still remains an important direction in the struggle for air purity. A catalytic method of neutralisation is the most economical and effective for large-scale waste emission. So the development of new active and selective catalysts for the deep oxidation of organic compounds seems to be an actual and practical task.

The systems of the deep oxidation of hydrocarbons and their derivatives, being used in industry as solvents (toluene, xylene, ethylacetate, butylacetate, *n*-butanol, acetone, dimethylformamide, pyridine, trichloroethylene) have been investigated. The main products of hydrocarbon conversion are carbon dioxide and water, of dimethylformamide and pyridine are carbon dioxide, nitrogen, and water, of trichloroethylene are carbon dioxide and chorine absorped with a catalyst.

The deep oxidation was carried out in the conditions of flowing system within 200-700^{0}C at the volume rate up to 25 l/h in the presence of catalysts containg different compounds of transition metals. The condition of their functioning were selected so that the conversion degree was about 100%.

It has been established that in the presence of oxide catalysts containg compounds of copper, chromium and iron and having the spinel structure all the studied compounds but trichloroethylene have the 100% conversion degree. Spinel structures work effectively within 200-300^{0}C. Trichloroethylene and pyridine are oxidized most hardly. Their 100% conversion can be achieved at temperature not less than 450-500^{0}C.

Catalytical systems created on the base of a nature carrier being early used for the sorption purification of halvanic wastes (they are enriched with Cu, Ni, Cr ions, 0.5-5.0%) take a specific place. They provide the 100% conversion degree of dimethylformamide at 200^{0}C and the volume rate up 15 l/h.

The commercial alumoplatinum catalyst AP-64 was tested. In its presence pyridine, beginning with 650^{0}C, is fully converted with forming molecular nitrogen and carbon dioxide. This process can be promoted by means of preliminary activitation of the catalyst at low temperature, oxygen dissolving in the surface layers of metal and taking part in the oxidation.

Copper-containig contacts (0.5% Cu/Al_2O_3), being typical catalysts of redox processes and easily activating oxygen with electron trasfer, convert pyridine by 100% within 500-600^{0}C. These results were compared with those obtained for the catalyst cantaining copper oxide of the same concentration, and providing 96.7-100% conversion of pyridine at 600^{0}C.

The introduction of palladium into these catalysts (1:1) shows that the copper-palladium oxide catalyst is practically inactive within 500-600^{0}C. In the presence of copper-palladium metal-containing contact the pyridine conversion approaches 100% only beginning with 650-700^{0}C. The monometal palladium catalyst 0.5% $Pd-Al_2O_3$ works under more severe conditions.

The results obtained can be used for developing a techology of the purification gas wastes from organic impurities.

CATALYTIC PURIFICATION OF WASTE GASES FROM CARBON AND NITROGEN OXIDES

S.G.Shcheglova, E.V.Pletneva, R.I.Kuzmina,
M.R.Kakhiani, and V.P.Sevostianov

Saratov State University
Scientific Research Institute of Chemistry
Saratov, Russia

The enhancement of the world car fleet is accompanied by the increase of exhaust gases volumes. Car exhaust gases account for more than 60% of the overall waste volume. In this connection the question of the creation of catalytic systems for complex purification is getting urgent. As there is a number of compounds to be simultaneously and fully deleted from exhaust gases, any development of such systems will be very laborious. Reviewing the developments in this field shows the usage of catalytic neutralizers to be very effective.

The end of the present work is selecting and testing a number of catalyst samples, both industrial and developed by the laboratory of technical chemistry and catalysis for clearing model gas mixtures from nitrogen and carbon (II) oxides and hydrocarbons.

The test were performed using a plant of flowing type, under the atmospheric pressure, within the range 200-550^{0}C. The model mixture was composed on the base of the average real contents of CO, NO_x and CH_x in exhaust gases. The volume rate was varied within 800-5000 g^{-1}.

To be tested there were chosen: a number of metal-cement catalyst samples (got from the Novomoskovskii Institute of Nitrogen Industry), samples of mark GTT modified with noble metals, and a number of metal-plate catalysts obtained by means of modifying the surface of pore metal substrate with transition metal compounds.

The tests have shown all the sample to have a certain activity in the studied process. The activity of the metal-cement catalysts of different marks is approximately the same: for instance, CO at 250^{0}C is oxidized by 60%, NO is by 10%. The sample activity rises with temperature and at 550^{0}C CO is oxidized fully, and NO is by 60%.

The deposition of 0.05 weight % of a noble metal on the samples of the metal-cement catalysts of mark GTT has lead to 100% purification of the model mixture from CO within the whole temperature range, as we expected. The significant activity increase was observed in the process of purification from NO as well: just at 250^{0}C the puritication degree is 67%, and at 550^{0}C is 100%.

The test of the metal-plate catalysts modified with transition metal compounds have shown the sharp increase of its activity to occur after the high-temperature (600^{0}C) annealing in air. The treatment provides such an activity as it is after the noble metal modification, but within 450-550^{0}C the catalysts are even more active regarding the oxidation of NO.

It should be noted that the specific surface of the metal-plate catalysts by a factor of 10^2 less than that of the metal-cement ones. One can conclude that the reaction proceeds on the surface of catalyst.

The increase in the activity after the oxidizing annealing of samples can be explained by the formation of spinel-structure compounds ($NiAlO_x$, $CuAlO_x$, $FeAlO_x$) on the surface.

The data obtained are in favour of using both metal-cement and metal-plate catalysts for the purification ot waste gases. However, such properties as thermal conductivity, suitability for constructing, ease of making alloy and surface are in favour of metal-only contacts.

A CATALYST FOR NEUTRALIZING NITROGEN AND CARBON OXIDES IN WASTE GASES

S.Y.Molina, L.P.Mukhina, and V.P.Sevostianov
Saratov State University, Saratov

The neutralization of nitrogen oxides is a significant ecological problem. To solve it one can use the reaction between NO and CO, that is especially important for industrial waste gases and car exhaust ones where these two toxic component are present together.

A highly-effective catalyst for neutralizing nitrogen and carbon oxides has been developed at the Institute of Chemistry of Saratov State University. It meets all the requirements to catalysts of complex purification: high degree of transformation of both the components (80-90%), reducing NO in the presence of O_2 to N_2. The catalyst is pressed from nickel powder and aluminium oxide distinguished by high mechanic strength, good heat and mass transfer, low aerodynamic resistance, high termostability, that is of special significance while using it in engines.

The catalyst activity was estimated using the reaction of NO reducing with CO both in the O_2 presence (air being the reducing gas) and in the O_2-less medium (nitrogen or helium being one). The amount of the components was 0.5-1.7 %, simulating waste gases of gas turbine engines and car exhauste gases.

It has been shown that NO is reduced with CO to N_2 with a high selectivity (~80%) in the presence of O_2 at the volume rate of the reagents feeding up to 1500 g^{-1} within 350-500°C. It should be noted that the NO:CO ratio was varied from 0.25 to 1.5. The higher the NO content in the source gas, the lower the degree of CO conversion within the whole temperature range (100% at NO:CO=0.25-1.0; 88% at NO:CO=1.5). It reveals the competitative desorption of the reagents and the Langmoir-Hinshel-Wood mechanism of the reaction.

Performing the reaction in the absence of O_2 has shown that at NO:CO up to 1.1 the degree of NO conversion is 100% even at 400°C. Together with an increased (in comparison with the source one) amount of N_2, CO_2 (up to 1.3%), traces of N_2O, O_2, CO are present in waste gases.

Therefore, the results obtained show the scope for using the catalyst for clearing waste and exhaust gases from nitrogen and carbon oxides with their joint present.

CATALYTIC SYNTHESIS OF ACETIC ANHYDRIDE BY MEANS OF OXIDIZING ACETALDEHYDE

S.V.Borisova, E.V.Pletneva, and V.P.Sevostianov

Institute of Chemistry, Saratov State University
Saratov

In industry acetic anhydride (AAn) and acetic acid (AAc) are synthesized via liquid-phase oxidizing acetaldehyde (AAl) in the presence of copper and cobalt-containing homogeneous catalyst. The oxidation goes under the atmospheric pressure at 50-60^{0}C and is most profitable and ecologically pure, the AAh yield being 50-55 mass %.

The selectivity by AAh can be increased by means of changing the technological conditions and developing new catalytic systems which will be able to perform a directed synthesis of the reaction endproducts. However, the simplest way seems to be selecting of highly-effective promoting additives to the industrial system or changing the ligand composition of the catalyst.

We have studied the liquid-phase oxidation of AAl in the presence of the industrial catalytic system promoted with complex compounds of cobalt, nickel, rare-earth elements, palladium salts of different nature. The oxidation of AAl was carried out in a laboratory unit of the bubble type, being a 1:30 mock-up of the industrial apparatus. The reaction products were analyzed by means of the gas-liquid chromatography.

The optimal additive concentration providing the highest selectivity and productivity by AAn has been determined for each developed system. The influence of the composition of both solvent and impurities on the catalytic properties of the modified systems has been studied.

It has been established that in the presence of all the studied compositions a change in the direction of the AAl oxidatyion toward the AAn formation is observed.

Of rare-earth element compounds the highest promoting effect is characteristic for yttrium and lantanum acetates, they increase the AAn formation selectivity up to 70 mass %.

A spectrophotometric investigation of the catalytic systems has been carried out. On the base of the visual and UV spectra we have established the formation of some intermediate complexes involuing the catalyst components, the solvent, and AAl, their decomposition providing the promoting effect while AAl oxidizing to AAn. The correlation between the system's catalytic activity and the optical density has been found.

Suggestion concerning the mechanism of the modifying additives functioning in the oxidation are made, they are related to the redox transformations of the catalyst metals.

The cobald (III) acetylacetonate and palladium acetate-containing catalysts are proposed for using in industry.

USING ULTRADISPERSE METALS IN THE ORGANIC AND ECOLOGICAL CATALYSIS

A.V.Pletnev, N.V.Vorobiova,
E.V.Pletneva, and V.P.Sevostianov

Recent years much attention was paid to researching and developing new untrivial materials and catalyst-producing methods. A particular interest is attracted by catalysts based on ultradisperse systems (UDS).

Such an interest is related to the fundamental features of the UD state which is characterized by an unusual combination of electrical, magnetic, superconducting, optical, chemical, and other properties. The investigation of UDS takes place on the seam of some important scientific and practical fields such as physics, surface chemistry, colloidal chemistry, and chemistry of heterogeneous catalysis.

Catalysts containing UD powders of copper, nickel, iron, molybdenum have been developed. They were prepared by means of ultrasonic mixing UD metals and the carrier - γ-aluminium oxide together

UD metals were synthesized by means of different methods: molybdenum and copper - by the plasma overcondensation method; nickel and iron - by the electrical explosion of conductors. The sizes of UD metal particles were 200-300, 150-240, 100-200, 100-160 A for molybdenum, copper, iron and nickel respectively.

The catalyst activity was studied in flowing and impulse microcatalytic equipment in reactions of both the saturated and unsaturated hydrocarbons C_4-C_{10} and alkylbenzenes.

There were prepared and examined catalysts containing the only component Ni, or Mo, or Fe, as well as and their combinations such as Cu-Mo, Fe-Mo with differend metal concentrations.

The Fe-, Mo- and Fe-Mo catalysts were shown to be polyfunctional and to catalize hydrocracking, isomerization and cyclization reactions of the hydrocarbons C_6-C_{10}. There was determined the influence of the metal nature, its concentration, the catalyst activation method on the activity and selectivity in different transformation directions.

The investigation of the Fe-Mo catalysts activity in the oxidizing dehydrogenation of alkylbenzenes was of particular interest. The ethylbenzene and isopropylenbenzene conversions were carried out at the atmospheric pressure and at 400-500^{0}C using varying the injection rate and the component composition of the reaction mixture. The optimal conditions for the styrol synthesis by means of oxidizing dehydrogenation of ethylbenzene have been determined. The selectivity of the styrol formation at 400-440^{0}C, on the catalyst containg 5% Fe- 5% Mo/γAl_2O_3, at the ethylbenzene conversion being more than 82% was 60-80%. A correlation between the catalyst activity and the Fe-, Mo-UD-particles grade was established.

The catalysts containing Cu and Fe UD-powders were examined for the utilization in solving ecological problems. These catalysts were tested in the process of industrial waste gases purification from carbon (II) oxide and trichloroethylene. When waste gases containing 0.5·10 vol. % of CO, their oxidation degree was 60-95 % at 80-120^{0}C and 100% at temperatures above 120^{0}C.

The trichloroethylene oxidation was studied in the presence of catalysts containing 8% Cu, 8% Fe or 16% Cu. In the first case the conversion degree was determined to be 45-60 vol.% al 400-500^{0}C. In the second case it was 60-80 %. These results indicate perspectives of the UD-metals utilization in catalytic reactions of hydrocarbons and in the ecological catalysis.

CONTENT

Part I

ORAL PRESENTATIONS

OP-15 Suk Bong Hong
Korea Institute of Science and Technology, Korea
LOCATION OF Tb(III) IONS IN Na-Y ZEOLITE DETERMINED BY LUMINESCENCE SPECTROSCOPY 5

OP-5 Seung-Doo Park, Ji-Hoon Jung*, Suk-In Hong
Korea University, Korea
*Hanseo University, Korea
SELECTIVE OXIDATION USING CATALYTIC ELECTRODE SUPPORTED BY SOLID ELECTROLYTE 7

OP-11 Kyung-Byung Yoon
Sogang University, Seoul, Korea
IONIC CLUSTERS OF ALKALI METALS WITHIN ZEOLITES 9

OP-18 Jeong-Kyu Lee, Ho-Taek Lee and Hyun-Ku Rhee
Seoul National University, Korea
ISOMERIZATION OF C_5/C_6 PARAFFINS OVER PLATINUM LOADED ZEOLITES 11

OP-17 Jong-Sung Yu and Larry Kevan*
Han Nam University, Taejon, Korea
*University of Houston, Houston, Texas, USA
ELECTRON SPIN RESONANCE ANALYSIS OF PARAMAGNETIC Pd (I) SPECIES IN Pd(II)-EXCHANGED H-Rho ZEOLITE 13

OP-4 Sun Hee Choi and Jae Sung Lee
Pohang University of Science and Technology, Pohang, Korea XAFS CHARACTERIZATION OF SUPPORTED $PdCl_2$-$CuCl_2$ CATALYSTS FOR CO OXIDATION 15

OP-16 Son-Ki Ihm and Jin-Ho Lee*
Korea Advanced Institute of Science and Technology, Taejon, Korea
*Chungbuk National University, Cheongju, Korea
CHARACTERISTICS OF METALLIC IRON IN Y-ZEOLITE CATALYST REDUCED BY HYDROGEN ATOM BEAMS 17

OP-25 Jong Rack Sohn and Man Young Park
Kyungpook National University, Taegu, Korea
ETHYLENE DIMERIZATION AND POLYMERIZATION OVER TRANSITION METAL-EXCHANGED MONTMORILLONITE CATALYSTS 19

OP-19 Sang-Eon Park
Korea Research Institute of Chemical Technology, Taejon, Korea

SELECTIVE CATALYTIC REDUCTION OF NO OVER METAL OXIDES INCORPERATED WITH ZEOLITES 21

OP-6 Chong Soo Han
Chonnam National University, Kwangju, Korea
I-V CHARACTERISTICS OF ZnO-ZnO CONTACT DURING OXYGEN ADSORPTION 23

OP-21 A.S. Belyi
Omsk Branch of Boreskov Institute of Catalysis SB RAS, Omsk, Russia
NEW NOTIONS OF ACTIVE SURFACE COMPOSITION OF REFORMING CATALYSTS 25

OP-7 V.A. Chumachenko, L.N. Bobrova*, A.S. Noskov*
Katalyzator Company, Novosibirsk , Russia
*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
UNSTEADY-STATE TECHNOLOGIES FOR CATALYTIC DETOXICATION OF GAS WASTES 27

OP-20 V.K. Duplyakin, G.A. Urzhuntsev
Omsk Branch of Boreskov Institute of Catalysis SB RAS, Omsk, Russia
NEW CATALYSTS FOR ENVIRONMENTALY FRIENDLY FUELS PRODUCTION 29

OP-10 K.G. Ione
Scientific Engineering Center "Zeosit", Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
THE INVESTIGATION AND DEVELOPMENT OF ENVIRONMENTALLY FREINDLY PROCESSES ON ZEOLITE CATALYSTS 31

OP-28 Z.R. Ismagilov, R.A. Shkrabina, N.A. Koryabkina
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
DEVELOPMENT OF NEW TECHNOLOGY FOR PRODUCTION OF ALUMINA SUPPORTS 33

OP-2 B.N. Kuznetsov
Institute of Chemistry of Natural Organic Materials SB RAS, Krasnoyarsk, Russia
CATALYST APPLICATION IN PRODUCING OF ORGANIC COMPOUNDS FROM PLANT BIOMASS 35

OP-30 V.A. Likholobov
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
DESIGN OF CARBON-CARBONACEOUS COMPOSITES FOR CATALYTIC AND ADSORPTIVE TECHNOLOGIES TO ABATE ENVIRONMENTAL DAMAGE 38

OP-29 I.A.Makaryan, S.M.Baturin, P.E.Matkovsky, V.I.Savchenko
Institute of Chemical Physics in Chernogolovka, Russia
NEW COMMERCIAL TECHNOLOGIES ON THE BASIS OF FUNDAMENTAL RESEARHES ON CATALYSIS WORKED OUT AT THE INSTITUTE OF CHEMICAL PHYSICS IN CHERNOGOLOVKA OF RUSSIAN ACADEMY OF SCIENCES 39

OP-8 V.A. Makhlin, B.N. Okunev

State Research Centre of Russian Federation, Karpov Institute of Physical Chemistry, Mocsow, Russia
AN AUTOTHERMAL REGIME OF CATALYTIC REACTOR FOR WASTE GAS CLEANING 41

OP-26 K.I. Matveev, E.G. Zhizhina, V.F. Odyakov, N.S. Kotsarenko, V.P. Shmachkova
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
NEW CATALYTIC METHODS FOR SYNTHESIS OF VITAMINS OF K FAMILY: VITAMINS K_3, K_4 AND VIKASOL 43

OP-22 N.M. Ostrovskii, N.M. Bukhavtsova
Omsk Branch of Boreskov Institute of Catalysis SB RAS, Omsk , Russia
CATALYTIC REACTIONS ACCOMPANIED BY CAPILLARY CONDENSATION 45

OP-1 V.N. Parmon
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
HORIZONS OF CATALYSIS IN ENERGETICS OF THE FUTURE 47

OP-9 N.M.Popova, A.K. Umbetkaliev, K. Dosumov and N.A. Antonova
Institute of Organic Catalysis and Electrochemistry, National Academy of Sciences of Republic of Kazakstan, Almaty, Kazakstan
INTERACTION OF SO_2 WITH O_2 OVER MIXED Pt, Pd; Pt-Pd and Pt-Ru CATALYSTS OF OXIDATION AND COMBINED TREATMENT OF AUTOMOBILE EXHAUST GASES 49

OP-12 B. V. Romanovsky and A. G.Gabrielov
Lomonosov Moscow State University, Moscow, Russia
ZEOLITE-ENCAPSULATED METALLOCOMPLEXES AS NANOSCALE MATERIALS 51

OP-23 A.Ya. Rozovskii
Topchiev Institite of Petrochemical Synthesis, Moscow, Russia
THE PROBLEMS OF NATURAL GAS PROCESSING INTO PETROCHEMICALS AND FUEL 53

OP-24 O.N. Temkin, L.G. Bruk
Lomonosov State Academy of Fine Chemical Technology, Moscow, Russia
NEW TRENDS AND RESULTS IN CARBONYLATION OF ALKYNES..54

OP-27 G.A. Tolstikov
Institute of Organic Chemistry SB RAS, Novosibirsk, Russia
METAL-COMPLEX CATALYSIS IN THE SYNTHESIS OF INSECT SEX PHEROMONES AND JUVENOIDS 56

OP-14 K. I. Zamaraev and John M. Thomas*
Boreskov Institute of Catalysis SB RAS , Novosibirsk, Russia
*Royal Institution of Great Britain
REACTION PATHWAYS, KEY INTERMEDIATES AND PORE CONFINEMENT EFFECTS IN DEHYDRATION OF BUTANOLS OVER H-ZSM-5 ZEOLITES AND AMORPHOUS ALUMOSILICATE 57

OP-13 G.M. Zhidomorov, I.V. Yudanov, N.A. Kachurovskaya
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

QUANTUM CHEMICAL TREATMENT OF ACTIVE SITES IN ZEOLITE 59

POSTER PRESENTATIONS

ZEOLITE CATALYSIS

PP-1 A.V. Abramova, E.V. Slivinsky, B.K. Nefedov, Yu.Ya. Goldfarb, E.K. Trusova
Topchiev Institute of Petrochemical Synthesis, Moscow
CATALYSTS ON BASE OF ULTRASTABLE ZEOLITES FOR OIL CHEMISTRY 63

PP-2 L.Yu. Dolgikh, N.I. Ilchenko, N.V. Pavlenko
L.V. Pisarzhevskij Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Kiev
RELATIONSHIP BETWEEN PHYSICO-CHEMICAL AND CATALYTIC PROPERTIES OF ZEOLITES OF DIFFERENT STRUCTURAL TYPES IN THE ETHENE-TO-HIGHER HYDROCARBONS CONVERSION 65

PP-3 V.P. Doronin, V.A. Drozdov. T.P. Sorokina, M.D. Smolikov, T.V. Kireeva
Omsk Department of Boreskov Institute of Catalysis SB RAS, Omsk
MICROPOROSITY OF KBaL ZEOLITE, Pt LOCALIZATION AND CATALYTICAL PROPERTIES 67

PP-4 E.E. Knyazeva, G.M. Telbiz, N.F. Meged
L.V. Pisarzhevskij Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Kiev
PARAFFIN CONVERSION OVER MATALCONTAINING PENTASIL ZEOLITES 69

PP-5 Yu.N. Kochkin, N.V. Pavlenko
L.V. Pisarzhevskij Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Kiev
EFFECT OF ACIDITY ON THE CATALYTIC ACTIVITY OF ACID ZEOLITES FOR THE SYNTHESIS OF ETBE 71

PP-6 S.N. Orlik, V.L. Struzhko
L.V. Pisarzhevskij Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Kiev
REDUCTION OF NITROGEN OXIDES BY C_1, C_3 - C_4 - HYDROCARBONS IN OXIDIZING ATMOSPHERE ON METAL EXCHANGED ZEOLITES 73

PP-7 V.N. Romannikov
Boreskov Institute of Catalysis SB RAS, Novosibirsk
BASE CATALYSIS ON ZEOLITES IN THE FORMALDEHYDE-DIMETHYLAMINE TRASFORMATIONS 75

PP-8 V.A. Sadykov, G.A. Alikina, R.V. Bunina, S.L. Baron, S.N. Pavlova , S.A. Veniaminov, A.Ya. Rozovskii*, V.F. Tretyakov*, V.V. Lunin**, V.A. Matyshak***
Boreskov Institute of Catalysis SB RAS, Novosibirsk

*Topchiev Institute of Petrochemical Synthesis, Moscow
**Chemical Department of the Lomonosov Moscow State University
***Semenov Institite of Chemical Physics RAS, Moscow
ZEOLITE-BASED CATALYSTS FOR SELECTIVE REDUCTION OF NITROGEN OXIDES BY LIGHT HYDROCARBONS UNDER OXYGEN EXCESS 77

PP-9 E.A. Stepanova, A. Rat'ko
Institute of General and Inorganic Chemistry, Belarus Academy of Sciences, Minsk
ZEOLITE-CONTAINING CATALYSTS ON THE BASIS OF HIGH SILICA HTsVM ZEOLITE AND LAYER-PILLARED MONTMORILLONITE 80

PP-10 N.A. Zakarina, G.V. Artyukhina, L.D. Volkova
D.V. Sokolsky Institute of Organic Catalysis & Electrochemistry of National Academy of Sciences of the Republic of Kazakhstan, Almaty
HETEROPOLY ACIDS AS ZEOLITE-TYPE MODIFIERS OF CATALYSTS SURFACES 82

PP-11 G.D. Zakumbaeva, Sh.A. Gilmundinov, N.Ph. Toktabaeva, G.N. Kotova, D.T. Nurgalieva, R.I. Egizbaeva
D.V. Sokolsky Institute of Organic Catalysis & Electrochemistry of National Academy of Sciences of the Republic of Kazakhstan, Almaty
SELECTIVE REDUCTION OF NITRIC OXIDE BY PROPYLENE ON BLOCK ZEOLITE-, Pt- AND Pd-CONTAINING CATALYSTS 84

CATALYSIS FOR ENVIRONMENTAL PROTECTION

PP-12 S.N. Bukeikhanova, O.E. Lebedeva
Al-Faraby Kazakh State National University, Almaty, Republic of Kazakhstan
UTILIZATION OF ELECTROTHERMOPHOSPHORUS SLAG AS COMPONENTS OF CATALYSTS 89

PP-13 E.D. Chekurovskaya, L.G. Zubanova, R.I. Kuzmina, T.M. Tarasova and V.P. Sevostianov
Saratov State University
Scientific Research Institute of Chemistry, Saratov
METALCOMPLEX-SUPPORTED CATALYSTS FOR THE CONVERSION OF HYDROCARBONS AND THEIR DERIVATIVES 91

PP-14 R.I. Kuzmina, L.G. Zubanova, E.D. Chekurovskaya, T.M. Tarasova and V.P. Sevostianov
Scientific Research Institute of Chemistry, Saratov
Saratov State University
CATALYTIC PURIFICATION OF WASTE GASES FROM HYDROCARBONS AND THEIR O-, N-, AND CL-DERIVATIVES 93

PP-15 S.G. Shcheglova, E.V. Pletneva, R.I. Kuzmina, M.R. Kakhiani, and V.P. Sevostianov
Saratov State University
Scientific Research Institute of Chemistry, Saratov

CATALYTIC PURIFICATION OF WASTE GASES FROM CARBON AND NITROGEN OXIDES 95

PP-16 S.Y. Molina, L.P. Mukhina, and V.P. Sevostianov
Saratov State University
A CATALYST FOR NEUTRALIZING NITROGEN AND CARBON OXIDES IN WASTE GASES 97

PP-17 S.V. Borisova, E.V. Pletneva, and V.P. Sevostianov
Scientific Research Institute of Chemistry, Saratov
Saratov State University
CATALYTIC SYNTHESIS OF ACETIC ANHYDRIDE BY MEANS OF OXIDIZING ACETALDEHYDE 99

PP-18 A.V. Pletnev, N.V. Vorobiova, E.V. Pletneva, and V.P. Sevostianov
Scientific Research Institute of Chemistry, Saratov
Saratov State University
USING ULTRADISPERSE METALS IN THE ORGANIC AND ECOLOGICAL CATALYSIS 101

Part II

PP-19 Y.A. Demyanenko, A.V. Sachivco, V.P. Tverdokhlebov, V.A. Fejdorov
State Thechnology Academy, Krasnoyarsk
ISC Achinsk Refinery, Achinsk
A NEW ENVIRONMENTAL SAFE CATALYST FOR USE IN HIGH TEMPERATURE PROCESS, DERIVED FROM FERROCEN 103

PP-20 A.I. Dzhumabaeva, A.N. Sartaeva, K.A. Zhubanov
Al-Faraby Kazakh State National University, Almaty, Republic of Kazakhstan
INFLUENCE OF RARE EARTH OXIDES ON ACTIVITY OF SUPPORTED ALUMINA-CHROMIUM CATALYSTS OF SULFUR DIOXIDE OXIDATION 104

PP-21 V.N. Efremov, G.M. Tesakova, N.K. Ikonnikov, E.Z. Golosman
AOOT Novomoskovsk Institute of Nitrogen Industry, Novomoskovsk, Russia
COMBINED CATALYTIC PURIFICATION OF WASTE GASES IN NITRIC ACID PRODUCTION FROM NITRIC OXIDES, CARBON AND AMMONIA 106

PP-22 N.R. Gazimzyanov , V.I. Kvashonkin
Elektrogorsk Institute of Petroleum Refining, Elektrogorsk
SELECTIVE WATER EXTRACTION OF ACTIVE COMPONENTS FROM HYDROTREATING CATALYSTS AS AN ESTIMATION METHOD OF THEIR CATALYTIC PROPERTIES IN OXIDE FORM 108

PP-23 M.A. Kipnis, L.G. Danilova, A.Yu. Shashkov, V.F. Dovganyuk, M.A. Porublev, Yu.N. Zelentzov
Elektrogorsk Institute of Petroleum Refining, Elektrogorsk
Angarsk Petrochemical Company, Angarsk
ALUMINA AND CARBON CARRIERS FOR PALLADIUM "EGGSHELL" CATALYSTS 110

PP-24 M.A. Kipnis, V.S. Agaronov, N.R. Gazimzyanov
Elektrogorsk Institute of Petroleum Refining, Elektrogorsk
THE NEW Ni-Mo/ Al_2O_3 CATALYST FOR HYDROGENATION OF ORGANIC SULPHUR COMPOUNDS IN NATURAL AND REFINERY GASES 112

PP-25 M.A. Kipnis, A.Yu. Kalinevich, V.F. Dovganyuk, L.G. Danilova, M.A. Porublev, Yu.N. Zelentzov
Elektrogorsk Institute of Petroleum Refining, Elektrogorsk
Angarsk Petrochemical Company, Angarsk
THE NEW CATALYSTS FOR HYDROGEN, AMMONIA, AND SYNGAS PRODUCTION 114

PP-26 T.V. Turkova, M.A. Kipnis, A.Yu. Shashkov
Elektrogorsk Institute of Petroleum Refining, Elektrogorsk
LOW PALLADIUM CONTENT "EGGSHELL" CATALYSTS 116

PP-27 O.M. Ilinitch and Yu. S. Vetchinova
Boreskov Institute of Catalysis SB RAS, Novosibirsk
LIQUID PHASE OXIDATIVE DETOXICATION OF SULFIDES IN CATALYTIC MEMBRANE REACTOR 118

PP-28 N.N. Kundo, W.E. Myzlish, G.A. Faddeenkova, T.L. Stuchinskaya
Boreskov Institute of Catalysis SB RAS, Novosibirsk
POTENTIALITIES OF PHTHALOGYANINE CATALYSTS FOR DESULPHURIZATION OF GASES AND SOLUTIONS 121

PP-29 V.F. Lyakhova, N.N. Sazonova, A.V. Simakov, G.B. Barannik, T.A. Nikoro, O.V. Komova, Z.R. Ismagilov, H. Veringa*
Boreskov Institute of Catalysis SB RAS, Novosibirsk
*Energy Research Foundation, ECN, Petten, The Netherlands
THE CATALYSTS FOR DIRECT OXIDATION OF AMMONIA INTO MOLECULAR NITROGEN 123

PP-30 M.G. Martsenyuk-Kukharuk, V.A. Ostapyuk, S.N. Orlik, A.D. Tereshchenko, I.F.Mironyuk
L.V. Pisarzhevskij Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Kiev
SUPPORTED BLOCK CATALYSTS FOR SCR PROCESS OF NITROGEN OXIDES 125

PP-31 A.Y. Mil'chenko, T.A. Kremleva*, A.Y. Yuffa*
Institute of North Assimilation Problems SB RAS, Tyumen
*Tyumen State University, Tyumen
NOVEL ECOLOGICALLY PURE METHOD OF PHENOLIC ALCOHOLS PRODUCTION - ALKOXYLATION OF PHENOL WITH FORMALDEHYDE CATALYZED BY SILICA BASED SULPHOCATIONITES 127

PP-32 Z.P. Pai and A. Ermakova
Boreskov Institute of Catalysis SB RAS, Novosibirsk
CATALYTIC PROCESSING OF H_2S CONTAINING GASES OF OIL-REFINING AND COKE-CHEMISRTY 129

PP-33 Z.P. Pai and A. Yermakova

Boreskov Institute of Catalysis SB RAS, Novosibirsk
LIQUID CATALYTIC PURIFICATION OF GASES FROM SO_x AND NO_x 131

PP-34 A.N. Pestryakov, E.N. Yurchenko*, A.E. Feofilov*, O.V. Pestryakova
Tomsk State Academy of Civil Engineering, Tomsk
*Russian Scientific Center "Applied Chemistry", St. Petersburg
CATALYSTS BASED ON FOAM METALS FOR EXHAUST GAS PURIFICATION 133

PP-35 N.N. Sazonova, L.T. Tsykoza, A.V. Simakov, G.B. Barannik
Boreskov Institute of Catalysis SB RAS, Novosibirsk
WO_3 AND Nb_2O_5 ADDITIONS FOR MONITORING OF V_2O_5 - TiO_2 CATALYST RESISTANCE TO SULPHUR OXIDE POISONING 135

PP-36 R.A. Shkrabina, A.A. Kirtchanov, N.A. Koryabkina, H. Veringa*, P. Pex*, Z.R. Ismagilov
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
*ECN, Petten, The Netherlands
POROUS ALUMINA CERAMICS AS A SUPPORT OF CATALYSTS AND MEMBRANES 137

P-37 A.V. Simakov, N.N. Sazonova, E.V. Rebrov*, O.V. Komova, G.B. Barannik
Boreskov Institute of Catalysis SB RAS, Novosibirsk
*State University, Novosibirsk
REACTION KINETICS AND DYNAMICS OF NO ADSORBED FORMS ON Cu-ZSM-5 AT THE SELECTIVE REDUCTION OF NO BY PROPANE 139

PP-38 A.D. Simonov, N.A.Yasykov, E.I. Yepifantseva
Boreskov Institute of Catalysis SB RAS, Novosibirsk
CATALYTIC PROCESSING OF SEDIMENTS AND PURIFICATION OF EFFLUENTS 141

CATALYSIS FOR ORGANIC SYNTHESIS AND PETROCHEMISTRY

PP-39 V.N. Antciferov, A.M. Makarov, I.V. Filimonova, M.U. Kalashnikova
Republican Engineering -Technical Centre of Powder Metallurgy, Perm
CATALYTIC SYSTEMS FOR THE ABATEMENT OF CARBON MONOXIDE AND UNBURNED HYDROCARBONS 145

PP-40 V.N. Antciferov, A.M. Makarov, I.V. Filimonova, M.U. Kalashnikova
Republican Engineering -Technical Centre of Powder Metallurgy, Perm
CATALYSTS BASED ON HIGHLY POROUS CELLULAR MATERIALS (HPCM) 147

PP-41 M.A. Arellano, O.N. Temkin, N.Kh. Allakhverdova* and I.V. Cherepnov
Lomonosov Academy of Fine Chemical Technology, Moscow
*Azizbekov Azeri Technological University, Baku, Azerbaidzhan
HETEROGENEOUS GASE PHASE CATALYTIC OXIDATION OF ETHANOL TO ACETIC ACID OVER THE Sn-Mo OXIDE CATALYST 149

PP-42 Yu.V. Belokopytov
L.V. Pisarzhevskij Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Kiev
THE CATALYTIC TREATMENT AND DISPOSAL OF CHLOROORGANIC WASTE 151

PP-43 A.G. Dedov, M.V. Vyshneckai, M.N. Kartasheva, L.E. Tskhai, A.P. Poliokov, E.M. Rudik
I.M. Gubkin State Academy of Oil and Gaz, Moscow
THE FLUORINE-CONTAINING CATALYSTS IN OXIDATIVE-COUPLING OF METHANE 153

PP-44 Ya.A. Dorfman, G.S. Polimbetova, L.V. Levina and R.R. Abdreimova
D.V. Sokolsky Institute of Organic Catalysis & Electrochemistry of National Academy of Sciences of the Republic of Kazakhstan, Almaty
NOVEL OXIDATIVE ALKOXYLATION AND AMINATION OF PH$_3$ AND P$_4$ CATALYZED BY Cu (II) CELLULOSE ANCHORED COMPLEXES 155

PP-45 M.V. Dorogov, E.M. Alov, Y.A. Moskvichev, V.V. Plahtinskii
Yaroslavl State Technical University, Yaroslavl.
CATALYTIC HYDROGENATION OF NITRO- AND DINITROPOLYAROMATIC SUBSTANCES WITH DIFFERENT FOOT-PATH GROUPS - THE WAY OF SYNTHESIS OF MONOMERS FOR THERMOSTABLE AND THERMOPLASTIC COMPOSITIONS 157

PP-46 A.V. Fionov, E.V. Lunina
Lomonosov Moscow State University, Moscow
CONTROL OF ACCEPTOR AND DONOR PROPERTIES OF ALUMINA BY MEANS OF TREATMENT BY ACIDS AND BASES 159

PP-47 S.L. Hladiy, M.K. Starchevsky, Yu.A. Pazdersky, M.N. Vargaftic* and I.I. Moiseev*
"Syntez" Research Institute, Borislav, Ukraine
*N.S. Kurnakov Instutute of General & Inorganic Chemistry RAS, Mocsow
GIANT PALLADIUM CLUSTERS IN SOFT OXIDATION OF ETHANOL 161

PP-48 O.M. Ilinitch, N.E. Kim*, B.M. Khlebnikov* and V.A. Likholobov
Boreskov Institute of Catalysis SB RAS, Novosibirsk
*Research Institute of Chemical Technology, Novosibirsk
POLY(PHENYLENE OXIDES) - CATALYTIC SYNTHESIS AND MEMBRANE APPLICATION 163

PP-49 A.S. Ivanova, E.M. Al'kaeva, T.V. Andrushkevich, V.M. Mastikhin, E.A. Paukshtis
Boreskov Institute of Catalysis SB RAS, Novosibirsk
ACIDITY EFFECT ON ALUMOSILICATE CATALYTIC PERFORMANCE AT β-PICOLINE SYNTHESIS VIA ACROLEIN CONDENSATION WITH AMMONIA 165

PP-50 S.R. Ivanova, K.S. Minsker
Bashkirian State University, Ufa

ABOUT THE CONNECTION OF THE EFFECTIVENESS OF ELECTROPHILIC CATALYSTS OF SEMIFUNCTIONAL ACTIVITY WITH THEIR ACID STRENGTH MEASURE 167

PP-51 Y.G. Kim, V.D. Stytsenko*, V.A. Khavkin*, J.S. Lee
Research Center for Catalysis and Catalytic Technology, Pohang, Korea
*Topchiev Institute of Petrochemical Synthesis RAS, Moscow
**All-Russian Research Institute of Petroleum Refining, Moscow
HYDROCONVERSION OF AROMATIC HYDROCARBONS OVER NEW TRIMETALLIC CATALYSTS.. 169

PP-52 A.V. Kondratiev, V.S. Markevich
Joint-stock company "All-Russian Research Institute of Organic Synthesis", Novokuibyshevsk
POTASSIUM ACETATE - CATALYST FOR ACID KETONIZATION... 170

PP-53 A.V. Kravtsov, E.D. Ivanchina and T.V. Kravtsova
Polytechnic University, Tomsk
COMPUTER PREDICTION OF Pt-CATALYST ACTIVITY OIL REFINING 171

PP-54 V.A. Kreuchkov, D.I. Slovetsky, V.T. Popov, A.V. Prokophjev, E.J. Bogolepova, T.S. Vinogradova, E.V. Slivinsky, G.S. Yeurjev *
Topchiev Institute of Petrochemical Synthesis RAS, Moscow
*Boreskov Institute of Catalysis SB RAS, Novosibirsk
THE NEW CATALYSTS FOR METATHESIS REACTIONS OF OLEFINS AND SUBSTITUTED OLEFINS WITH FUNCTIONALY GROUPS 173

PP-55 S.Yu. Kuz'mitskaya, N.A. Vasilyeva
Boreskov Institute of Catalysis SB RAS, Novosibirsk
EFFECT OF MODIFIED MAGNESIUM OXIDE ON N-BUTANE HIGH-TEMPERATURE DECOMPOSITION 175

PP-56 L.V. Manuilova, N.D. Parshukova and T.S. Sukhareva
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
CATALYTIC PRODUCTION OF 4-METHYLTHIAZOLE...................... 176

PP-57 A.V. Mashkina, Yu.A. Savostin*
Boreskov Institute of Catalysis SB RAS, Novosibirsk
"KATALYZATOR Ltd", Novosibirsk
CATALYTIC SYNTHESIS OF ORGANIC SULFUR COMPOUNDS 178

PP-58 S.V. Mezcheryakov, K.D. Korenev, V.A. Zavorothny
I.M. Gubkin State Academy of Oil and Gaz, Moscow
THE MINERAL-ORGANIC SULFOCATIONITES-CATALYSTS FOR THE OIL PERFORMING AND OIL CHEMISTRY PROCESSES.......... 180

PP-59 K.S. Minsker, S.R. Ivanova
Bashkirian State University, Ufa
CATALYST HYDROCARBONS PYROLISIS ON CHLORIDS OF ALKALINE EARTH METALLS 182

PP-60 K.Ya. Motovilov*, K.I. Matveev, E.G. Zhizhina, V.F. Odyakov, E.V. Gusamova*
Novosibirsk State Agriculture University, Novosibirsk
Boreskov Institute of Catalysis SB RAS, Novosibirsk

EFFICIENCY OF VITAMIN K (VIKASOL) PRODUCED VIA "VIKASIB" TECHNOLOGY AT POULTRY NUTRITION 184

PP-61 E.A. Mushina, I.F. Gavrilenko, Yu.Ya. Podolsky, V.M. Frolov, B.A. Krenzel, I.N. Borodina, M.S. Gabutdinov*, C.B. Medvedeva*, A.Z. Vakhbreit*, S.A. Solodyankin*, V.F. Cherevin*
Topchiev Institute of Petrochemical Synthesis RAS, Moscow
*Stock Company "Kazanorgsintez", Kazan
BINUCLEAR METAL COMPLEX CATALYSTS IN POLYMERIZATION PROCESSES 185

PP-62 V.N. Postnov, A.G. Novikov
St. Petersburg State University, St. Petersburg
SYNTHESIS OF SUBSTRATUM-ORIENTED HETEROGENEOUS CATALYSTS BASED ON SILICA AND INVESTIGATION OF THEIR PROPERTIES 187

PP-63 I.V. Sablukova, B.S. Strelchik, E.Z. Golosman, O.V. Lysova, V.A. Vekslina
AO VNIIOS NK, Novokuibyshevsk, Russia
AO NIAP, Novomoskovsk, Russia
Aerocosmic Iniversity, Samara, Russia
COPPER CATALYSTS FOR THE DEHYDROGENATION REACTION OF THE ETHANOL TO THE ETHYL ACETATE 189

PP-64 U.M. Schindler, A.G. Sarmuzina, G.Sh. Tlepieva
Al-Pharaby Kazakh State National University, Almaty, Republic of Kazakhstan
State Research-and-Production Association of Industrial Ecology, "Kazmekhanobr", Almaty, Republic of Kazakhstan
COMPLEX EXPLOITING OF SORBABLE CATALYTIC TECHNOLOGIES OF GAS-WATER 190

PP-65 V.A. Semikolenov
Boreskov Institute of Catalysis SB RAS, Novosibirsk
CATALYTIC SYNTHESIS OF 1-ETHYL-2-AMINOMETHYLPIRROLYDINE FOR THE PRODUCTION OF PHARMACEUTICALS 192

PP-66 F.K. Smidt, Kim En Hwa and K.P. Zhdanova
Irkutsk State University, Irkutsk
PHYSICO-CHEMICAL AND CATALYTIC PROPERTIES OF ALUMOMOLYBDENUM CATALYSTS 194

PP-67 E.F. Stefoglo, O.P. Zhukova
Institute of Carbon, Kemerovo
ANESTHESINE CATALYTIC PRODUCTION VIA LIQUID-PHASE HYDROGENATION OF ETHYL ETHER OF PARA-NITROBENZOIC ACID OVER Pd/C 196

PP-68 A.R. Suzdorf, S.V. Morozov*, A.M. Kovalev, A.G. Anshits
Institute of Chemistry of Natural Organic Materials SB RAS, Krasnoyarsk
*Institute of Organic Chemistry SB RAS , Novosibirsk

HYDRODECHLORINATION OF CHLOROAROMATIC COMPOUNDS ON NICKEL CATALYSTS 198

PP-69 E.G. Zhizhina, A.P. Krysin*, V.F. Odyakov, K.I. Matveev
Boreskov Institute of Catalysis SB RAS, Novosibirsk
*Institute of Organic Chemistry SB RAS,Novosibirsk
CATALYTIC SYNTHESIS OF 1-NAPHTHYLACETIC ACID VIA CARBONYLATION OF 1-(CHLORMETHYL)NAPHTALENE IN THE PRESENCE OF Pd(O)-TRIPHENYLPHOSPHINE COMPLEX............. 200

Russian-Korean Seminar on Catalysis

Editor: Prof. V.A. Likholobov

The present abstracts underwent a rather mild editing process.
For this reason responsibility for all presentations rests with the authors.

Technical editors: T.V. Zamulina
E.L. Mikhailenko
Cover: E.E. Razgulina

Подписано в печать 05.05.95 Формат 60×84/16
Печ.л. 12,8 Заказ № 98 Тираж 150

Отпечатано на полиграфическом участке издательского отдела Института катализа
6300090, Новосибирск, пр. Ак. Лаврентьева. 5.

Russian-Korean Seminar on Catalysis
Novosibirsk, May 16-19, 1995

ABSTRACTS

PART II

Russian Academy of Sciences

Korea Science and
Engineering Foundation

BORESKOV INSTITUTE OF CATALYSIS
RUSSIA

Russian Academy of Sciences
Korea Science and Engineering Foundation
Scientific Council on Catalysis and its Industrial Use
of RAS and the Ministry of Science

RUSSIAN-KOREAN SEMINAR ON CATALYSIS
Novosibirsk, May 16-19, 1995

ABSTRACTS

(Part II)

Novosibirsk 1995
Russia

УДК 541.128

A NEW ENVIRONMENTAL SAFE CATALYST FOR USE IN HIGH TEMPERATURE PROCESS, DERIVED FROM FERROCEN

Y.A.Demyanenko*, A.V.Sachivco, V.P.Tverdokhlebov, V.A.Fejdorov

KRASNOYARSK STATE TECHNOLOGY ACADEMY, KRASNOYARSK
*JSC ACHINSK REFINERY, ACHINSK**

One of the ferrocen first uses was as an anti detonator for motor fuels. However use of ferrocen was limited in this situation due to the fact that when the temperature decreases the concentration of ferrocen also decreases thereby causing an unstable composition.

ФК-4* , which is derived from ferrocen, has good technical and economical properties. It has been used as an additive for petroleum. A concentration of 0.01% increases the octane number by 5-6 points and reduces emission of nitrogen oxide and carbon monoxide by 40-70%.

ФК-4 additive to diesel fuel in concentration 0,001% reduces smoky emisson by 60%. For comparison, «laprasol», which is used in USA reduces smoky emission by only 40%. Use of diesel fuels with ФК-4 additive will allow an increase in productivity of works in mines shattered areas and railway stations because the time for ventilation will be reduced. Both mentioned advantages of ФК-4 have patents protection.

Recently it test have shown that when ФК-4 is used as additive during the production of anodes for the aluminium industry, the amount of cancerogenic L-benzpyrene substance reduced is twice as much as before.

For detail investigation of physical-chemical properties of ФК-4 in different mediums was studied ФК-4 solubility in petroleums and organic solvents which are included in composition of petroleums, in different water solutions of electrolytes and its acid-alkali properties.

It has been determined that ФК-4 solubility in petroleum is considerably more then ferrocens solubility.ФК-4 solubility has little temperature dependence in range -35°C+35 °C and its solubility is additive value in mixture of organic solvents. Elec-trolytes additives in water and water organic solvents cause the ФК-4 content to weaken. If the quantity of organic components is increased the weakening effect is reduced.

Reduction-oxidation potential of ФК-4 cation ФК-4 system is reduced with increasing of concentration of electrolytes in solution.

It was revealed the approximation functions between this potential and salt background and non-water additives.

Acid-alkali properties of ФК-4 are expressed insignificant.

---

*ФК-4 - Ferrocenildimethilcarbinol

INFLUENCE OF RARE EARTH OXIDES ON ACTIVITY OF SUPPORTED ALUMINA-CHROMIUM CATALYSTS OF SULFUR DIOXIDE OXIDATION

A.I.Dzhumabaeva, A.N.Sartaeva, K.A.Zhubanov

Al-Faraby Kazakh State National University

Waste gases of the industrial enterprises containing the toxic sulfur compounds damage to the nature and the people health. The great number of the sulfuric gases being thrown out is the heating gases of the combustion of sulfur-containing fuel, black mineral oil and coal in the power engeneering and technological plants.

There are many methods for the waste industrial gases cleaning with the purposes of the sulfur dioxide removing. One of them is the catalytic oxidation of sulfur dioxide to sulfur trioxide with the following receipt of the sulfuric acid.

Many compounds are used for that process, for example the oxides of vanadium (V), chromium (III), alumina, copper and others. Besides that the compounds of rare earth elements are used as promotors too. The using of these compounds promotes not only the common catalytic activity but the thermal stability of the samples.

Our research is devoted to the results of the studing of the promotor influence of cerium, ittrium and scandium oxides on the activity and thermal stability of the supported alumina-chromium catalysts on diatomyte at the sulfur dioxide oxidation process. So we wanted to find optimal conditions of that process. The transformation degree of sulfur dioxide was taken as the measure of activity.

Synthesis of catalysts was carried out in by saturation of the mixture of diatomyte and alumina-rare earth oxides with the solutions of chromium acid.

The reaction was carried out in following conditions: concentrations of sulfur dioxide and oxygen in the initial gaseous mixture are 0.6 - 1.0 and 20.8% by volume accordingly, the common rate of gaseous mixture's feed is 2000 1/h.

As a result of our researches it was established that the promoting ability of rare earth compounds was different and depended on bearer's kind and the quantity and nature of the promotors.

The common fact for all investigated promotors is that activity gets through the maximum depending on quantity of promotors. So, the transformation degree of the sulfur dioxide on the catalysts with the ittrium oxide (III) is 90%, scandium oxide (III) - 92% and cerium dioxide (IV) - 89%. It's necessary to mark that the promoted catalysts with 10% chromium oxide have more activity than samples with contents of chromium oxide - 5 and 15%..

Thus, the optimal conditions of the sulfur dioxide oxidation process were found. And these catalysts may be recommended for using at the process of the oxidation of the low-concentrated sulfur dioxide.

COMBINED CATALYTIC PURIFICATION OF WASTE GASES IN NITRIC ACID PRODUCTION FROM NITRIC OXIDES, CARBON AND AMMONIA

V.N. Efremov, G.M. Tesakova, N.K. Ikonnikov, E.Z. Golosman

AOOT Novomoskovsk Institute of Nitrogen Industry, Novomoskovsk

Waste gases of nitric acid production contain up to 0,1-0,2 vol% of nitric oxides, 0,1--0,3 vol% of carbon monoxide and 0,007-0,18 vol% of ammonia. The main method for purification of waste gases from nitric oxides up to sanitary norms is the high-temperature catalytic reduction on alumino-palladium catalyst A K-2, ensuring the purification from nitric oxides. From scientific and technical points of view the problem of combined purification was solved by using developed nickel-copper cement-containing catalyst free of noble metals.

The waste-free process for production of nickel-copper catalyst HKO-2-3 as rings, tablets or extrudates based on chemical mixing has been developed. It is established that during catalyst synthesis the solid nickel-copper solution (alloy) is formed which shows the catalytic properties like those of platinum and causes the high catalytic activity as well as oxidation stability at high temperature. The catalyst reduction by hydrogen, hydrogen-containing gas and working gas containing nitric oxides, natural gas, hydrogen, oxygen, nitrogen has been studied. The reduction goes on most actively at 350 °C.

The catalyst activity was studied in a laboratory flow reactor over a temperature range of 100-800 °C and space velocity of 5000-50000 h^{-1}. During the reduction of nitric oxides by hydrogen the ignition temperature of the catalyst developed and contact AK-2 is 250 °C and breakthrough temperature (0,005 vol%) of nitric oxides are in the range of 170-180 °C. The ignition temperature of HKO-2-3 catalyst in reduction of nitric oxides by natural gas is 600-620 °C, that is somewhat higher in comparison with the similar AK-2 parameter (440-460 °C). Over the temperature range of 600-800 °C the catalytic activity of both catalysts is comparabe and the residual content of nitric oxides is 0,002-0,004 vol% which is below the sanitary norms.

The results most close to practice were obtained by use of working gas from turbine TT-3M. The tests were carried out at the space velocity of 42000 h^{-1} over a temperature range of 400-700 °C. At 460 °C the purification degree from carbon monoxide was 100%. The purification degree from nitric oxides varied from 38% at 400 °C to 85% at 700 °C. At 700 °C 100% purification from ammonia was achieved.

It was revealed that the prereduced catalyst shows the higher catalytic activity. The optimum natural gas/oxygen ratio was determined at which the maximal purification degree of waste gas from toxical components is achieved The laboratory investigations have shown that HKO-2-3 catalyst is resistant to oxidizing atmosphere at the temperatures up to 800 °C following which the activity does not change in fact.

The large-scale tests of HKO-2-3 catalyst were carried out in the catalytic purification unit of YK-7-71/76 plant at HAK «AZOT». For decreasing the ignition temperature the spent catalyst AK-2 was used as a frontal layer in a 0,15-0,25 ratio with the tested contact. At the reactor temperature of 700-730 °C HKO -2-3 catalyst ensured the purification from nitric oxides up to 0,001-0,004 vol%, carbon monoxide up to 0,003-0,005 and ammonia up to 0,001-0,003 vol%.

SELECTIVE WATER EXTRACTION OF ACTIVE COMPONENTS FROM HYDROTREATING CATALYSTS AS AN ESTIMATION METHOD OF THEIR CATALYTIC PROPERTIES IN OXIDE FORM

N.R.Gazimzyanov, V.I.Kvashonkin

Elektrogorsk institute of petroleum refining, Elektrogorsk

Surface analogue of heteropolymolibdate (HPM) is considered to be the oxide precursor of the active sulfide phase of hydrotreating catalysts. The water extractable phase of oxide Ni-Mo/Al_2O_3 (ANM) catalysts, as it has been shown, pertains to HPM and so the method of selective water extraction (SWE) can be used for the HPM determination and for the estimation of catalytic properties of ANM hydrotreating catalysts in oxide form.

In this report the experience of using SWE in the study of influence the preparation conditions on the phase composition and catalytic properties of ANM catalysts is summarised.

1. Influence of one step impregnation technique. Among the studied techniques (with ammonia, phosphoric acid (B) and by using $(NH_4)_4[NiMo_6(OH)_6O_{18}]$ (C)) the technique B is found to provide the most HPM formation. The catalyst via technique C has "shell" distribution of Mo and Ni within the carrier.

2. Influence of Ni and Mo content. By using the method of statistic design of an experiment the ANM catalysts were obtained varying the content of MoO_3 within 12-19 % and NiO within 3,5-5 % mass. The procedure of preparation involved the kneading Mo and Ni salts with alumina powder followed by peptization with nitric acid. Mo/Ni value is found to be constant for all extracts and the amounts of extracted Mo and Ni ($C^{Mo(Ni)}$) to be described by an equation of the following type:

$$C^{Mo(Ni)}=A_0+A_1*CM+A_2*CN,$$

where A_0, A_1, A_2 - coefficients of the regression, CM and CN - Mo and Ni contents. It's interesting to note that oxygen chemisorption is described by an equation of the same type . The HPM amount determined by SWE correlated with catalytic activity in thiophen hydrogenolysis, with the exeption of the samples with the highest HPM contetnt. This fact is probably connected with unoptimal presulfiding conditions.

3. Influence of alumina phase composition. The catalyst were prepared by kneading technique with various alumina modifications: pseudoboehmite, boehmite, γ-, θ-, α-Al_2O_3. The using of pseudoboehmite provides obtaining the catalyst with the highest mechanical strength, however the lowest HPM formation is observed in this case. The highest HPM content is observed for the catalyst with γ-Al_2O_3.

With the results obtained, the new ANM catalyst has been developed: ГО-30-7 modifications (ГО-30-8, ГОЭ-1) and impregnated КПС-like catalyst Г-1. The representative comparative characteristics of the ANM catalysts are shown in a table:

Comparative characteristics of the ANM catalysts

Catalyst	Compos., %		Diameter, mm	Stren. kg/mm	Amount of Ni extr., mole*10^{-5}/g cat.	Relat. act.,* %
	MoO_3	NiO				
ГО-30-7	18,0	4,5	2,0	1,2	6,04	107
ГО-30-8	18,0	4,5	1,6	1,4	4,10	105
ГОЭ-1	17,0	4,0	2,0	1,2	8,38	111
КПС-16Н	15,0	5,0	2,8	1,1	5,18	108
Г-1	15,0	4,0	2,8	1,2	9,44	114

* - standard procedure - ОСТ 38.01130-77: feed - diesel fraction with 1 % sulphur content; T - 380°C; P - 2,1 MPa; LHSV - 6 h^{-1}.

A very important advantage of catalyst ГОЭ-1, besides its high activity, is the preparation technique, which excludes formation of the toxic exhausts during calcination. High mechanical strength of catalyst ГО-30-8 allows to obtain extrudates with a diameter less than 2 mm. Catalyst Г-1, as catalyst КПС-16Н, has "shell" Mo and Ni distribution. Additionally, it is more active than catalyst КПС-16Н.

Thus, the proposed SWE method can be siutable for solving of the following tasks:

- for estimation of HPM content to find out optimal technique and conditions in catalyst preparation;
- for choosing optimal presulfiding conditions;
- for the controling catalyst production.

ALUMINA AND CARBON CARRIERS FOR PALLADIUM "EGGSHELL" CATALYSTS

**M.A.Kipnis, L.G.Danilova, A.Yu.Shashkov, V.F.Dovganyuk,
M.A.Porublev, Yu.N.Zelentzov**

Elektrogorsk institute of petroleum refining, Elektrogorsk
Angarsk petrochemical company, Angarsk

The activated alumina (mainly mark A-64) and activated carbon (mark APБ) are usually used as carriers for production of home-made catalysts of selective hydrogenation and oxidation processes. The carrier A-64 has two substantial disadvantages - a low crush strength and a strong destruction during the impregnation and as a result - the loss of the catalyst. The carrier APБ has a low crush strength and a low attriction index as well.

The technology of new carrier with high crush strength ШГН was worked out in AO "ElIPR" and test-operated in the pilot scale. This technology allows to manufacture the alumina carrier with optimal form and size without destruction during impregnation due to the addition of the special promoters in alumina extrusion paste.

Spherical carriers are known to exibit a high resistance to attriction which is important both: either for a high-rate gas steam processes, or for processes of liquid-phase hydrogenation.

The attrition testing of developed and commercial carriers was carried out under following conditions: medium -hexane, reaction volume - 120 cm3, oscillate frequency - 120 osc./min, amplitude 60 mm, period - 60 min, relationship solid:liquid - 1:1. The results of the testing are presented in the Table 1. There are also presented empirical data on the new carbon carrier ФАС produced in the pilot scale.

As a result the designed alumina carrier ШГН considerably exceeds the traditional γ-alumina ones in attriction and crush strength. The new carbon carrier ФАС has the better caracteristic in comparison with the carbon carrier APБ.

Both the developed alumina carrier ШГН, and carbon carrier ФАС were employed to recieve the palladium "eggshell" catalysts with 0,2 % Pd. They aren't worse the catalysts ПК-25 and MA-15 in activity and selectivity and considerably exceed them in crush strength. The carbon carrier ФАС is more available than the similar carrier СИБУНИТ (SIBUNIT) and stronger than activated carbon АРБ used for Pd-catalysts production.

Table 1.

Characteristics of carriers on the attrition resistance in liquid phase (hexane).

No	Specimen of carrier, manufactory	Form	Attrition %	Bulk density kg/dm3	Pore volume %	Crush. stren. kg/mm
1.	А-64, Ryasan Refinery	extrud.	5,0	0,6	76,0	0,6
2.	ШН-2, Redkino "TEKHNOROZ"	sphere	15,0	0,8	44,5	-
3.	ПК-3Ш Severo-donezk "AZOT"	sphere	13,4		34,6	-
4.	ШГН (SAC)	sphere	0,5	1,2	25,0	-
5.	ФАС	sphere	0,1	0,6	80,0	-
6.	Carbon АРБ Perm KHZ	extrud.	1,7	0,6	60,0	-

In conclusion, the developed alumina carriers ШГН can be used for preparation of the other catalysts, for example Ni-containing ones because they have satisfied pore volume together with high crush strength.

THE NEW Ni-Mo/Al_2O_3 CATALYST FOR HYDROGENATION OF ORGANIC SULPHUR COMPOUNDS IN NATURAL AND REFINERY GASES

M.A.Kipnis, V.S.Agaronov, N.R.Gazimzyanov

Elektrogorsk institute of petroleum refining, Elektrogorsk

In most of the units for ammonia, methanol, hydrogen production in the CIS, as the analysis shows , the Co-Mo catalysts (AKM, ГО-70, C-49-1), developed for hydrotreating of oil distillates and with rather high content of active metals (totally more 16 %, as oxides) are being exploited. The use of these catalysts was connected, firstly, with high content of organic sulphur compounds (OSC) in natural gas (NG) at the moment of the putting these units into operation (up to 80 mg/m^3), secondly, with the absence of special home-made catalysts for NG hydrotreating. Nowadays, because of improved refining, the real OSC content in NG, supplied to most of the plants, and in refinery gases (RG) doesn't exeed 25 mg/m^3. Additionally, the OSC, mainly, consist of mercaptanes, which are easily hydrogenated at 250-350°C. In this connection the use of catalysts with high content of active metals seems to be not effective.

As a rule, the Co-Mo catalysts are more active than the Ni-Mo ones in the hydrogenation of OSC. But if the hydrogenation gas contains carbon oxides (COx) the Co-Mo catalystsloose their activity due to the coking, whereas the Ni-Mo ones are less sensitive to COx. Besides, as the operation practice of catalysts AKM and ГО-70 shows , if NG contains hydrocarbons C_2-C_4, the reactor heating is observed caused by hydrocracking of C_2-C_4 hydrocarbons, followed by the fast cocking.

On the basis of the facts, mentioned above the new special ANM catalyst for hydrotreating of natural and refinery gases has been developed - ГПВ (ТУ 38.40184-92). It is characterized by rather low content of active metals (about 1,5 times) and by specially selected carrier. Catalyst ГПВ is comparable with catalysts AKM and ГО-70 in main technological properties (table 1). Moreover, it has low hydrocracking activity (HC). The special method for estimation of HC activity has been designed, based on determination of the lowest temperature on which the hydrocracking of n-hexan is observed.

Table 1

Comparative characteristics of the catalysts, used for hydrogenation of OSC in natural and refinery gases

Catalyst	Content, %			Shape	Bulk dens. g/cm^3	Diameter, mm	Stren. kg/mm	Hydrocracking temp., $^{\circ}$C	Conv. OSC*, %
	MoO_3	CoO	NiO						
ГО-70	13,4	4,5	-	extr.	0,78	2.4	1,9	350	100
АКМ	12,0	4,0	-	extr.	0,70	4,0	1,8	350	100
С-49-1	12,0	4,0	-	extr.		3,2		400	100
ГПВ	8,0	-	2,0	extr.	0,90	2.5**	1,9	450	100

* feed - n-hexan + 0,2 % butilmercaptane, temperature - 360°C, pressure - 2,0 MPa, W.H.S.V. - 0,5 $ч^{-1}$ (on liquid hexan);

** the producing of extrudates of desirable diameters is also possible.

Catalyst ГПВ is produced at the catalyst plant of Angarsk petrochemical company and by now it is loaded on the hydrogenation reactors of hydrogen producing units in Ufa and Pavlodar and is being successfully operated.

On the basis of this technology a new set of NG hydrotreating catalysts is being developed which takes into account the feed composition and the units' operation specification.

THE NEW CATALYSTS FOR HYDROGEN, AMMONIA, AND SYNGAS PRODUCTION

M.A.Kipnis, A.Yu.Kalinevich, V.F.Dovganyuk, L.G.Danilova, M.A.Porublev, Yu.N.Zelentzov

Elektrogorsk institute of petroleum refining, Elektrogorsk
Angarsk petrochemical company (APCC), Angarsk

At present the modernization process of the Hydrogen-, Ammonia-, Syn. Gas units is going. A number of hydrogen units has been recently put into operation. These circumstances and the increasing demands for efficiency, competitability of home-made catalysts have brought to the development of the new catalysts for sulphur purification and steam reforming of hydrocarbons.

The new sulphur absorption catalyst ES-1 (ЭС-1) on the basis of zink carbonate is being produced in AO "APPC". Its absorption capacity is increased in comparision with traditional home-produced sulphur absorption catalysts.

The special technology of activation permits to recieve the activated zink oxide with the developed specific surface and optimal porosity. ЭС-1 is manufactured in 4 mm extrudates or 5×5 mm tablets.

The industrial batches of ЭС-1 have been operated in Lisitchansk Refinery since 1993 (15 t) and Ufa Refinery since 1994 (45 t).

The activation technology of zink oxide feed can be used for the industrial production of zink oxide with the developed specific surface.

The new technological units for production of Hydrogen-, Ammonia- and Syn. Gas, operating at lower relationship steam: carbon, require coke resistant catalysts. The industrial production of K-87 and AKH (AKN) catalysts, containing alkali, alkali-earth- and rare-earth element oxides, has begun in "APCC" (TU 38.40182-92).

Catalyst K-87 (mark K-87-3) has been succesfully exploited in the unit of steam-carbon dioxide conversion of methane, the catalyst AKN - in the conversion of naphtha. Catalyst K-87 (mark K-87-2) is exploited in the ammonia production on the stage of shaft conversion instead of traditional ГИАП-8.

Catalyst K-87 (mark K-87-3) has been put into operation in the tubular furnace of the steam-carbon dioxide conversion of methane, since 1989 at the plant "Neftechimik" in Perm, catalyst K-87 (mark K-87-2) - in the shaft conversion at "Salavatnefteorgsyntez".

Catalyst K-87, containing up to 12 % NiO considerably exceeds the known commercial catalysts: ГИАП-8, ГИАП-3-6Н, ГИАП-19, ГИАП-16 and corresponds to the best foreign BASF, Haldor Topsoe, Dyson Refractories (Dycat International) catalysts.

Catalyst АКН has succsessfully substituted for ICI catalysts: 46-1/46-4 (two-layer loading) at the plant of mineral fertilizers. Catalyst K-87 can be used in the units of protective atmosphere production.

LOW PALLADIUM CONTENT "EGGSHELL" CATALYSTS

T. V. Turkova, M. A. Kipnis, A. Yu. Shashkov

Elektrogorsk institute of petroleum refining, Elektrogorsk

A number of the "eggshell" Pd/Al_2O_3 catalysts with low palladium content has been developed [1]. Analysis of the industrial requirements showed that the most essential volume of the palladium catalysts consumption was connected with the processes of selective hydrogenation of the olefins, purification of the technological and exhaust gases from the nitrogen oxides, hydrocarbons and CO.

Catalysts obtained by the new technique were tested in olefins selective hydrogenation, NOx reduction by the methane and oxygen (hydrogen) deep purification.

"Eggshell" catalysts with 0,01 - 0,2 % Pd content on the alumina spherical support (diam. 3 - 6 mm, Angarsk PCC) have improved attrition resistance. These catalysts have been developed for the selective hydrogenation of acetylene compounds in gaseous mixtures and also acetylene and diene ones in pyrobenzines and pyrocondensates. They are found to be as well as known commercial contacts ПК-25, МА-15, ПУ-2 in selectivity, being tested according the model mixture of the phenyl-acetylene with styrene plenty in the dimethylformamide media. These commercial catalysts on the γ-Al_2O_3 and carbon supports not yield to experimental alumina supported ones in attrition resistance. The main parameters of the new catalysts will be specificated according to the scale up testing in the real product hydrogenation.

Technique of Pd-impregnation also allows to obtain the contacts on the carbon supports. For example, low content ПУ-2 analogue (carbon extrudate, АРБ) exceeds the proto-type in nitro-benzene hydrogenation in activity. Granular spherical carbon sorbent ФАС (diam. 0,5 - 6 mm), possesing unique attrition resistance seems to be more preferable as a support. Experimental samples are under testing in intermediate product hydrogenation at the pharmaceutical works now.

In comparison with common commercial catalyst АПК-2 (continuous Pd distribution in support's granule) the new "eggshell" АПЭК-0,5 has 4-time low palladium content with the higher activity in NO_x reduction by the methane. Activity test has been made according to technical reglament for the АПК-2 with the reactor changed for loading of the undestroyed granule at the plant laboratory. Adjusting batch АПЭК-0,5 (640 kg) has been put into operation in the УКЛ apparatus (AO "Dorogobuzh").

The new catalyst for deep oxidation of the organic contamination, CO and purification of the oxygen or hydrogen (ПЭК-20, 0,2 % Pd on γ-Al_2O_3) exceeds the known commercial contacts ШПК-1, ШПАК-0,1, АПН used for these purposes in activity, having lower cost price and Pd content. Adjusting batch is run for the deep oxygen purification on the technical glass plant (Gus Khrustalnij). 200 kg of the trial catalyst was produced and put into the reactor for protactive exogase purification at the metallurgical plant (Kolchugino).

Technology of the catalyst production has been approved in commercial scale (AO "Dorogobuzh", AO "TEKHNOROS", Angarsk PCC).

1. T. V. Turkova, M. A. Kipnis et al. "Neftepererabotka i neftekhimija", ZNIITEneftekhim, M., 1994, No. 5, p. 15 - 17 (Russ.)

Liquid Phase Oxidative Detoxication of Sulfides in Catalytic Membrane Reactor

O.M.Ilinitch and Yu.S.Vetchinova
Boreskov Institute of Catalysis, Novosibirsk 630090, Russia

Introduction

Catalytic reactions combined with various methods of separation form the basis for technologies in chemistry and related industries. Traditionally, these stages were being investigated and developed independently, until the pioneering findings of membrane catalysis have demonstrated the promising potentials of their integration. At present, membrane methods are mostly employed in the processes based on enzymatic and heterogeneous catalysis. Prospects of these techniques applied to the liquid phase catalysis have been far less studied. This study is focused at the investigations of the porous catalytic membranes employed in the liquid phase process of sulfide oxidative detoxication.

Results and discussion

The reaction under consideration

$$S^{2-} + n\,O_2 \rightarrow S,\ SO_3^{2-},\ S_2O_3^{2-},\ SO_4^{2-}$$

occurs in aqueous solutions at ambient temperature and pH range ca. 7-13. It is catalyzed by the sodium salt of tetra(sulfophthalocyanine)-cobalt(II), briefly Co-TSPC, dissolved in the solution being treated. The reaction selectivity is principally determined by pH value of the solution; at pH close to 7, sulfur is the main product, while oxygen-containing compounds are typically produced at high pH.

For this reaction, the problem of the catalyst heterogenization is not solved yet. In the search for an appropriate support for the catalyst, the porous membrane was found capable to adsorb Co-TSPC in appreciable quantities. Two samples containing Co-TSPC in different surface concentrations (M-1 and M-2) were prepared and tested for the catalytic performance. For the both samples the Co-TSPC concentration at the membrane surface was within a monolayer. For the M-1 sample, the average surface concentration of Co-TSPC was 50-fold larger than that for the M-2. The samples were cut into pieces ca. 3×3 mm and dispersed in the thoroughly stirred reaction solution. No catalytic activity was registered for the M-1 membrane, while for the M-2 the activity, although ca. five-fold lower than that found for the homogeneous Co-TSPC, was clearly observed.

Two reasons for the activity decrease of the Co-TSPC fixed to the membrane were considered: (1) the catalyst deactivation upon adsorption onto the membrane, and (2) diffusion of the reactants within the pores of the membrane.

The catalyst deactivation upon adsorption is unlikely to take place, as UV-VIS spectra of the membrane-bound Co-TSPC catalyst were identical to those of the homogeneous one which is perfectly active. Apparently, it is due to the the slow reactants diffusion within the pores of the membrane that the catalytic reaction was not observed with the M-1 membrane of the high surface concentration of the catalyst, while it became noticeable as soon as the catalyst concentration was decreased in the M-2 membrane. This assumption is supported by the calculations of the Thiele modulus which revealed strong diffusion limitations for the M-1 sample.

The above results indicate that the homogeneous Co-TSPC catalyst apparently can not be fixed to the surface of typical grained porous supports without a substantial decrease of the catalytic activity caused by the internal diffusion. On the other hand, a porous membrane when used as the catalyst support may provide a new solution of the diffusion problem. A forced flow of the reacting liquid mixture through the uniform pores of the membrane instead of a slow diffusion of reactants in the pores of a grained support may improve the conditions for the reactants transport to and from the catalytic surface.

A validity of the latter assumption has been verified experimentally. For that, new samples of the membrane-bound Co-TSPC were prepared and tested in the stirred membrane reactor with Na_2S solution flowing through the membrane under oxygen pressure. The experimental results are shown in Table 1.

Although no Co-TSPC was found in the reaction solutions, an appreciable catalytic conversion of sulfide was detected (Run No.1). For comparison, a special experiment had been carried out at the same conditions, with the only exception that there was no flow of the reaction solution through the catalytic membrane. In this run (No. 2), no sulfide conversion was observed.

These results confirm the assumption that the reaction is strongly affected by the reactants diffusion in the pores of a supporting material. Besides, our expectation to overcome the diffusion limitations by the use of a forced flow of the reaction solution through the porous catalytic membrane appears to be fulfilled.

Table 1. Na_2S oxidation in the catalytic membrane reactor

Reaction conditions: T=298K, $P_{O2} = 0.115$ MPa, $C_{Na2S} = 0.04$ M, pH = 13,

Run No.	Amount of Co-TSPC, mg	Membrane surface, m^2		Contact time, minutes	Conversion of S^{2-}, %
		external	total		
1	1.7	0.011	10.6	11	23
2	1.7	0.011	10.6	no flow through the membrane	0

Acknowledgement

Financial support of this work from Russian Foundation for Fundamental Investigations (grant No. 93-03-4849) is gratefully acknowledged

POTENTIALITIES OF PHTHALOCYANINE CATALYSTS FOR DESULPHURIZATION OF GASES AND SOLUTIONS

Kundo N.N., Myzlish W.E., Stuchinskaya T.L., Faddeenkova G.A.
Federal Scientific Center "Boreskov Institute of Catalysis" of the Russian Academy of Sciences Novosibirsk 630090, Russia

Liquid-phase oxidation of H_2S and mercaptans occurs at some gas cleaning and oil refining processes, as well as at sewages processing. Comparing the stability and activity of different catalysts containing salts, transition metal complexes, organic redox complexes, phthalocyanine complexes, we have found that the latter are the most promising catalysts for the liquid-phase oxidation of H_2S and mercaptans. Among these, cobalt phthalocyanines stand out as being much more active than the other ones. We have studied the catalytic oxidation of H_2S and mercaptan in alkaline solutions in the presence of cobalt phthalocyanines containing various substituents in the benzoic nuclei. Based on our experiment, we can conclude that cobalt phthalocyanines, containing both sulpho-groups and clorine or bromine atoms, are the most active in a homogeneous medium. Phthalocyanines with -COOH, -OH, $-NH_2$ and $-NO_2$ groups are less active. Cobalt phthalocyanines are easily adsorbed from solutions. This favors their use for heterogeneous catalysts production. In order to obtain catalysts for the sulphide compounds oxidation, we have deposited cobalt phthalocyanine sulphonates on polyorganosiloxanes. These catalysts exhibit a much higher activity than that obtained via adsorption of cobalt phthalocyanine sulphonates by medicinal charcoal.

Spectral analysis of the H_2S liquid-phase oxidation, catalyzed by soluble derivatives of cobalt phthalocyanine, has shown that the catalyst activity depends on at least two factors.

(1) An easy redox transition between Co(I)Pc - Co(II)Pc -Co(III)Pc forms affects most significantly the catalyst activity. The complex forming ligands stabilize strongly the Co(III)Pc state in solutions, thus providing a decrease in catalyst activity.

(2) A critical aggregation of phthalocyanine molecules also affects the catalyst activity. Comparing the catalytic activity and absorption spectra, we have found the optimum Co(II)Pc aggregation degree whereby the catalyst has the highest specific activity.

Thorough studies of the reaction mechanism allowed to determine various oxidation process conditions and to advise different additions, which can increase the rate and selectivity.

Almost a complete oxidation of H_2S and mercaptans was observed at the sewages oxidation by air in the presence of cobalt phthalocyanine sulphonates. We can use both dissolved phthalocyanine catalysts with sulpho- and carboxy groups (10^{-5}-10^{-6} M concentration) or catalysts supported on a carbon or any other suitable support. The oxidation proceeds via the sewages blowing with air at ambient temperature.

The liquid phase purification appears to be very promising for phthalocyanine catalysts. H_2S, dust, resins, NO_2, NH_3, HCN complicate the gas purification by conventional technologies. At H_2S absorption, all these admixtures can be removed from the gas and solution regenerated by the air blowing.

Thus, the dissolved cobalt phthalocyanine catalyst successfully assists the coke gas purification from hydrogen sulphide and hydrogen cyanide at a pilot plant. The absorber and solution regeneration by air allows to obtain a 95% and higher gas cleaning, if the initial concentration of H_2S and HCN are 3 and 2 g/m^3, respectively. Sulphur and sodium thiocyanate are commercial products.

At present our rather powerful plant produces various cobalt phthalocyanine catalysts, which can facilitate the solution of many technological and environmental problems.

THE CATALYSTS FOR DIRECT OXIDATION OF AMMONIA INTO MOLECULAR NITROGEN

V.F.Lyakhova, N.N.Sazonova, A.V.Simakov, G.B.Barannik, T.A.Nikoro, O.V.Komova, Z.R.Ismagilov, H.Veringa*

Federal Scientific Centre "Boreskov Institute of Catalysis", Novosibirsk, 630090, Russia
**Energy Research Foundation , ECN, Petten, The Netherlands*

A catalytic oxidation of ammonia is a process of heterogeneous catalysis valuable with regard to the fundamentals of oxidative heterogeneous catalysis. It is also of importance for practice, considering the urgent problems of environment protection. Conventional methods for exhausts purification from ammonia (extraction and combustion) are quite efficient in some cases, but it is rather hard to use them, when cleaning a complex mixture of various components. Based on relationship between the energy of oxygen bonding with a catalyst surface, Golodets et al. [1,2] have considered the theoretical aspects of selective catalytic ammonia oxidation on metal, simple oxides, zeolites and other catalysts.

In the present paper we report the investigation of activity of catalysts of various origin to select an active and selective catalyst for direct oxidation of ammonia into molecular nitrogen suitable for exhaust gases purification from ammonia, e.g., at coal gasification. Beside, there is a problem of unused ammonia removal after selective catalytic reduction of nitrogen oxides by ammonia.

We have studied several catalytic systems: oxide catalysts both bulk (Fe_2O_3, Bi-Mo-O, Fe-Bi-Mo-O) and deposited on various supports (V_2O_5/MeO, where MeO= TiO_2, SiO_2, MgO); Cu/TiO_2; copper promoted zeolites (Cu/HZSM-5); perovskites ($La_{0.8}Sr_{0.2}CoO_3$, $LaCoO_3$). Some samples of V-Ti catalysts were modified with MoO_3 and WO_3 admixtures (3, 9, 27 mass.%). Vanadium content in the samples varied from 1.5 to 15 mass.%.

Catalyst activity was measured in a flow-circulation set up at the following conditions: the mixture composition - ammonia (800-900 ppm); oxygen(2vol.%). balance helium. Temperature was 250. 300 and 400°C. catalyst sample weight -0.4g, mixture flow rate - 10.8 L/h, the circulation factor about 70-80.

According to our data V-Ti. Cu-Ti catalysts and Cu-promoted zeolites provide the highest reaction rate (at 400°C ammonia conversion -100%) in the catalytic ammonia oxidation. Moreover, at nitrogen formation we observe only small amounts of nitrous oxide and no nitrogen oxide. The rate of nitrogen formation on the modified V-Ti catalysts and the effect of modifiers depend on reaction temperature. Obtained kinetic data have been analyzed according to a parallel-successive scheme of selective ammonia oxidation. Relationships between the catalyst surface properties and their activity and selectivity in the reaction under investigation have been discussed.

The catalysts, considered here, are also promising, since they have been prepared as honeycomb monoliths. Such a shape of catalyst increases significantly the catalysts efficiency in processing of a large amount of gas.

REFERENCES

1. N.I.Il'chenko, G.I.Golodets, J. Catalysis, 39, 57 (1974)
2. N.I.Il'chenko, G.I.Golodets, J. Catalysis, 35, 73 (1974).

SUPPORTED BLOCK CATALYSTS FOR SCR PROCESS OF NITROGEN OXIDES

M.G.Martsenyuk-Kukharuk, V.A.Ostapyuk, S.N.Orlik,
A.D.Tereshchenko, I.F.Mironyuk

L.V.Pisarzhevskij Institute of Physical Chemistry,
National Academy of Sciences of Ukraine, Kiev, (044)265-62-16

The supported oxide block honeycomb catalysts for the process of selective reduction of nitrogen oxides by ammonia (SCR-process)(V_2O_5-TiO_2/SiO_2; Fe,Cu,Cr/γ-Al_2O_3) were developed. The physico-chemical characteristics of the developed catalysts (resistance to sulphur compound, XP-spectrum and acidity of surface) and kinetics of the SCR-process were studied. The results obtained were used during pilot-commercial tests on power-and-heating plant flue gas cleaning of nitrogen oxides by SCR-method.

The supported block honeycomb vanadium-titanium catalysts (V_2O_5-TiO_2/ SiO_2) for the selective reduction of nitrogen oxides by ammonia was developed. For impruving the moldability of the mass plus raising the mechanical strength of the honeycomb structure elements the mixture was prepared using additions of Transcarpatian clays.

Settling of an ultra thin layer of anatase on the surface of pores of honeycomb structure elements was realized owing to the adoption of aqueous solutions of titanium tetraacetate and hydrochloric solutions of titanium chloride. The $\equiv$Ti-O-Si$\equiv$ chemical bond is implemented between the SiO_2 matrix (substrate) and the TiO layered. The settling of titanium dioxide was alternated with that of vanadium pentoxide to boost the activity of the catalyst plus resistance to sulphur compounds and its mechanical strength.

The conversion of NO was 80-90% for the reaction mixture of the next composition: 0,05% NO + 0,045% NH_3 +6% O_2; V=15 ths h^{-1} in the temperature interval of 250-350^0 C. One requirement catalysts for SCR-process should meet is their resistance to sulphur compounds, therefore we studied the influence of sulphur dioxide on the process in detail. Two types of the SO_2 influence on the process have been singled out: the first one results in the fact that in the cold sections of the mounting and the reactor sulphur dioxide combines with ammonia, causing deceleration of the reaction of NO reduction, proportional to the concentration of sulphur dioxide. In the second scenario (when directly introducing SO_2 into the hot zone of the reactor) its impact on the reaction rate is not definitive: there may be acceleration, retardation or no marked effect of sulphur dioxide on the process; the degree of the SO_2 influence increases with increasing SO_2 concentration.

The acidic-basic properties of V-Ti catalysts were studied by the method of TPD of NH_3 and showed that SO_2 increases the surface acidity of the catalysts and not only the quantity of acidic centres is increasing but the new centres with high bond energy of ammonia are appeared and that's may be the cause of increasing activity of the catalysts in the SCR process of NOx.

Supported catalysts of intricate composition for SCR process have been also developed . They contain a mixture of oxides and sulphates of Fe, Cu, Cr, Ni and Zn as the active components and are not inferior on their V-Ti counterparts in activity and the resistance to sulphur, while conciderably excelling them on many economic accounts.

An investigation of starting and used catalysts has been carried out by XPS-technique with a view to analyzing the composition and valence state of elements in the catalysts. Comparative analysis of binding energy values and relative intensities of the Ti 2p, V 2p lines in the spectra of starting and used catalysts evidences no perceptiblechanges in the valent and structural state of the active phase. For Cr-containing catalyst in the course of operation a Cr6+ - to - threevalent Cr reduction effect is observed plus increasing surface concentration of the active phase on Al_2O_3.

The developed catalysts were used successfully during pilot-commercial tests on power-and-heating plant flue gas cleaning of nitrogen oxides by SCR-method. Purification degree of NOx at 300-315°C and space velocity 10-20 ths h^{-1} was more than 80%.

NOVEL ECOLOGICALLY PURE METHOD OF PHENOLIC ALCOHOLS PRODUCTION - ALKOXYLATION OF PHENOL WITH FORMALDEHYDE CATALYZED BY SILICA BASED SULPHOCATIONITES.

A.Y.Mil'chenko, T.A.Kremleva*, A.Y.Yuffa*

Institute of North Assimilation Problems (Russian Academy of Sciences, Siberian Dept.), p/box 2774, Tyumen 625003, RUSSIA

*Tyumen State University, 10 Semakova, Tyumen 625003, RUSSIA

It's known industrial condensation of phenol and formaldehyde to be carried out under homogeneous catalytic conditions in presence of basic or acidic catalysts. In the former case main products of the reaction are phenolic alcohols (PA), whereas in the latter case bis(dihydroxyphenyl)methanes (DHPM) become final products, PA being only intermediate compounds. PA can't be isolated under conditions of usual homogeneous acidic catalysis because the rate of DHPM formation is 10-13 times higher than that of intermediate PA generation. But it is PA obtaining that is of prime chemical and commercial interest since they are widely used as binders in production of thermoinsulating materials. Existing technologies of PA industrial preparation posess a number of disadvantages such as: high residual concentration of phenol and formaldehyde (about 10%); the necessity of neutralization of large amounts of acidic solutions and, therefore, the problem of utilization of salt wastes, high additional expenses of acid, that causes losses of money and damages environment.

Our method of PA production is a radical departure from conventional practice because it is based on utilization of ecologically pure heterogeneous acidic catalysts. These catalysts are silicas with definite size of pores (S-120 or MSA-750) chemically coated with layer of $-C_6H_4SO_3H$ groups. The interaction of phenol with formaldehyde (1:1 molar ratio) in presence of such sulphocationites at 60-85°C during 3h permits to obtain PA with quantitative yield (residual content of monomers in reaction mixture doesn't exceed 3%, slight amounts of DHPM are also detected).

Thus, the use of our technique allows to solve serious problems of traditional technologies, such as:

i) the ease of catalyst isolation after finishing the reaction;

ii) the possibility of multiple usage of catalyst without regeneration with keeping the same catalytic activity;

iii) the elimination of any salt wastes and, hence, the lack of the great problem of their utilization or neutralization;

iv) low residual contents of toxic, volatile, chemically active monomers in obtained product, that is particularly important on storing and further utilization of PA;

v) essential reduction of corrosive activity of reaction medium;

vi) minimum expenditures of time, ancillary reagents, energy and labour to isolate final products.

All factors mentioned above can be considered not only as a good way to save money and resources but, mainly, as contributory ones for the process of reduction of chemical influence on environment.

CATALYTIC PROCESSING OF H_2S CONTAINING GASES OF OIL-REFINING AND COKE-CHEMISTRY

Z.P.Pai and A.Yermakova

Federal Scientific Center "Boreskov Institute of Catalysis", Novosibirsk 630090, Russia

Acid gases, obtained at the adsorption-desorption purification of associated oil gases and coke-oven gases, contain about 40-90 vol.% of H_2S. Such H_2S-containing gases are usually utilized via the gas-phase Claus process [1]. Yet the process has some drawbacks, arising from reversible reaction (1) and from some peculiarities of catalysts performance [2]

$$2\,H_2S + SO_2 \rightleftharpoons 2\,H_2O + 3/x\,S_x \qquad (1)$$

Nowadays, the gas-phase Claus reactors have no alternative and competitive analogs in utilizing the huge amounts of H_2S containing gases, when a single reactor produces about 100 thousand tons of sulfur per year, as in the gas industry. However, such reactors are not good for the oil-refining and coke industry, since their capacity attains only 10-15 thousand tons of sulfur per year.

A liquid-phase Claus process [3] seems to be most advantageous for utilizing 500-6000 m^3 of acid gases per hour, that contain 20-90 vol.% of H_2S.

The main stages of the process scheme are: heating, catalysis and sulfur isolation from solution (Fig. 1). As in the gas-phase Claus process, H_2S is thermally oxidized to SO_2 and S in the Claus furnace (1). About 70% of H_2S converts to sulfur, which condenses in tank (2) and then is used as a commercial

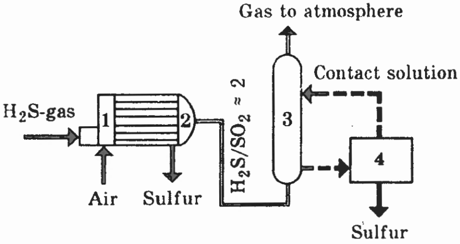


Fig. 1. Scheme of sulfur production from hydrogen sulfide containing gas

product. Gas, containing H_2S and SO_2 ($H_2S : SO_2 \approx 2$) goes to catalytic absorbing reactor (3), filled with homogeneous catalyst IC-27-1, where occurs the Claus process producing the elemental sulfur. Simultaneously, gas is purified from admixtures. After cleaning it either goes to atmosphere or is used commercially.

Solution containing sulfur crystals undergoes sulfur isolation (4). This stage should be analyzed with regard to economy. It depends on reactor capacity [4]. If the latter is about 1 ton of sulfur per day, then decantation combined with filtering is be efficient. For reactor producing 1-5 ton of sulfur per day, a flotation followed by melting should be used. Continuously produced melters are expedient if more than 5 tons of sulfur are produced daily.

Our method, based on the liquid-phase catalytic interaction, allows to obtain efficient sulphur recover from reaction volume unit. Moreover, it has the following advantages. The stoichiometric relation $H_2S : SO_2 = 2$ is no longer needed all the time in the gas phase after the thermal stage. Our method allows to isolate NH3 and HCN from the off-gases of coke-productions and to convert cyanides to environmentally safe compounds, rhodanide. Oil-refinery gases can be separated from COS, sulfur steam and H_2O as well.

References

1. V.R. Grunvald, Technology of the Gas Sulphur, Khimiya, Moscow 1992.
2. L. Parnell, Hydrocarbon Processing, N.9 (1985) 114-118.
3. Z.P.Pai, A.Yermakova, N.N.Kundo et al., Coke and Chemistry, N.6 (1993) 36-42.
4. L.C. Hardison, Hydrocarbon Process, 64 (1985) 70-71.

LIQUID CATALYTIC PURIFICATION OF GASES FROM SO_X AND NO_X

Z.P. Pai and A. Yermakova

Federal Scientific Center "Boreskov Institute of Catalysis", Novosibirsk 630090, Russia

Electric power plants (EPS) pollute environment with nitrogen and sulfur oxides most severely. Thus, in 1991 they vented $3.06 \cdot 10^6$ t of SO_2 and $1.64 \cdot 10^6$ t of NO_2, that is 26% of their total amount discharged into the atmosphere in Russia [1]. NOx concentration in flue gases varies between 200 and 1000 mg/m^3, that of SO_2 attains 4 g/m^3.

In most countries, these impurities are removed separately at the EPS. Note that SO_2 is removed via wet procedures, while for NO_x, dry methods are used.

Existing technologies for a simultaneous purification of waste gases from NO_x and SO_x are not efficient enough and only the least part of them has been tested on real flue gases.

Absorption seems to be most suitable for the flue gases purification from nitrogen oxides. It can be arranged in three ways: oxidation-absorption, absorption-oxidation and absorption-reduction.

The latter is mostly interesting, since it allows to reduce NO to N_2 [2,3].

Oxygen-containing sulfur compounds when used for NO reduction allow to purify simultaneously flue gases containing nitrogen and sulfur dioxides. NO content being 80-90% with respect to all NO_x present.

Our studies [4] have shown the activity of reductants to increase in the following series:

$$SO_3^{2-} \rangle HS^- \rangle \left(S_2O_3^{2-} + IC-27-1\right) \rangle S_2O_3^{2-}$$

The system consisting of thiosulfate and homogeneous catalyst IC-27-1 is the most appropriate for practice. More detailed studies on the liquid phase NO reduction in the presence of catalyst IC-27-I allowed to design a process for simultaneous purification of flue gases from sulfur and nitrogen oxides.

The process is carried out under mild conditions: the optimal pH of a contact solution is 6.0-7.0 and T=60°C. The maximum NO conversion degree is 92-94% and for SO_2 it is 99.2%. However, taking into account that NO partially transforms into N_2O, the total amount of removed NO_x is 80%.

The process scheme suggested for industrial scale consists of two principal stages: SO_2 and NO_x absorption and solution regeneration with a hydrogen sulfide-containing gas. Here, the final products are elemental sulfur and ammophoska which is a valuable fertilizer.

References

1. V.A. Zaitsev, A.A. Kucherov, T.B. Pyatina and A.P. Kovalenko, Khim.Prom., N.3-4 (1993) 119-127.
2. H. Takeuchi, M. Ando and N. Kizawa, Ind. End. Chem. Process. Des. Dev., V.16, N.3 (1977) 303-308.
3. S.B. Oblath, S.S. Markowitz, T. Novak and S.G. Chang, J.Phys.Chem., V.86 (1982) 4853-4855.
4. Z.P. Pai, S.V. Kapterev and N.N. Kundo, Sib.Khim.Zh., 1 (1993) 5-10.

CATALYSTS BASED ON FOAM METALS FOR EXHAUST GAS PURIFICATION

A.N.Pestryakov, *E.N.Yurchenko, *A.E.Feofilov, O.V.Pestryakova
Tomsk State Academy of Civil Engineering, Tomsk
*Russian Scientific Center "Applied Chemistry", St-Petersburg

A number of previous studies showed that foam metals and foam ceramics with the supported active cover are effective catalysts for deep oxidation of hydrocarbons. Catalytic, mechanical, structural and gas-dynamic properties of foam-metal catalysts with the supported oxide active cover have been studied in the processes of deep oxidation of CO, propane and methane.

Foam materials are high-porous metal or ceramic blocks with cellular structure. Their elementary cell has a dodecahedron form. Changing the preparation conditions structural-mechanical characteristics of the blocks can be varied within wide range: cell average diameter - 0.8-5.0 mm; porosity - 80-98 %; volume density - 0.1-1.0 g/cm^3. High gas permeability, strength and catalytic activity are the main advantages of the foam materials permitting to use them efficiently in different catalytic processes.

As catalytically active metals (Cu, Ni, Fe, Cr) are included in the foam material composition, the foam metals may be used in the deep oxidation processes directly. However, due to small surface area (0.05-0.1 m^2/g) efficiency of pure foam metals is moderate in the kinetic temperature range (>300°C). In order to increase the surface area and catalytic activity we have worked out the methods of deposition of oxide active cover on the foam metal directly or with using the intermediate -Al_2O_3 support. The first method permits to raise the surface area up to 3-8 m^2/g. Efficiency of the catalysts with the supported active cover in the processes of deep oxidation of hydrocarbons is vastly superior to the index of pure foam-metal support. The experiments reveal that fine-cellular catalysts are more active than large-cellular ones. But according to the catalyst service conditions it is necessary to strive for optimal relation between catalytic properties of the samples and their strength and gas-dynamic characteristics.

Applying the intermediate Al_2O_3 layer allows to increase the surface area up to 20-30 m^2/g. This complicates the process of the catalyst preparation but raises catalytic activity of the samples. Efficiency of the foam catalyst exceeds the index of the honeycomb catalyst with the same composition of active cover and similar diameter of channels in the processes of CO and propane oxidation. Three-dimensional cellular structure of the foam catalysts gives rise high turbulency of gas flow. This affords better contact of the reacting molecules with the catalyst surface as compared with honeycomb catalysts, where part of molecules short-circuits in laminar flow. Activities of the foam and granular samples are close to each other. But foam catalysts are more effective than granular ones on permeability and strength.

Catalytic activity of the foam materials in methane oxidation is shifted to high-temperature region. This is the known phenomena attributed to stability of methane molecule. But the generality of the process pattern over foam catalysts is analogous with CO and propane oxidation. Fine-cellular samples with Al_2O_3 layer are more effective. However, when using the catalysts with the intermediate support it is necessary to take into account that Al_2O_3 layer somewhat lows strength and permeability of the foam metals, especially fine-cellular ones. Moreover, distinct amount of Al_2O_3 can be supported on different foam metals. The foam metals are able to keep from 6 to 20 wt.% Al_2O_3, foam ceramics - more than 35 %. Surface area of the catalysts changes in accordance with these values.

It is essential to note that in air at high temperature the stock of foam support corrodes. So such metals and alloys as Cu, Cu-Ni do not fit for preparation of foam catalysts performing at high temperature (>300°C). Foam ceramics is the most corrosion-resistant, but catalysts based on foam ceramics are friable and may fail when using at hard mechanical load. So foam supports on the base of steel or Nichrome are optimal for application under hard conditions. Moreover, Al_2O_3 layer protects in large part the catalyst surface from corrosion at high temperature. Catalysts based on foam ceramics may be efficiently used in the processes without strong mechanical attacks.

WO_3 and Nb_2O_5 ADDITIONS for MONITORING of V_2O_5-TiO_2 CATALYST RESISTANCE to SULPHUR OXIDE POISONING

N.N. Sazonova, L.T. Tsykoza, A.V. Simakov, G B. Barannik.

Federal Scientific Centre "Boreskov Institute of Catalysis", Novosibirsk 630090, Russia

Selective catalytic reduction (SCR) of NO_x by ammonia on monolith V-Ti-O catalysts is widely used to remove NO_x from exhaust gases. Like NO_x sulphur dioxide is a very toxic admixture of flue gases. It can produce SO_3 and solid salts at the reaction with oxygen and ammonia. As the effluent gases temperature decreases these salts can pollute heating surfaces or poison the catalyst. Thus the catalyst applied for SCR should be highly resistant to the sulphur oxides poisoning. It is known [1,2], that doping of SCR catalysts by various admixtures increases their resistance to the sulphur poisoning.

Monolith V-Ti SCR catalysts based on Russian raw materials have been developed at the Boreskov Institute of Catalysis. In order to improve the catalyst thermal resistance, tungsten or niobium oxide additives are used.

We have studied the activity of catalysts of various composition at sulphur dioxide oxidation and selective catalytic reduction of NO by ammonia.

Model catalysts with controlled composition were prepared by mixing of titanium dioxide powder with an active component solution. Then the samples were subsequently dried in air and under an IR lamp, heated at 500^0C for 4 h in air. $VOSO_4 \times 3H_2O$ or NH_4VO_3 were initial active components. Catalysts were modified by tungsten and niobium oxides added at the mixing. Vanadium concentration varied within 1.5-5 wt.% of V_2O_5. 2.59-9 wt.%. Nb_2O_5 was added to the catalyst. $V_2O_5/WO_3=1/2$. Titanium dioxide of 15 m^2/g specific surface having 1.5 wt.% of admixtures (Cl^-) was used for the catalyst preparation. In some runs, the initial titanium dioxide comprised already tungsten and niobium oxides as natural admixtures. Extruded samples of monolith catalysts were prepared with various plasticizers and moulding agents.

The catalyst activity at SO_2 oxidation to SO_3 was measured in a flow-pulse set up at 400^0C. The mixture contained: SO_2=1.2%; O_2=9.2%, balance nitrogen. The sample weight was 3 g. Contact time was varied by changing the rate of initial mixture feed (5-50 L/h). Oxygen content in the initial and final mixture was analyzed by chromatography, SO_2 content- by iodometry. The catalyst activity was characterized by SO_2 conversion.

The catalyst activity at the selective reduction of nitrogen oxide by ammonia (0.4 g sample, 0.5-1.0 mm fraction) was determined as the NO conversion by a flow technique: 225-400°C, initial mixture contained 0.05 vol.% of NO, 0.5 vol.% of O_2, 0.05 vol.% of NH_3, feed rate was 3 ml/s.

On the basis of our study one can to conclude that:

- The addition of tungsten to the catalyst is very advantageous, since it increases the catalyst activity at the SCR reaction and decreases the oxidation of sulphur dioxide.
- Niobium additives also decrease the catalyst activity at the sulphur dioxide oxidation.
- Tungsten additives decrease the catalyst activity with respect to ammonia oxidation at the selective reduction of NO with ammonia.
- The catalyst resistance to sulphur oxide poisoning increases if tungsten or niobium oxides are added. The catalyst activity at the SCR was measured before and after oxidation of sulphur dioxide as well as after the catalyst regeneration by its heating at 500°C in air. Niobium-free catalyst used for oxidation of SO_2 to SO_3 has showed a considerably lower activity at the SCR at temperatures below 350°C. While niobium doped catalyst appeared to be more resistant to sulphur poisoning. The catalyst regeneration returns its starting activity.

Thus, tungsten or niobium oxides added to V-Ti oxide catalyst decrease significantly oxidation of sulphur dioxide and increase the catalyst activity at NO selective catalytic reduction by ammonia of real exhaust gases which contain sulphur oxides. The latter opens up a wide field of application for this catalysts.

REFERENCES

1. Chen, R.T. Yang, Appl. Catal. A:General, 80, 135, (1992).
2. Kozo Tanabe: Catalysis Today, 8, 1 (1990).

Porous alumina ceramics as a support of catalysts and membranes.

R.A.Shkrabina, A.A.Kirtchanov. N.A.Koryabkina, H.Veringa*, P.Pex*, Z.R.Ismagilov.

Boreskov Institute of Catalysis, Novosibirsk, Russia.
** ECN, Petten, The Netherlands.*

Alumina is widely used as material for the preparation of granulated catalyst support. Also in many years aluminas are applied as supports for membranes.

The pore structure of membrane support materials used as catalysts is one of the most important characteristics, and the making preparation of ceramics with the required properties is the most important problem to be solved as well.

The known route for obtaining of the pore structure - burning out organic additives - does not allow modification of the pore structure over a wide range and, for instance, to produce ceramics (calcinated at high temperature) with pore diameters of 150÷1000Å.

The goal of this work is the development of a preparation technique of alumina ceramics as single tubes and multihole structures with the required pore structure.

Studies are carried out in the following directions:

- study of the oxide/hydroxide aluminium materials (precursor) with the different physical-chemical properties;
- preparation of masses (from precursors) with rheological properties suitable for extrusion;
- study of the influence of the extrusion mass compositions (ratio between initial components in these masses) and thermal conditions on the pore structure of alumina ceramics;
- preparation of porous alumina as single tubes (ST) and multihole structure (MHS) and their characterization.
- the development of the experimental procedure and the construction of measurement equipment for determing the gas permeability (G/P).

It is shown that for the preparation of the extrusion masses it is possible to use (instead of burning out organic compounds) aluminium hydroxide as a binder agent.

It is also established, that by variation of the ratio between binder (aluminium hydroxide) and the main alumina component (α-Al_2O_3) in the extrusion masses and thermal conditions, a well defined pore structure can be prepared.

The results obtained extent the possibilities of pore structure control compared to the chemical method of burning out of the organics.

The properties of the samples prepared as single tubes and multihole structure (with monomodal distribution of pore size) are given in the Table.

Table. *Properties of ceramic samples (single tubes and multihole structure).* *

№	S_{BET}, m²/g	V_{tot}, cm³/g	D_{av}, mkm	P_{av}, kg/cm²	Porosity, %	$G/P(N_2)\cdot 10^6$, mol/cm²·s·Pa	Shape, size, mm
1.	2,9	0,13	0,18	-	35	21,28	ST $d_{out} = 4,3$; $d_{inn} = 2,0$; L = 100÷150.
2.	5,3	0,17	0,12	7,5	40	23,50	-"-
3.	10	0,26	0,09	12	51	17,11	-"-
4.	2,5	0,16	0,12	210	40	-	MHS $d_{out} = 50$; $d_{inn} = 1,0$; L = 50÷100.
5.	6,8	0,12	0,07	-	33	-	-"-

*) Thermal treatment conditions of samples were the same (final temperature 1200°C).

The work is carried out by the cooperation between BIC and ECN and supported by a grant of NWO in the Netherlands.

REACTION KINETICS and DYNAMICS of NO ADSORBED FORMS on Cu-ZSM-5 at the SELECTIVE REDUCTION of NO by PROPANE

A.V.Simakov, N.N.Sazonova, E. V. Rebrov*, O.V.Komova, G.B.Barannik

Federal Scientific Centre «Boreskov Institute of Catalysis», Novosibirsk, 630090, Russia
**State University, Novosibirsk, 630090, Russia*

Recently, considerable attention is focused on the detail investigation of the selective catalytic reduction (SCR) of NO with propane on copper-exchanged zeolites. SCR appears to be the most promising method for the NO removal from exhaust.

In the present work we have studied the kinetics of SCR NO with propane and direct decomposition of NO in the presence of oxygen at the steady and non-steady state of a catalyst. The reaction rate as a function of the reagent concentration, reaction temperature and time of contact in a full-mixed reactor has been obtained.

Cu-ZSM-5 catalyst (1.18 wt.% of Cu) was prepared by the traditional ionic exchange between H-ZSM-5 and aqueous solution of the copper-amino complex.

The interaction of the reaction media and catalysts surface was studied by TPD. On order to elucidate the nature of adsorbed reagent form we have compared their spectra with the spectra of model systems (CuO/SiO_2, CuO/Al_2O_3, CuO). Spectra are shown in Fig.1. Kinetic parameters of the reagents desorption were calculated by mathematical simulation of TPD spectra.

As the oxygen concentration increases, the rate of NO decomposition rises (Fig.2). The rate of the selective reduction of NO with propane is characterized by maximum at $[O_2]=0,7\%$. The increase in propane concentration provides either increase or decrease of the reaction rate depending on the temperature.

Several types of NO adsorption were identified over the catalyst surface under reaction conditions. The amount of adsorbed NO depends on both the reagent concentration and reaction temperature (Fig.3).

Mathematical kinetic model of the selective reduction of NO with propane on Cu-ZSM-5 and dynamics of adsorbed reagents form on the catalysts surface are under discussion.

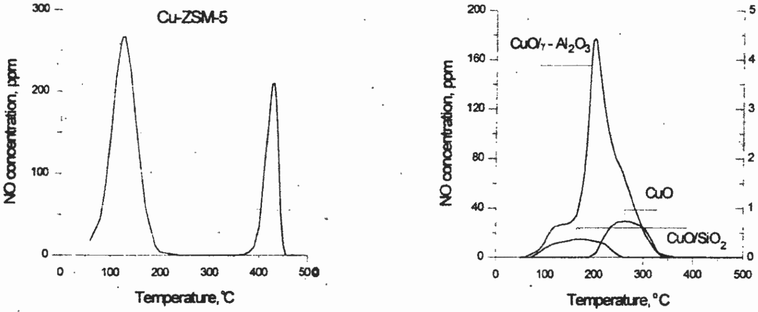


Fig.1

TPD spectra of NO over Cu-containing systems. Adsorption of NO + O_2 at 50°C.

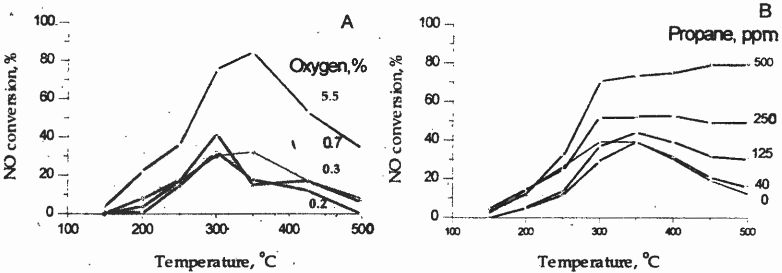


Fig.2.

Activity of Cu-ZSM-5 catalyst at NO decomposition (A, NO=500 ppm) and NO reduction with propane (B, NO=500 ppm, O_2=2.2%) as a function of oxygen (A) and propane (B) concentrations. Space velocity is 7500 h^{-1}.

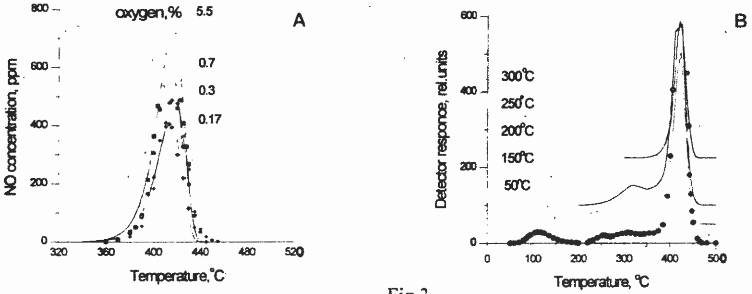


Fig.3.

TPD spectra of NO as a function of oxygen content (A, reaction of NO decomposition, T_{reac}=300°C, NO=500 ppm) and reaction temperature (B, reaction of NO reduction with propane, C_3H_8=75 ppm, NO-500 ppm, O_2=2.2%). Space velocity is 7500 h^{-1}.

CATALYTIC PROCESSING OF SEDIMENTS AND PURIFICATION OF EFFLUENTS

Simonov A.D., Yasykov N.A., Yepifantseva E.I.

Boreskov Institute of Catalysis, 630090 Novosibirsk, Russia.

We need to provide optimal conditions for catalyst action on a solid organic waste to make the catalytic combustion efficient [1]. In many cases we can arrange this creating a developed surface for the catalyst contact with the solid waste using a fluidized bed of dispersed catalyst. In this case we obtain a good mass exchange at considerably low temperatures (400-700°C) and efficient interaction of solid organic particles with air, while the intermediate products evolving due to this interaction are burnt on the catalyst surface [2]. Meanwhile, nitrogen combined in the organic waste is oxidized mainly to molecular nitrogen. Sulfur compounds do not evolve into the gas phase due to the low combustion temperatures but remain combined in the mineral fraction of organic waste. The catalyst presence increases also the combustion degree. The similar dependencies were obtained upon the combustion of active sludge, micellar wastes from the production of drugs, municipal sewages and some agricultural wastes. The flue gases after the catalyst bed contain considerably less amounts of toxic products than after the inert bed. After the catalyst bed the amount of nitrogen oxides does not exceed 150 mg/m^3 (it is 300 mg/m^3 or even higher after the quartz bed), the amount of CO is about 0,01% vol. (after the quartz bed about 1.0% vol.). No sulfur oxides were registered after the catalyst bed, while after the quartz bed at 700°C SO_x concentration was 200 mg/m^3.

Varying the stay period of particles in the catalyst bed via changing the bed height or fluidization rate, we can change the combustion degree, decrease the evolution of volatile components and increase carbonization of coke. The yield of the solid product can attain 50-60% with respect to the sediment type. Investigation of the product texture shows, that we can obtain adsorbents with a high specific surface due to the low process temperatures. In the inert bed, where combustion proceeds in the diffusion region, the particle temperature is noticeably higher - 800-1000°C. This burns out micropores and mesopores and decreases specific surface of products. Production of adsorbents via the catalytic processing of solid industrial wastes [3] allows to combine efficiently utilization of sediments and purification of industrial effluents. Now, the scheme is implemented at "Grigishkes" (Lithuania) for purification of effluents provided upon fiber wooden plates and paper production. The industrial large scale tests have shown the possibility to implement the cyclic sediment treatment with a following utilization of solid product for adsorption/coagulation purification of effluents. The excess of the solid product is removed from the process and used as commercial adsorbent. In comparison to the known methods for detoxication of sediments and purification of effluents the new method allows to: reduce size and metal weight of apparatus by factor 20; arrange an autothermal process (that is without any additional fuel) at the wetness of sediments less than 75%; liquidate or reduce considerably gas ejections intoxicated with organics, oxides of carbon, nitrogen and sulfur; provide a high degree of effluent purification from the dissolved and condensed materials without expensive or deficit flocculants and coagulants.

REFERENCES

1. B.N.Kuznetsov. Catalysis for chemical treatment of coals and biomass. Kranoyarsk, Krasnoyarsk State University, 1988, p. 66 (in Russian).
2. Volkova G.G., Simonov A.D., in: "Chemical physics of explosion and combustion. Combusiotn of condensed systems. Chernogolovka, institute of Chemical Physics, 1986, p. 24 (in Russian).
3. A.D.Simonov. Catalytic purificaion of effluents. Zh.V.Kh.O. im Mendeleeva, 1990, vol. 35, No1, p.107 (in Russian).

POSTER PRESENTATIONS

CATALYSIS FOR ORGANIC SYNTHESIS AND PETROCHEMISTRY

CATALYTIC SYSTEMS FOR THE ABATEMENT OF CARBON MONOXIDE AND UNBURNED HYDROCARBONS

Antciferov V.N., Makarov A.M.,
Filimonova I.V., Kalashnikova M.U.,

Republican Engineering-Technical Centre of Powder Metallurgy
(RETC PM), Perm

In order to reduce or overcome the problems of environmental pollution caused by pollutants such as carbon monoxide, nitrogen-oxide compounds and toxic organic compounds that are produced in the exhaust of power plants or transportation vehicles, a need exists to provide catalytic processing equipment. For this purpose, it is important to create catalytic systems that can withstand high temperatures so that it is possible to reduce the overall dimensions of the catalyst system and diminish the power consumption, while still realizing effective catalytic removal of the noxious components.

The nickel-chromium micro-rod surfaces were then coated with a carrier layer of γ-aluminum oxide by submerging the highly porous nickel-chromium open cell foam structure in a saturated solution of sodium aluminate. About 20 g/mm^2 of the γ-aluminum oxide layer having a thickness of about 60-100 microns and a specific surface area of about 200 m^2/g adhered to the surface of the nickel-chromium micro-rods. A platinum-rhodium catalytic layer was then formed on the surface of the γ-aluminum oxide carrier layer by impregnating the specimen in a solution of platinum chloride and rhodium chloride and subsequently reducing to produce a finely dispersed metallic layer of platinum-rhodium. The content of platinum and rhodium was about 0.25 and 0.1 weight percent, respectively , as compared to the total weight of the catalyst.

The results in Table show the high efficiency of CO-to-CO_2 conversion at low temperatures for the test samples as compared with the Volvo reference.

The degree of conversion of CO to CO_2 at T(°C),the reference was a Volvo-740 catalytic converter:

T (°C)	20	140	160	180	200	300
Test	33	48	53	57	60	98
Reference	4	8	12	50	69	100

Suggested areas of application.

Cleaning of gaseous effluents from automotive engines and from industrial enterprises (industries manufacturing synthetic acids, phthalic anhydride, plastics) by oxidizing their constituent hydrogen, carbon monooxide, hydrocarbons, aldehyde, odorous and other organic substances.

Catalytic systems insure a 90-100% oxidation of carbon monooxide (200-400 C), 80-100% oxidation of methylethylketone, cyclohexane (200-300 C), xylol, ethylacetate, benzol, ethelene phthalic anhydride (300-400 C), nitrogen oxide decomposition to a conversion factor of 0.7-0.9 (270-400 C).

RESULTS OF ANALYSIS WASTE GASES FROM ENAMEL FURNACE PLANT "KAMKABEL"

Date, place taking a sample of waste gas	Chemical compositions, mg/m^3			
	tricresol	phenol	xylol	CO
10.01.91				
before catalyst	101,20	6,47	80,0	125,0
after catalyst	6,16	0,93	43,3	12,5
% combustion	94,00	85,60	45,8	90,0
28.01.91				
before catalyst	238,90	55,30	400,0	866,3
after catalyst	11,20	0,41	55,0	15,1
% combustion	95,30	99,20	86,2	98,2
18.02.91				
before catalyst	186,00	81,70	450,0	1250,0
after catalyst	50,00	0,07	25,0	20,8
% combustion	73,10	99,90	94,4	98,3

CATALYSTS BASED ON HIGHLY POROUS CELLULAR MATERIALS (HPCM)

Antciferov V.N., Makarov A.M.,
Filimonova I.V., Kalashnikova M.U.

Republican Engineering-Technical Centre of Powder Metallurgy
(RETC PM), Perm

These are solid, "block-type" catalysts; compared to the bead-type catalysts they offer a much lower gas-dynamic resistance, a large reduction of the catalytically active material mass and a substantially more efficient use of the volume. Using metals as a porous CELLULAR medium does away with the low impact strength and thermal conductivity, characteristic of the more traditional ceramic matrix materials. Metals provide for low heating-up times which enables rapid changes of operating regimes; they preclude local hot spots formation due to high thermal conductivity and they possess high mechanical properties, in fact the highly porous structure of the metal matrix ensures higher mechanical properties than any known matrix structures of comparable density while the permeability of HPCM's is higher by 3 to 5 order of magnitude.

Catalytic block systems for reforming of gasoline, preventing the build-up of hydrogen in air of plants by low temperature oxidation (at 25 °C and concentration <1%). Typically, excessive hydrogen levels may be reduced by using devices employing high temperature catalytic systems or flames actually increase the risk of hydrogen explosion under certain circumstances. "Block type" catalysts of the HPCM type with a hydrophobic coating are developed to oxidize hydrogen in the presence of large quantities of steam, (up to saturation level) for a hydrogen removal system for nuclear power plants.

The highly porous open cell foam structures may be combined with a catalyst by covering the micro-rods of a metallic open cell foam structure with a support layer comprised of metal oxides such as Al_2O_3, ZrO_2 or TiO_2 and then coating the surface of the support layer with a catalyst such as platinum, platinum-rhodium, palladium, cerium, Cu, Ni, etc. The highly porous metallic open cell structures may be formed from metals such as Ni, Cr, Mo, Co, W, alloys thereof, or stainless steel.

Selected characteristics.

Matrix material microstructure -	a highly regular, meshed, cellular structure.
Cell geometry -	pentagondodecahedron.
Size of blok, mm	600x300x300
Mean cell size, mm	1-5
Density, g/cm^3	0.2-1.0
Porosity, %	85-95
Permeability (as specified to the USSR Standard GOST 25283-82), m^2	10^{-6}
Compression strength (for plate-type HPCM), kg/cm^2	2-70
Resistance to scaling (for HPCM material), degrees C	700-800
Specific heat capacity, kJ/kg/degree	0.4-0.6
Thermal conductivity at 800 C, W/m/degree	1-5
Specific surface area of coating-second carrier Al_2O_3, m^2/g	120-140
Relative content of the Al_2O_3 coating, %	10-40
Specific surface area of the catalytic system, m^2/g	15-25

Catalysts or catalyst supports based on open cell foam structures are known; J. Brockmeyer and J.F. Pizzirusso, "Ceramic Foam Offers Surprising Properties," J. Materials Engineering, pp. 39-41, July 1988 and Antsiferov, V.N., Kundo, N.N., Ovchinnikova, V.E., Nokhrina, T.F., Porozova, S.E. and Fedorov, A.A., "Methane Conversion Catalyst Support Produced by Means of Powder Metallurgy," Russian J. Appl. Chem., 1990, No. 9, pp. 1993-2003.

HETEROGENEOUS GASE PHASE CATALYTIC OXIDATION OF ETHANOL TO ACETIC ACID OVER THE Sn - Mo OXIDE CATALYST

M.A.ARELLANO*, O.N. TEMKIN,*N.Kh. ALLAKHVERDOVA, and I.V. CHEREPNOV***
*Lomonosov Akademy of Fine Chemical Technology, Moscow, Russia
** Azizbekov Azeri Technological University, Baku, Azerbaidzhan

Alcohols obtained from the natural biomass, which are renewable resources, can be considered as possible key source of raw materials. This especially the case of those countries in which there are no deposits of natural hydrocarbons. In particular, ethanol is a universal raw material in chemical industry; for instance, ethanol can be used to obtain acetaldehyde and acetic acid.

Earlier it was found that the solid solution of Mo and Sn oxides is capable of catalyzing the oxidation of diluted (~ 20%) solutions of ethanol to acetic acid at a substantial selectivity (up to 60%) [1,2]. The goal of this paper is to study the metods of increasing the selectivity and the concentration of acetic acid in the condensate of process on this catalyst.

The catalyst (atomic ratio Sn: Mo = 9 : 1) was prepared using the literature procedure [1]. The activity of the catalyst was measured in the quartz continuos flow fixed bed reactor. Ethanol was oxidized on the granulated catalyst (the size of granules is 1-2 mm) under athmospheric pressure at 170 - 380 °C. Liquid and gas-phase products were analyzed by the chromatography.

We studied the effect of dilution of the catalyst with quartz on the process characteristics (the ethanol : H_2O : air molar ratio = 1 : 10 : 8 , the volume rate 2500 h^{-1}). The portion of catalyst (α) was 20, 80, and 100 % (Figs. 1, 2)

It was found that optimum temperatures for acetaldehyde and acetic acids differ considerably from each other. The yield of acetaldehyde of 80 % can be achieved at 210 ° C and (α) = 20 %. The yield of acetic acid at 300 ° C and (α) = 80 % is 60 %.

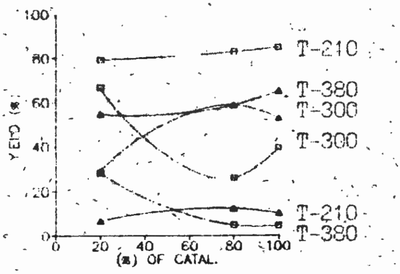


Fig. 1 (Δ) Acetic acid, (□) Acetaldehyde

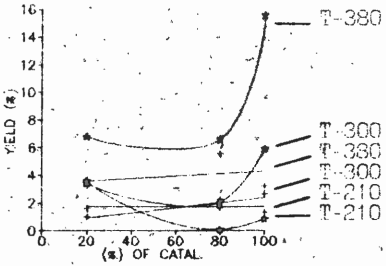


Fig. 2 (★) CO, (+) CO_2

The decrease in (α) was found to facilitate more uniform distribution of temperature along the reactor, especially when the ethanol concentrations increases. If one takes into account that the process occurs via the following scheme: ethanol ⇒ acetaldehyde⇒ acetic acid, the data obtained points to different conditions of these two steps.

An effect of alcohol concentrations studied shows that the yield of acetaldehyde slightly depends on the alcohol concentration, whereas the yield of acetic acid decrease with alcohol concentration. As this take place the concentration of CO increases, while the concentration of CO_2 remains virtually constant.

Additional experiments showed that when acetaldehyde is prepared from ethanol under optimum conditions, its oxidation to acetic acid also can be optimized. In this case, if the ethanol conversion is complete, the acetic acid can be obtained from 60 - 70 wt % alcohol at ~ 60% yield at the acetic acid concentration in condensate of ~ 35 - 40 %.

References

1. G.O. Tuarsheva.
HETEROGENEOUS CATALYTIC OXIDATION OF ETHANOL TO ACETIC ACID OVER THE Sn - Mo SYSTEM. Ph.D. Tesis. Baku, 1988.

2. N.Kh. Allakhverdova, K.Y.Adzhamov, T.G.Alkhazov.
KINET. CATAL. 1992, VOL. 33, Pg. 327-331
OXIDATION OF ETHANOL TO ACETIC ACID OVER THE Sn - Mo CATALYST

THE CATALYTIC TREATMENT AND DISPOSAL OF CHLOROORGANIC WASTE

Yu.V.BELOKOPYTOV

L.V.Pisarzevsky Physical Chemistry Institute Ukrainian National Academy of Sciences, 252039, Kiev,prospect Nauki,31, Ukraine.

It was known that the highly toxic compounds could be formed at the incineration of chloroorganic substances in the usual flame, for example dioxines. The catalytic methods, of utilization and disposal of the waste are the most perspective.

Our investigations were directed to the clearing up of the mechanism of the catalytic conversion of chloroorganic compounds with the purpose of simplification of the syntheses of the valuable chlorine-containing products as well as the determination of optimum conditions for the utilization and the complex treatment of the waste of the chloroorganic productions. The processes of the partial oxidation of chloro-(CB), dichloro- (DCB), trichloro-(TCB), tetrachloro- (TTCB) and hexachlorobenzenes (HCB) were studied on the promoted vanadium-molybdenum catalysts by different physical-chemical methods. It was shown that the maleic (MA), chloro- (CMA) and dichloromaleic anhydrides were formed at the oxidation of chlorine-containing benzenes. Besides, there are both less and more chlorinated benzenes in the reaction products. Thus, at the oxidation of CB there are benzene, o- (ODCB) and p-dichlorobenzenes (PDCB) in the reaction products besides MA and CMA. It is significant that the ratios MA:CMA and ODCB:PDCB do not practically depend on the temperature of the reactor. It was found that the chlorine in the chloro-derivative benzene molecules is mobile and the presence of high proton-donor acidity on the surface of the oxide vanadium- molybdenum catalyst favours both the isomerization reaction and disproportionation reaction.

The processes of complete oxidation of chloroorganic compounds on the oxide catalysts were investigated. The thermodynamic approach to the selection of the optimum catalyst of complete oxidation of chloroorganic compounds was considered. It was shown that the deep oxidation of benzene and its chloro-derivatives is realized for the same mechanism in which the limiting stage is the rupture of the C-C bond in the benzene ring. The more chlorinated benzenes could be formed at the deep oxidation of chlorobenzenes. It was explained by the proceeding on the catalytic surface of the reaction between the chemisorbed chlorine and the initial molecule.

It was studied the hydrogenolysis process of HCB, CTC, TCE, and hexachlorobutadiene (HCBD). The catalysts were produced and the conditions of dechlorination of the above mentioned compounds were determined. It was shown that the less chlorinated hydrocarbons would be predominated in the reaction products as a reaction temperature, the contact time and the ratio hydrogen:reagent increase.

The experiments on the catalytic oxidation and hydrogenolysis of real waste of CTC and TCE production containing mainly HCB, hexachloroethane, HCBD and CTC were carried out . It was shown that the combined application of catalytic processes of partial and complete oxidation as well as hydrogenolysis would make possible utilization and removal of the chloroorganic waste completely.

THE FLUORINE-CONTAINING CATALYSTS IN OXIDATIVE-COUPLING OF METHANE

A.G.Dedov, M.V. Vyshneckai, M.N. Kartasheva, L.E. Tskhai, A.P.Poliokov, E.M.Rudik.

State Academy of Oil and Gaz, Moscow, Russia.

The study of the methane activation and its selective transformations into valuable products is the fundamental problem and one of the key moment in the alkanes functionalyzation. So, during the last years the interest in oxidative transformations of methane was increased, in particularly the interest in oxidative coupling of methane (OCM). There are a lot of publications connected with OCM, but the ways of OCM still is not studied enough, the role of oxygen, oxygen and substrate intermediates forms nature is also not clear enough. Some authors described the formation of high hydrocarbons from methane on oxides systems, served as catalyst-reagent[1].

We studied the methane transformation on a number of catalysts: zeolite (Na- and H-forms) modified by fluorine in comparison with such systems as Fe-zeocar, zirconia and 10%-MnNaZVK. The fluorine-ion influence on the methane conversion was

Table 1. The OCM Results under t = 800 °C (v = 1000 h^{-1}, CH_4:air = 0,65 mol.)

Catalyst	Conv. tot.	Select. C_2		Products % mass.				AC_2	A by CO, CO_2	VC_2	V by CO, CO_2
			H_2	CO, CO_2	CH_4	C_2H_4	C_2H_6				
NaZVK	8,0	77,0	0,4	1,4	92,0	2,5	3,7	341	81	136	33
2% F-NaZVK	3,6	59,0	3,8	1,1	96,4	1,28	0,85	117	63	47	25
11% F-NaZVK	4,4	80,0	0,4	0,6	96	2,4	1,2	196	31	78	12
HZVM	6,2	18,0	0,8	4,3	93,8	0,7	0,4	66	250	26	100
0,2%F-HZVM	2,0	51,0	0,4	0,6	98,0	0,6	0,4	78	77	31	31
0,4%F-HZVM	3,0	46,0	0,3	1,2	97,0	0,6	0,6	65	65	26	26
0,5%F-HZVM	5,0	52,0	0,3	2,1	95,0	2,1	0,5	147	120	59	48
Quarts	1,5	74,0	0,3	0,07	99,0	0,52	0,59	-	-	21	1,6
Fe-zeocar	3,3	41,0	0,5	1,5	97,0	0,42	0,9	67	74	30	33
ZrO_2	8,0	15,0	0,5	6,2	92,0	0,5	0,6	57	314	26	141
10%Mn-NaZVK	17,0	50,0	0,5	8,0	83,0	6,0	3,0	380	374	190	187

AC_2, A, CO, CO_2 - productivity by C_2-hydrocarbon and carbon oxides, mmol/h · g · Ct

VC_2,VCO- speed of products form, mmol/h investigated.

The catalytic experiments were carried out at atmospheric pressure and temperature 700 - 850 °C, V=1000 h^{-1}, methane:air=0,65 mol in a flow quartz reactor. The reaction products were analysed by gas-liquid chromotography by using two columns: 5 metres, Al_2O_3 modified by $NaHCO_3$, 3 metres, the coal-carrier. The standard deflexion is 0,5.

The experimental results are introduced in Table 1. The best value of C_2- hydrocarbon selectivity is observed for sample 11%F-NaZVK. It is 80% under conversion 4,4%(mass).

It was shown that the results of reaction depend essentially on catalyst acid-base properties. The conversion is changed weakly and the C_2-hydrocarbon selectivity on F-NaZVK (80%) is much more greater than the selectivity on F-HZVM (50%). Besides there are some liquid oxidative products on the H-ZVM catalysts modified by fluorine.

The fluorine-ion modification of NaZVK does not influence on reaction, and fluorine-ion modification of HZBM increases the C_2-hydrocarbon selectivity from 18--22% to 52-57%. The fluorine perhaps prevents the more deep oxidation. The conversion on zirconium oxide -11%- at temperature 850°C was the best, but C_2-hydrocarbon selectivity was not high - 20 %.

Literature.

1.Keller G.E., Bhasin M.M. Synthesis of ethylene via oxidative coupling of methane. 1.Determination of active catalysts //J.Catal., 1982, v.73, p.9.

NOVEL OXIDATIVE ALKOXYLATION and AMINATION of PH_3 and P_4 CATALYZED by Cu(II) CELLULOSE ANCHORED COMPLEXES

Ya.A.Dorfman, G.S.Polimbetova, L.V.Levina and R.R.Abdreimova

Institute of Organic Catalysis and Electrochemistry of National Academy of Sciences, Kunaev St., 142, 480100 Almaty, KAZAKHSTAN

Copper(II) complexes coordinative anchored to cellulose throught its glycol HO-groups (1) catalyze the new reactions of phosphine (2) and tetraphosphorus (3) oxidative alkoxylation and amination.

$$[C_6H_7O_2(OH)_3]_n + nCuX_iL_jY_m \rightleftarrows [C_6H_7O_2(OH)_3CuX_iL_{j-1}Y_m]_n + nL, \qquad (1)$$

η^1– X = HO^-, RO^-, NH_2^-, $R'HN^-$, R'_2N^-; η^2– X= $H_2NC_2H_4NH^-$, $C_3H_5(OH)_2O^-$, $C_2H_4(OH)O^-$, $C_4H_8(OH)O^-$, $C_2H_4OC_2H_4(OH)O^-$; L = HX ; Y = $R''CO_2^-$; R = Me, Et, Pr, i-Pr, Bu, i-Bu, Am, i-Am, Oct ; R' = Et , i-Pr , $PhCH_2$, C_6H_{11}; R" = CH_3, C_3H_7, $C_{17}H_{35}$.

$$PH_3 + 2O_2 + 3HX \longrightarrow X_3PO + 3H_2O, \qquad (2)$$
$$P_4 + 5O_2 + 12HX \longrightarrow 4X_3PO + 6H_2O \qquad (3)$$

This catalysts were used in the manufacture of the light valveless respirators for protection from high toxic PH_3 and P_4 (2-20 mg/m^3).The highest specific activity at room temperature and contact time about 10^{-2}– 10^{-1}s has been achieved by the heterogenization of the badly solved in organic solvents Cu(II) complexes.

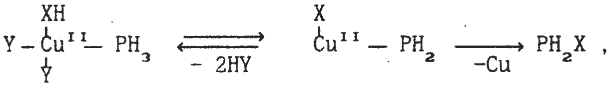
The catalytic processes (2,3) were studied by methods of differential kinetics, chemical modelling and inhibition of free radicals; the products have been analyzed by GC and ^{31}P NMR - spectroscopy. The intermediate Cu(II)complexes and transition states were investigated by XPS-, UV-, IR-, EPS-spectroscopy and quantum-chemical methods CNDO , MWG, PMO.

Mechanistic studies reveal a redox coordination mechanism of the new reactions (2,3) comprised of two major steps :

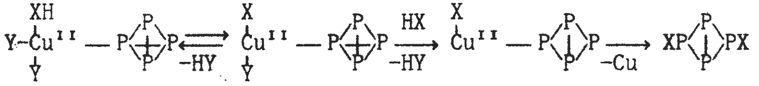
a) reduction of Cu(II) by PH_3 or P_4 , liberating Cu(0) and the phosphororganic product;

b) oxidation of Cu(0) by O_2 again into Cu(II).

Both low-polar PH_3 and non-polar P_4 are activated upon coordination. The bonds P-H and P-P become weaker and can be broken by innerspheric bases; P-atoms acquire a positive charge and form donor-acceptor bonds with covalent bonded X-ligands. At rate determining step the innerspheric bi - electron redox colapse of PH_3- or P_4- including Cu(II) complexes is realized.



$$Y-\underset{\downarrow \atop Y}{\overset{XH}{Cu^{II}}}-PH_3 \underset{-\,2HY}{\rightleftarrows} \overset{X}{Cu^{II}}-PH_2 \xrightarrow[-Cu]{} PH_2X\ , \qquad (4)$$

 (5)

The following oxidation of PH_2X or P_4X_2 proceed by the same way. In contrast to the complemental Cu(II) complexes noncomplemental Fe(III), Co(III), Mn(III) ones are not active in reactions of type (4,5). The calculations of the surface profile of potential energy of the innerspheric reaction between PH_3 and X- ions show that change of the angle between Cu-PH_3 and Cu-X bonds leads to the appearance of potential barrier. The altitude of latter depends on the nature and number of coordinative and covalent bonded ligands and can be correlated with kinetical and activation parameters of reaction (4). At the movement of PH_3 along the reaction the P-H bond become considerably weaker and the forming P-X bond stronger.

The composition of PH_3, P_4 oxidation products depends on the nature of the anchored catalyst ligands. In the presence of HO^-- ligands the reactions of PH_3, P_4 oxidative hydroxylation to H_3PO_4 are carried out. Alkoxyd-, glicoxyd-, glycerate- and amid-ligands can react with PH_3 or P_4 only in the absence of hydroxyd -ligands to give predominantly the linear alkyl- and amidophosphates. Ammonia and coordinative bonded cellulose do not undergo oxidative phosphorylation by PH_3, P_4. Only covalent bonded ligand heteroatoms (O,N) can react with coordinated PH_3 or P_4. The stabilization energy of innerspheric reaction between PH_3, P_4 and covalent bonded with Cu(II) heteroatoms is on order higher than with donor-acceptor bonded ones. Therefore the product composition depends also on the capacity of substrates (H_2O, NH_2R, ROH) to deprotonization.

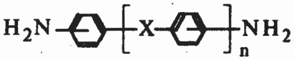
The research described in this publication was made possible in part by Grant No MY1000 from International Science Foundation and Grant No TA-MOU-CA 13-041 from US AID.

CATALYTIC HYDROGENATION OF NITRO- AND DINITROPOLYAROMATIC SUBSTANCES WITH DIFFERENT FOOT-PATH GROUPS - THE WAY OF SYNTHESIS MONOMERS FOR THERMOSTABLE AND THERMOPLASTIC POLYMIDE COMPOSITIONS

M.V. Dorogov, E.M. Alov, Y.A. Moskwichev, V.V. Plakhtinskii

Yaroslavl State Technical University, Yaroslavl

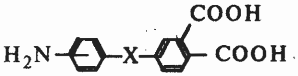
Recent publications in scientific literature has demonstrated big interest to fundamental and applied research in the field of nitrogen bearing heterociclic polymers, first of all - polyimides and polyamides. Aromatic diamines and dianhydrides are traditional monomers for polyimides. Authors used catalytic hydrogenaion of dinitroaromatic substances for receipt following diamine-monomers:



where $n=1...5$; X= -O -, -CO-, $-CH_2-$, $-C(CH_3)_2-$, -S-, $-SO_2-$, -O(CO)- or σ-bond; $-NH_2$ - in meta- or para-position in regards to foot-path groups.

On base of this diamines and aromatic anhydrides of 1,2,4,5-benzentetracarboxylic; 3,3′,4,4′ -diphenyloxydtetracarboxylic; 3,3′,4,4′ - benzophenonetetracarboxylic acids received poly- imides with low glass transition temperatures (210...240 °C), low melting points (330...350 °C), excelent thermostable and high adhesion properties, more easily processing.

Besides that, we use catalytic hydrogenation for synthesis aminophthalic acids, that have both parts of imide fragment in their structure - anilyne and phthalic acid groups:



where X=-O-, -CO-, $-SO_2-$; $-NH_2$ - in meta- or para-position in regards to foot-path groups.

Applications of this types of homopolycondensation monomers have some advantages, first of all, absence of necessity to regulate equimolar correlation diamine - dianhydride.

Autors conduct investigation, concerning elaboration synthesis of aromatic amines by catalytic hydrogenation of correspon-ding nitrocompounds.

We discuss following questions in our report:

1. The impact of different parametrs (temperature, hydrogen pressure, structure and initial concentration of nitrosubstrate, nature of solvent or pH of water phase) upon the reaction rate, selectivity and aminoproducts yield.
2. Adsorption model of catalytic heterophase hydrogenation.
3. Determination of kinetics parametrs.
4. Promoting action of water on the rate of catalytic hydrogenation in organic solvents.

5. The relation conversion - reaction time (on base of kinetics).
6. The most effective conditions of catalytic hydrogenation.
7. Problem of intermediate products.
8. The catalysts (deactivation and methods of regeneration).
9. Isolation and identification of aminoproducts.

Control of Acceptor and Donor Properties of Alumina by means of Treatment by Acids and Bases.

A.V.FIONOV, E.V.LUNINA

Chemistry Department, Moscow State University, 119899, Moscow, Russia. Fax: 095 9390067.

Alumina, especially η- and γ-phases, is used as catalyst and as component in the complex catalytic compositions. In connection with this a great attention is paid to the search of the ways of the modification of the alumina surface to obtain desired catalytic properties. One of these ways is the impregnation of the alumina by water solutions of inorganic acids and bases with the following drying and calcination. In spite of the wide use of the such treatment in practice, conceptions about the surface structure are insufficiently developed. Many of experimental methods, used for the study of electron-acceptor properties of the alumina (calorimetry, titration with Hammett indicators, IR-spectroscopy), give the information about the strength and the concentration of the electron-acceptor centers (Lewis acid sites - LAS). However, these methods give no direct evidence of the structure of the LAS.

Data of the EPR of paramagnetic complexes of the probe molecules - anthraquinone and tetramethylpiperidine-N-oxyl (TEMPO) [1] permit to obtain the information about both the structure of LAS and its relation with the crystal structure of the alumina. As it has been shown on the dehydroxylated (T=720-920 K, P=10^{-5} Torr) γ- and η-Al_2O_3 surfaces the local concentrations of LAS - three coordinated aluminium ions (Al^{3+}) are high and these ions are arranged regulatively. These data confirm the concepts of Al^{3+} formation as a result of the terminal OH-groups removal from Al-ions in a tetrahedron coordination, disposed on (111)A and (110)C planes.

The obtained experimental data permit to confirm the crystallographic model of the alumina surface (Knozinger et al. [2]). The comparison of the IR-spectra of adsorbed carbon monoxide with the EPR data allows to assume that the presence of two bands 2230-2245 cm^{-1} and 2200-2215 cm^{-1} 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-acceptor properties among one family of Al^{3+} are accounted for the structure of the second coordination sphere, formed by hydroxyls, atoms of oxygen and vacancies of the external oxygen layer. The structure of the second coordination sphere depends on the calcination temperature, nature and concentration of the modifying agents.

Data on the anthraquinone adsorption have showed that the treatment by acids (H_3PO_4, H_3BO_3) and bases ($Ca(OH)_2$, NaOH) causes the blockage of Al-ions in a tetrahedron coordination and results in the decrease of the total and local concentration of LAS on the alumina surface. This blockage comes from the random interaction of the modifying agents with the surface hydroxyls. The TEMPO adsorption showed that the remaining LAS are weeker (especially at the treatment by H_3BO_3 and NaOH) than on the pure alumina. However, remaining LAS have the same structure of three coordinated aluminium ions.

The new acid sites appear at the treatment of the alumina (P-OH and B-OH in the case of H_3PO_4 and H_3BO_3; coordinately unsaturated Ca^{2+} in the case of $Ca(OH)_2$). The treatment of alumina by bases also increases the donor properties of alumina surface. The anthraquinone adsorbed on electron-donor centers forms the anion-radical anthrasemiquinone.

1. E.V.Lunina, in O.A.Petrij and V.V.Lunin (Eds). Catalysis. Fundamental and Applied Studies. MGU, Moscow, 1987, p.262.
2. Knozinger H., Ratnasamy P. // Catal. Rev. Sci. Eng. 1978, V.17, N.1, p.31.

GIANT PALLADIUM CLUSTERS IN SOFT OXIDATION OF ETHANOL

Hladiy S.L.*, Starchevsky M.K.*, Pazdersky Yu.A.*, Vargaftik M.N.** and
Moiseev I.I.**

* *"Syntez" Research Institute, 293760 Boryslav, Ukraine*
***N.S. Kurnakov Institute of general & Inorganic Chemistry,*
Russian Academy of Sciences, 117907 Moscow, Russian Federation

Giant palladium clusters Pd_{561} $phen_{60}$ $(OAc)_{180}$ (I) and Pd_{561} $phen_{60}$ $O_{60}(PF_6)_{60}$ (II) have been known to be active catalytic systems being able to catalyze processes that differ both character and direction [1,2].

In ethanol solutions of clusters (I) and (II) alcohol oxidation was revealed to flow actively in extremely soft conditions at the temperature 293-323 K even if cluster concentration was in scale 10^{-5} - 10^{-4} mol/dm^3 (see table). During oxidizing anhydrous ethanol besides acetic aldehyde, ethyl acetate, acetic acid and acetal there has been formed also acetic anhydride as a reaction product.

Acetic aldehyde and ethyl acetate have been found to be the primary reaction products. Ethyl acetate has been formed mainly through direct ethanol oxidizing:

$$2CH_3CH_2OH + O_2 \rightarrow CH_3CH_2OCOCH_3 + 2H_2O \quad (1).$$

Some ester amount has been a result of the Tischenko process:

$$2CH_3CHO \rightarrow CH_3CH_2OCOCH_3 \quad (2).$$

Alcohol acetylation with formed anhydride has not been catalyzed by clusters and is imperceptible under mentioned conditions.

The character of kinetic curves has showed acetic anhydride to be formed through following reaction sequence:

$$CH_3CH_2OH \rightarrow CH_3CHO \rightarrow (CH_3CO)_2O \quad (3).$$

Acetic anhydride formation rate increases up to stabilization of acetic aldehyde concentration and, after having achieved maximum, sharply falls. As the formed water has caused hydrolysis the concentration of acetic anhydride afterwards has decreased.

In ethanol solution cluster (I) has been found to be more active for oxidative reactions. Cluster (II) however has exhibited high catalytic activity for acetal formation.

Table

Product formation rates in oxidation of ethanol with oxygen catalyzed by (I) and (II) clusters

Cluster concentration () × 10^5,M	Temperature K	Initial formation rate $V_0 \times 10^4$,M/min				
		EtOAc	CH_3CHO	$(AC)_2O$	AcOH	$C_2H_4(OEt)_2$
(I) 7.24	303	3.0	70	0.5	1.2	< 0.02
(II) 7.10	313	6.5	120	1.7	2.0	< 0.02
(I) 7.49	323	13.0	258	3.4	4.2	< 0.02
(II) 7.06	313	1.6	42	0.3	1.6	0.93

Referenses

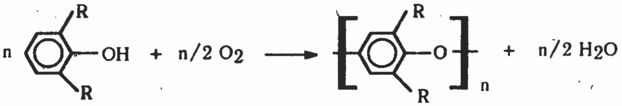
1. Vargaftik M.N., Zagorodnikov V.P., Stolarov I.P., Moiseev I.I., Kochubey D.I., Likholobov V.A., Chuvilin A.L. and Zamaraev K.I., J.Mol.Catal., 1989, 53, P.315-348.
2. P.I. Pasichnyk, M.K. Starchevsky, Yu.A. Pazdersky, V.P.Zagorodnikov, M.N. Vargaftik, I.I. Moiseev, Mondeleev Commun., 1994, P.1-2.

POLY(PHENYLENE OXIDES) - CATALYTIC SYNTHESIS AND MEMBRANE APPLICATION

O.M.Ilinitch [(a)], N.E.Kim [(b)], B.M.Khlebnikov [(b)] and V.A.Likholobov [(a)]

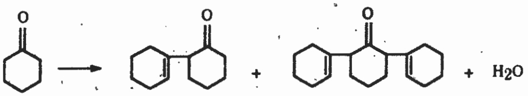
(a) Boreskov Institute of Catalysis
(b) Research Institute of Chemical Technology
Novosibirsk, Russian Federation

In the late fifties, the process for the poly(phenylene oxide) production had been commercialized by the General Electric Co. This process is based on the catalytic reaction of oxidative polycondensation of 2,6-dimethylphenol:

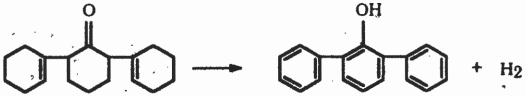


It is known that the properties of various polymers can be improved by means of copolymerization. Our work was aimed at the synthesis and application of the (co)polymers of poly(phenylene oxide) family. The materials comprised homo- and copolymers of 2,6-dimethylphenol and 2,6-diphenylphenol (i.e., in the above equation R = CH_3 or C_6H_5). The latter is not available commercially; therefore, the study on its catalytic synthesis have been carried out.

The catalytic synthesis of 2,6-diphenylphenol consists of the next four stages:
(1) condensation of cyclohexanone catalyzed by alkalis or acids with bi- and tricyclic ketones being the reaction products:



(2) isolation of tricyclic ketones;
(3) selective catalytic dehydrogenation of the tricyclic ketones to 2,6-diphenylphenol:



(4) isolation and purification of 2,6-diphenylphenol.

Purified 2,6-diphenylphenol is further used in the (co)polycondensation reaction catalyzed by the copper-amine organometallic complexes and producing the (co)polymers of poly(phenylene oxide) family. Regularities of all the above mentioned stages have been studied to form the basis for the pilot-scale production of the polymers with any desired ratio of the dimethyl- and diphenyl-substituted phenol (co)monomers. The copolymers were found to be superior to the conventional PPO (the homopolymer of 2,6-dimethylphenol) in thermal stability, resistance against oxygen, radiation etc.

The polyphenyleneoxides are being intensively studied as the potential gas separating membrane materials. Here we report on the properties of the homo- and copolymers of 2,6-dimethylphenol and 2,6-diphenylphenol in membrane separation of air. In this study, permeability, sorption and diffusivity of oxygen and nitrogen in the polymers have been investigated. The data are summarized in Figs. 1-2 and Table 1. As can be seen, poly(phenylene oxides) possess the relatively high separation selectivity for the oxygen/nitrogen pair, which is due to the much higher permeability of oxygen. In turn, high permeability of oxygen results from its high diffusivity compared to that of nitrogen, while adsorption of these gases in the polymers is about the same.

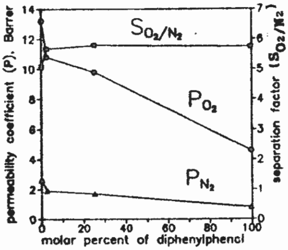


Fig. 1. Permeability coefficients and separation factor for air separation over poly(phenylene oxides) at 273K

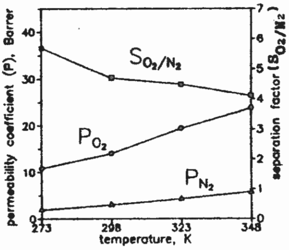


Fig. 2. Temperature dependence of permeability coefficients and separation factor in air separation over Copolymer 1

Table 1. Permeability, sorption and diffusion coefficients for nitrogen and oxygen in poly(phenylene oxides) at 298K:

PPO - homopolymer of 2,6-dimethylphenol;
PPhPO - homopolymer of 2,6-diphenylphenol;
Copolymer 1 - 97,5 mol.% of 2,6-dimethyl- and 2,5 mol.% of 2,6-diphenylphenol;
Copolymer 2 - 75 mol. % of 2,6-dimethyl- and 25 mol.% of 2,6-diphenylphenol.

Polymer	P_{O2} Barrer	P_{N2} Barrer	$S_{O2} \cdot 10^3$ cm^3 cm^{-3} cm Hg^{-1}	$S_{N2} \cdot 10^3$ cm^3 cm^{-3} cm Hg^{-1}	$D_{O2} \cdot 10^7$ cm^2 s^{-1}	$D_{N2} \cdot 10^7$ cm^2 s^{-1}
PPO	21	4.7	13.3	9.0	1.6	0.52
Copolymer 1	14	3.0	9.0	5.35	1.6	0.56
Copolymer 2	13	2.8	7.6	-	1.7	-
PPhPO	7	1.5	4.6	-	1.5	-

ACIDITY EFFECT ON ALUMOSILICATE CATALYTIC PERFORMANCE AT β-PICOLINE SYNTHESIS VIA ACROLEIN CONDENSATION WITH AMMONIA

A.S.Ivanova, E.M. Al'kayeva, T.V.Andrushkevich
V.M.Mastikhin and E.A.Paukshtis

Federal Scientific Center "Boreskov Institute of Catalysis",
Pr.Akademika Lavrentieva, 5, Novosibirsk 630090, Russia

β-Picoline serves as a feedstock at the synthesis of many pharmaceuticals, pesticides and biologically active substances. The ways to increase its yield at the acrolein condensation with ammonia are intensively studied today.

The aldehyde condensation with ammonia goes through the aldols formation, followed by their cyclization with ammonia [1,2]. OH-groups and the Lewis acid sites (LAS) participate in the aldols formation. According to [2,3], the Broensted acid sites (BAS) assist the cyclization reaction producing heterocycles. Amorphous alumosilicates comprise usually both acid sites and, thus they are promising for this reaction.

In the present work we have studied how the preparation procedure, composition and the treatment temperature affect the phase composition, surface, acidic and catalytic properties of Al-Si-O-samples at the acrolein condensation with ammonia. We have found that the phase composition of samples is a mixture of silicium and aluminium oxides of the corresponding modification. The latter depends on the calcination temperature. Amorphous alumosilicates, whose degree of ordering increases with the treatment temperature, are also present. According to the ^1H MAS NMR data, Al-Si-O-samples contain OH groups, connected with Al (I) and Si (II). A relationship between the amount of OH-groups of both types depends on the SiO_2 content and treatment temperature: as SiO_2 content increases from 19 to 50 mol.%, the portion of II increases from 0.6 to 1.0 (rel.units), while the amount of I does not practically change. The calcination temperature rise from 700 to 1250°C is accompanied by a simultaneous decrease of portion II from 1.0 to 0.3 (rel.units). The concentrations of BAS and LAS, related to m^2, increase as the silicium dioxide content decreases (Table). The LAS in distribution power is determined by the composition, preparation tecnique and temperature of calcination (Table).

Table.

Catalytic Properties of Al-Si Samples as a Function of Acidity

№ №	SiO$_2$ content, mol.%	T$_{calc}$, °C	BAS	LAS			T$_{reac}$, °C	X, %	S, %		B, %
				L:Py	L:CO				β-picoline	pyridine	
			μmol/m^2		μmol/g						
1	96.5	700	0.047	0.17	2197/63	2230/23	330	98.0	55.0	40.0	95.0
2							390	98.0	64.5	30.0	94.0
3	50.0	700	0.070	0.31	2195/80	2230/30	330	97.0	41.7	13.2	54.9
4							350	97.0	40.0	20.0	60.0
5	50.0	700	0.029	0.50	2195/140	0	350	98.0	60.3	19.7	80.0
6							390	98.2	69.2	20.1	89.3
7		1000	0.044	0.87	2195/155	0	390	96.0	70.0	20.4	90.4
8		1250	0	0.92	2195/45	2230/26	390	80.2	55.8	14.1	69.9
9		1000	0.044	0.87	2195/155	0	390	91.3	55.3	26.0	81.3
10	36.0	1000	0.058	1.13	2190/160	2230/7.5	390	92.8	43.4	25.0	68.4
11	19.0	1000	0.063	1.19	2190/175	2230/16	390	86.8	37.8	22.8	60.6

In runs 1-4 we used samples prepared by Al- and Si - components precipitation; in runs 5-11 samples were prepared by components mixing. Runs 1-8 were performed in an integral reactor and 9-11 - in a differential one.

The catalyst activity and selectivity depends on the content of surface OH-groups, LAS concentration and to a lesser extent on the BAS concentration. The yield of β-picoline, the main reaction product, increases if the concentration of strong (ν_{CO} = 2230 cm^{-1}) LAS decreases.

Al-Si-O-catalyst of the equimolar composition, obtained via mixing, exhibits the optimum surface state.

REFERENCES

1. A.E. Chichibabin, Fundamentals of Organic Chemistry, vol.1, Moscow 1963.
2. A.P. Ivanovskii, Heterogeneous Catalysis for the Chemistry of Heteropoly Compounds, p. 19, Moscow 1987.
3. E.S.Sirlibayev, A.Ikramov, G.Mukhtazo, N.V.Kryukova in Catalysis and Catalytic Processes for Chemical Productions, P.2, p. 223, Moscow 1989.

EFFICIENCY OF ELECTROPHILIC CATALYSTS OF SEMI-FUNCTIONAL ACTIVITY IN RELATION TO THEIR ACID STRENGTH

S.R.Ivanova, K.S.Minsker

Bashkirian State University, Ufa

Metal chlorides as weak Broensted acids, if compared to typical catalysts based on $AlCl_3$, $SnCl_4$, assisted by proton donors (H_2O, HCl, ROH) appear to be quite promising for many electrophilic processes: polymerization of olefins, destruction and depolymerization of polyolefins, alkylation of phenols and aminophenols by polyolefins, and destruction and hydrodesulfurization of various sulfur-containing organics.

The activity and selectivity of numerous electrophilic catalysts based on the chlorides of metals belonging to Groups IIa-Va, IIb, VIIb and VIII and of double and complex salts based on the chlorides of metals belonging to Groups IIIa and Ia and/or IIa,b have been studied experimentally. The conversion and yield of main reaction products appear to depend dramatically on the chemical structure of catalysts, the place of proper metal in the Periodic System as well as on the chemical origin of proton donors and solvents used.

The charges of hydrogen atoms (q_{H^+}) determine the electrophilic performance of the Broensted acid catalysts. These charges can be evaluated by quantum chemical semi-empirical method CNDO/2 using the model catalyst systems of stoichiometry catalyst:proton donor= 1:1. One can also use the universal acidity indicator (pK_α) that correlates with charge q_{H^+} according to equation $pK_\alpha = 25 - 100q_{H^+}$.

A relative acidity indicator is an alternative parameter to measure the strength of electrophilic catalysts. One can determine it via a differential non-aqueous titration without laborious quantum-chemical calculations.

You can follow a linear correlation like $pK_\alpha = f(q_{H^+})$ between POK and q_{H^+} or POK and pK_α in accordance to equation $POK = 13.32q_{H^+} - 1.03$ (the correlation coefficient equals 0.982 with a standard error of 0.187). For equation $POK = 2.3 - 1.22pK_\alpha$ the correlation coefficient equals 0.0996 with a standard error of 0.084.

The combination of experimental and theoretical results shows clearly that parameters q_{H^+}, pK_α and POK determine the strength of Broensted acid electrophilic catalysts and thus their activity and selectivity in all reactions involving carbon-ion.

One can notice 2 thresholds of catalysts efficiency in electrophilic reactions: the upper one ($pK_\alpha \geq +11$; $POK \leq 0.9$ g-akv/g.cat) and the lower one ($-10 \leq pK_\alpha$, $POK \geq 3.0$ g-akv/g.cat). The first one occurs when the catalyst activity is extremely low. The second one happens when the catalysts are very active but secondary and by-reactions provide a considerable contribution. Experiment shows that the quantitative evaluation of acid catalysts strengths in electrophilic reactions helps to predict the catalysts efficiency.

HYDROCONVERSION OF AROMATIC HYDROCARBONS OVER NEW TRIMETALLIC CATALYSTS

Y.G. Kim[1], V.D. Stytsenko[2], V.A. Khavkin[3], J.S. Lee [1]

1- Research Center for Catalysis and Catalytic Technology, Pohang, Korea

2- Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia

3- All-Russian Research Institute of Petroleum Refining, Moscow, Russia

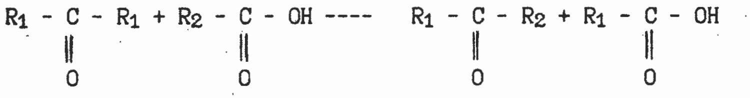
New trimetallic catalysts (TMC) for hydroconversion of aromatic hydrocarbons (AH) have been designed by modification of Ni/Al_2O_3 with organochromium compounds and phosphoromolybdic HPA. The catalysts were tested in hydrogenation of AH (T= 473-673 K, p = 0.1-1 MPa), hydrodemethylation of toluene (623-800 K, 0.1-1 MPa) and hydrotreating of a diesel oil (573-673K, 1-3 MPa) and theywere shown to possess a high activity, selectivity and sulfur tolerance under conditions of the processes above. The activity of TMC in these processes was much higher as compared with that of two-component (Ni-Cr, Ni-HPA) or conventional Ni/Al_2O_3 catalysts. Using TMC, toluene hydrodemethylation may be performed with improved selectivity in respect to benzene (>85%). The high sulfur tolerance of TMC was demonstrated by performing hydrodemethylation of toluene containing up to 0.03% S, as well as by hydrotreating diesel oil to decrease AH and sulfur content. The reasons for the sinergistic activity are considered to be interaction between Ni and Mo and acidity of HPA (to a minor extent). Thus, the trimetallic catalysts were shown to be very promising for hydroconversion of aromatic hydrocarbons and fuels containing thereof.

POTASSIUM ACETATE - CATALYST FOR ACID KETONIZATION

A.V. Kondratiev, V.S. Markevich

Joint-stosk company "All-Russian Research Institute of Organic Synthesis", Novokuibyshevsk, Russia

Receipt of asymmetric ketones by vapour-phase reaction between symmetric ketones and acids is realised on hard alkaline catalysts.

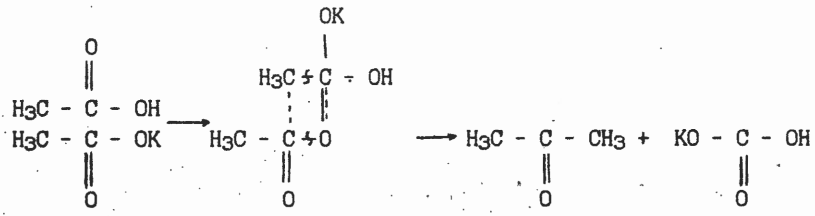


$$R_1-\underset{\underset{O}{\|}}{C}-R_1+R_2-\underset{\underset{O}{\|}}{C}-OH \;----\; R_1-\underset{\underset{O}{\|}}{C}-R_2+R_1-\underset{\underset{O}{\|}}{C}-OH$$

Presence of acid in the products of the reaction show possible formation of melt salt phase on catalyst surface area.

One can suppose, that catalytic act of ketonization is accepted to proceed through the intermediate formation of alkaline metal carbonate after salt decomposition. However, in products of acid ketonization (catalyst - melt potassium acetate) at high selective asymmetric ketones receipt potassium carbonate is absent.

Comparing the pyrolysis rates of potassium acetate and acetic acid in the melt of potassium acetate under conditions we discovered that in the second case the reaction proceeds several times as fast. So, acetic acid is supposed to be decomposed catalytically under the influence of potassium acetate by carbonyl coordination of ion-acetate.



For evidence of supposed catalytic mechanism instead of acetic acid propionic, butanoic, isobutanoic acids were utilised. Methylethylketone, methylpropylketone and methylisopropylketone are received accordingly.

COMPUTER PREDICTION OF Pt-CATALYST ACTIVITY OIL REFINING

A.V.Kravtsov, E.D.Ivanchina, T.V.Kravtsova

Polytechnic University , Tomsk, Russia

SUMMARY

The problem of computer prediction of Pt-catalysts activity depending on service life and technological conditions has been solved. The proposed method of computer prediction based on physical, chemical and technological lows of multicomponent hydrocarbons transformation on Pt - polymetal catalysts.

This method takes into account the dynamics of the acid and metal activity. It has the possibility of the automatic calculation of the optimum input of the activity enhancing additions.

RESULTS AND DISCUSSION

The proposed method of the elaboration of the effective technologies based on the kinetic oil refining models, isomerization, hydrocracking has possibility to produce the calculation of the multicomponent raw oil. It is necessary to take into account the mutual connection of reactional and seperating water and sulphur content for the reliable simulation.

We suggest generalized model of the thermal and catalytic transformation of individual hydrocarbons. It has been used to elaborate the effective complex technology for transformation of oil into the ecologically pure petrol and to predict the catalysts activity of different kinds and so its lifetime. The model is founded on the dehydrogenation, dehydrocyclization, isomerization and hydrocracking. The particular behaviour of catalysts and its deactivation and reactivation are assumed. Some industrial Pt-catalysts for reforming, isomerization and hydrocracking are studied. The intellectual knowledge base is made, that includes acid and metal activity variation of polymetal Pt-catalyst and the diagnosis of the possible deviation of the industrial process regulations. It gives the recommendations how to exclude this deviations. The kinetic formula is suggested that connects the reaction velocity with catalysts activity and number of its regenerations. This gives reliable opportunity to predict the work of the industrial reactors. The nonstationary model assumes some coke deactivation. In this model the poison of active catalytic centre by coke is taken into account.

The reactivation kinetic of Pt-catalyst is investigated and the calculation formula is suggested. Using them the optimum expenditure of the organic cloride may be assessed.

The digital assessment of differential promotor input in the numerical reaction zone was fulfilled. This input is function of water and harmful admixture contents. There is prediction of activity due to catalyst prehistory. This makes it possible to select the optimum technological regime and the raw materials supplying for reforming unit.

On base of proposed method we predicted reforming unit work depending on technological conditions and raw material quality:

1. Efficient technological schemes of different reforming variants.
2. Optimal construction solution of untraditional schemes.
3. Forecast of activity and duration of Pt-catalysts service life.
4. Investigations of influence of percomponent composition of start - materials with taking in consideration concentration of harmful additions and moisture of reforming product output and its quality.
5. Diagnostics of emergency conditions and recommendations for their removal.
6. Activity of Pt-catalysts reduction conditions and concentrations of chloro-organic compounds account.
7. Forecast of product compositions and its octane number depending on acid level and metallic activity of catalysts.
8. Computer evaluation of using different catalyst efficiency in reforming process.

This prediction system has been used in the oil refining plants.

THE NEW CATALYSTS FOR METATHESIS REACTIONS OF OLEFINS AND SUBSTITUTED OLEFINS WITH FUNCTIONALY GROUPS

Kreuchkov V.A., Slovetsky D.I., Popov V.T., Prokophjev A.V.
Bogolepova E.J., Vinogradova T.S., Slivinsky E.V.

Topchiev Institute of Petrochemical Synthesis RAS, Moscow

Yeurjev G.S.

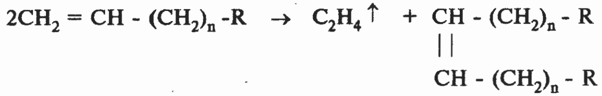
Boreskov Institute of Catalysis SB RAS, Novosibirsk

The metathesis of alkens or especially of substituted olefins with functional groups are interesting for synthesis of valuable organic products [1,2].

The rhenium oxide on γ-Al_2O_3 catalysts with high Re_2O_7 contents (about 15 w.%) are usually used for this reactions.

It is interesting to have rhenium systems containing less concentration of active metal. This may be achieved using more effective carrier. We use the new alumina carrier prepared with the original technology. It consists of the agglomerates (d~50-500 μ) with the capillar morphology and has the surface area in the range 180-400 m^2/g. The diameters of the through capillars are equal to about 0,1 - 0,5 μ. The phase compositions of the initial aluminium hydroxide is X-ray amorphous or amorphous with admixtures of pseudoboehmite, bayerite or even diaspore phases. After high-temperature treatment (500-700 ^0C) alumina consists of δ, θ and α-phases and surface area being little changed.

The reactions of metathesis have been conducted as models with the n-hexene-1 and allylchloride under normal conditions with the static type equipment under stirring and withdrawing one of the products (ethylene)



$$2CH_2 = CH - (CH_2)_n - R \rightarrow C_2H_4\uparrow + \begin{array}{c} CH - (CH_2)_n - R \\ || \\ CH - (CH_2)_n - R \end{array}$$

where R=-H; -Cl.

The activity and stability of the catalysts on the base of this carriers are shown to be dependent on initial alumina structure and composition and also on the parameters of the finishing preparing operations (temperature, treatment, time and etc.). The prepared optimal alumina - rhenium catalysts containing reduced concentration of Re_2O_7 (about 2,5 w.%) provide high rate of model metathesis reactions and high stability of the system. The productivites are increased by 1,4-2,9 times.

Thus using of alumina-rhenium catalysts on the basis of new alumina opens new opportunity for more effective synthesis of many valuable chemical products (such as pheromones, protaglandins, etc.) wich cannot be synthesied by any other way.

1. Mol J.C. Metathesis of Functionalized Olefins. - J.Molec. Catal.,1982, v.15, p.35
2. Bogolepova E.J. at all. Neftechimiya,1986,v.26,N 2, p.185-188

EFFECT OF MODIFIED MAGNESIUM OXIDE ON N-BUTANE HIGH-TEMPERATURE DECOMPOSITION

S.Yu. Kuz'mitskaya, N.A. Vasilyeva

Federal Scientific Center «Boreskov Institute of Catalysis», Novosibirsk 630090, Russia

Much attention is given to MgO-based catalysts in oxidative coupling of methane (OCM) all over the world. However, few papers are devoted to such catalysts in the oxygen-free hydrocarbons pyrolysis although magnesium oxide is known to accelerate radical-chain pyrolysis reactions [1].

Here, we consider the effect of a modifying component on n-butane high-temperature decomposition in temperature interval 600-800 °C. Two types of catalysts prepared via impregnating MgO with concentrated solutions of the salts with similar anions MgO/$MgAc_2$ and LiAc were studied. XRD data show the dry samples to have the structure of defect Mg hydroxide, while the structure of those calcinated at > 350 °C is typical for MgO. Specific surface of the samples obtained is 0.6-47 m^2/g.

MgO/$MgAc_2$ is shown to exhibit a higher catalytic activity in n-butane pyrolysis than initial MgO (at 700 °C, n-butane conversion degree for MgO/$MgAc_2$ is 15% higher than for MgO). MgO/LiAc is not active. For OCM (oxidation atmosphere), the above samples are also shown to be inactive. It is therefore concluded that formation of the active centers taking part in free-radical reactions depends on the reaction atmosphere composition.

Analysis of light paraffins distribution and yield indicates an additional generation of radicals into the bulk. Within the temperature interval 600-700 °C, C-H bonds tend to break thus increasing the yield of H_2. At higher temperatures, methane and ethane yields increase what sais for a predominant breaking of C-C bonds. So, it may be assumed that the catalyst MgO/$MgAc_2$ has at least two types of active surface centers.

N-butane conversion degree over MgO/LiAc differs slightly from that for thermal pyrolysis. In this case, surface centers typical for active MgO and MgO/$MgAc_2$ are either absent or blocked by Li surface compounds formed under these conditions.

Thus, analysis of catalytic activity of MgO modified with MgAc and LiAc has shown that the suggested preparation procedure provides the defect MgO structure and the centers active in n-butane pyrolysis.

References

1. N.A. Vasilyeva, R.A. Buyanov, Kinetika i kataliz, 1993, v.34, N.5, p.835.

CATALYTIC PRODUCTION OF 4-METHYLTHIAZOLE

L.V.Manuilova, N.D.Parshukova and T.S. Sukhareva
Federal Scientific Center "Boreskov Institute of Catalysis"
Novosibirsk 630090, Russia

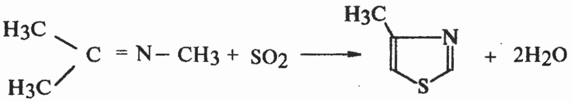
4-Methylthiazole (4-MT) is an important intermediate for the synthesis of thiabendazol (fungicide for diverse applications). The existing methods are mainly preparatory, thus limiting the accessibility of 4-MT [1]. 4-MT can be synthesized from methylisopropylidenimine (imine) and SO_2 on complex catalysts at 400-500°C. The yield of 4-MT is up to 60% on Fe_2O_3 (~ 90 mass %) - Cr_2O_3-Al_2O_3 [2] and 64 mass % on CaO (89 mass %) - NaOH (10 mass % - ZnO_2 (1 mass %) [3] catalysts. Yet this reaction is studied insufficiently.

In this paper we have studied the influence of the conditions of SO_2 interaction with imine on the yield of 4-MT, its formation rate on bulk (massive) and supported oxides and metal sulfides as well.

4-MT synthesis was performed in a fixed bed circular set up: P = 0.1 MPa, T = 300-500°C, imine concentration = 3-10 mol.%, SO_2 : imine = 1.3-3 (mol), τ = 0.2-4 s. The reaction products were analyzed by chromatography. Catalysts: γ-Al_2O_3, SiO_2, Mo and W sulfides, Fe, Mo and Cr oxides, both bulk and supported on a carbon carrier.

When no catalyst is used, the flow of imine and SO_2 vapors, passing through an inert gas (C_{im} = 4.5-5% and SO_2 : imine > 1) at 4 L/h, produces only 1-2% (400°C) and 9-10 mass.% (440°C) of 4-MT.

If catalysts are used, 4-MT forms under all studied conditions:



In both cases (with or without catalyst), the unreacted imine decomposes completely in the presence of SO_2 and H_2O under present conditions. By-products were not identified. Catalysts after experiments have shown the presence of C (up to 13 mass.%) and S (up to 11 mass.%).

At 400-440°C, the production of 4-MT is the most advantageous. For each catalyst, we have measured a 4-MT yield as a function of contact time at various temperatures. As the temperature and contact time increase, the yield of 4-MT also increase. We have found that the rate of 4-MT formation is proportional to the imine concentration.

Specific rates of the 4-MT formation related to the surface unit (at equal 4-MT yields) were used for catalysts estimation. According to the rate of 4-MT formation, the catalyst series is as follows:

$$Fe_2O_3 > Cr_2O_3 > MoO_3 > MoS_2 > \gamma\text{-}Al_2O_3 > WS_2 > SiO_2$$

	Fe_2O_3	Cr_2O_3	MoO_3	MoS_2	γ-Al_2O_3	WS_2	SiO_2
$W \cdot 10^3, g/m^2\ h$ (440^oC, $X_{4\text{-}MT}=30\%$)	45	26	25	4.2	1.9	0.9	0.4

The activity of Fe, Cr and Mo oxides is very close and an order of magnitude higher than that of sulfides. Though γ-Al_2O_3 and SiO_2 have a rather low specific activity, they are very promising for the 4-MT synthesis. They are more stable than Fe and Cr oxides. Moreover, γ-Al_2O_3 provides > 60 mass% and higher yields of 4-MT.

When Fe, Cr, or Mo oxides are supported on a C carrier, inert in this reaction, the regularities are similar to that observed for bulk samples. Yields and rates of the 4-MT synthesis on supported samples (5 mass.% of metal) are comparable to the values obtained for the bulk catalysts under similar conditions. They are respectively $\geq$ 60 mass.% and 0.4-0.8 $g/g_{cat.}$ h.

Thus, Fe, Cr, Mo, Al, Si individual oxides and Mo, W sulfides appeared to accelerate the 4-MT formation from imine and SO_2. For γ-Al_2O_3, the yield may be as high as 63 mass.% (400^oC, $\tau = 4$ s). Moreover, the catalyst appears to be more stable than the known one.

REFERENCES

1. Heterocyclic Compounds, Ed. V. Elderfield, vol. 5, Izdat. Inostr.Lit., Moscow 1961.
2. Sa V.Ho, St.Louis Mo, US Patent No 4 284 784 (1981).
3. J.S. Amato, S. Karady, L.M. Weinstock, US Patent No 4 282 364 (1981);
4. Amato, S. Karady, L.M. Weinstock, Heterocycles, 22, 1947 (1984).

CATALYTIC SYNTHESIS OF ORGANIC SULFUR COMPOUNDS

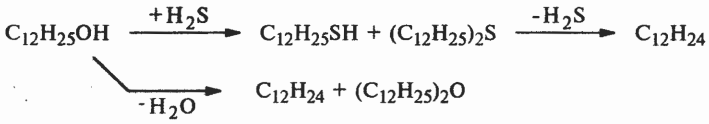
A.V.Mashkina, Yu.A.Savostin

Boreskov Institute of Catalysis, "KATALIZATOR Ltd", Novosibirsk 630090, Russia

A number of sulfur organic compounds are used in practice. Catalytic methods appear to be the most efficient for their synthesis.

Alkyl mercaptan synthesis from alcohols and H_2S have been studied.

n-Dodecyl mercaptan (polymerization regulator) was synthesized via the interaction of lauryl alcohol and H_2S at 250-350°C. n-Dodecyl mercaptan and dodecene are the main reaction products, while dodecyl ether and dodecyl sulphide are by-products. Reaction follows a consecutive-parallel mechanism:



$$\begin{tikzcd} C_{12}H_{25}OH \arrow[r, "+H_2S"] \arrow[dr, "-H_2O"'] & C_{12}H_{25}SH + (C_{12}H_{25})_2S \arrow[r, "-H_2S"] & C_{12}H_{24} \\ & C_{12}H_{24} + (C_{12}H_{25})_2O & \end{tikzcd}$$

Solid alkaline catalysts turned out to be very efficient for the n-dodecylmercaptan synthesis. ICT-38-7 catalyst is advised for this synthesis. Its preparation technique is already developed. On the basis of the kinetic study, we have determined the synthesis conditions providing a 70% yield of n-dodecyl mercaptan at a complete conversion of lauryl alcohol.

Methyl mercaptan, initial substance for methyonine production (medicine and food additive), is synthesized via the interaction of methanol and H_2S at 320-420°C:

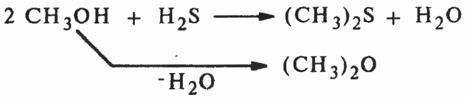
$$CH_3 + H_2S \longrightarrow CH_3SH + H_2O$$

Dimethyl sulfide, dimethyl ether, methane and carbon dioxide are by-products.

Different catalysts can assist the reaction. Catalysts with strong basic sites, which are conjugated with the weak Lewis acid sites, are the most active and selective towards methyl mercaptan. We have developed a method for the ICT-31-1 catalyst preparation, which provides a 100% selectivity towards methyl mercaptan.

Dimethyl sulfoxide (medicine, solvent and extracting agent) is obtained via a two-stage scheme, including dimethyl sulphide production and its oxidation by oxygen.

Heterogeneous-catalytic interaction of methanol and H_2S, proceeding on ICT-37-7 (catalyst surface has pair acid-basic sites), yields **dimethyl sulfide**:



$$2\,CH_3OH + H_2S \longrightarrow (CH_3)_2S + H_2O$$

$$2\,CH_3OH \xrightarrow[-H_2O]{} (CH_3)_2O$$

Our catalyst preparation procedure and dimethyl sulfide production conditions provide a 95% yield of the latter. We have also designed the reactor.

Dimethyl sulfide oxidation by oxygen provides **dimethyl sulfoxide**

$$(CH_3)_2S \xrightarrow{+\,O_2} (CH_3)_2SO$$

The process proceeds in the liquid phase in the presence of a transition metal (catalyst IC-23-3) in a reactor continuously working at 150°C and 5 MPa. Basing on our kinetic studies, we recommend the conditions which allow to synthesize dimethyl sulfoxide production with a 80 mol.% yield and 90% selectivity. Dimethyl sulfoxide output equals 1000 mol per hour per g-atom of active metal.

THE MINERAL-ORGANIC SULFOCATIONITES-CATALYSTS FOR THE OIL PERFORMING AND OIL CHEMISTRY PROCESSES

S.V.Mezcheryakov, K.D.Korenev, V.A.Zavorothny
(State Academy of Oil & Gas named by I.M.Gubkin, Moscow)

Catalysis by the polymeric sulfoacids (sulfocationites) is widely used in the oil chemistry and industrial organic synthesis [1]. But the little size of polymeric granuls (usually 0,3-1,5 mm), its swelling in the reagents and its limited termostability (up to 110°C) complicate the technological equipment. Therefore the producing and using of mineral-organic sulfocationites (MOS) in which the polymer's film are fixed on the surface of mineral's carrier having the size of 5 mm and more over is very interesting.

These MOS are produced by the spreading of polyaromatic polymers having conjugated bonds (followed by the sulfonaton) or the copolymers of perfluorinesulfoacids and ethene on the porous granuls of alumosilicates or moulded silicate articles. The statistic exchange capacity of MOS is a 0,3 meq/g, the specific surface - up to 300 m^2/g, the start's temperature of termic degradation - not more than 220°C [2].

The MOS - "Phthalosorb" - is produced by the thermal polymerisation (for 450°C) of phthalic anhydride adsorbed on the alumosilicate's surface and followed by sulfonation of the formed polyphenyleneketones. "Phthalosorb" is used in the isoprene synthesis through 4,4-Dimethyldioxane-1,3 (DMD). The proportion DMD: t.butanol: isobutylene is a 1:2,1:4,9, catalyst's quantity is a 10%, temperature - 170°C, pressure - 2,7 MPa. The content of isoprene reaches 57% closed values for the sulfuric acid's process (55- 60%).

"Phthalosorb" is used for the esterification of synthetic fatty acids C_{14}-C_{16} (or carboxylic acids produced from the rapseed oil) by methanol (1:7, moles). The esterification is carried out in current-flow plant under the reaction-rectification's conditions. The temperature of process is 210-220°C, pressure - 0,5 MPa. The yield of carboxilyc acids' methyl esters reaches 95%, acid number - 0,75 mg KOH/g. These esters are tested as a component of diesel fuel.

The testing of "Phthalosorb" in the preparation of the methyl- tert-butyl ether (MTBE) is carried out under following conditions: proportion isobutylene (isobutylene content mixture): methanol = 1:1,1 (moles), temperature 90-100^{0}C, pressure 1-1,2 MPa, volume's velocity of reaction mixture's feed 0,3 h^{-1}. The conversion of isobutylene reaches 90%. MTBE is isolated by the distillation of reaction's product. MTBE is a highoctane component of the autobenzine.

The copolymer of ethene and perfluorine-2-(fluorinesulfonyl- ethoxy)-propylvinyl ether, 6,5% weight is spread on the moulded ceramic carrier (Rachig's circles). This MOS is charged in the current-flow reactor.The mixture isobutane and n.butenes-2 (10:1, moles) is circulated through the reactor. The temperature is about 90^{0}C, pressure is about 2 MPa, velocity of reaction mixture's feed - 0,3 g/g catalyst in hour. The conversion of n.butenes-2 reaches 90%. The octane number of the liquid product is 96 (research's method).

The testing of same catalyst in the reaction of benzene and propene at temperature 170^{0}C, pressure 3,0 MPa and velocity of propene's feed 1,0 g/g catalyst an hour results in propene's conversion 92%.

Thus the producing and using of MOS can become a new step in the development of chemistry and technology of catalytic processes.

1. Korenev K.D. et al. The sulfocationits - catalysts of modern oil chemistry's processes//Central science-research's institute of the information and technique-economical researches of oil refining and oil chemistry's industry.-Moscow, 1990.-77 p. (reviews information).

2. Lunin A.F. et al. //Oil refining and oil chemistry.-1985.- № 3.-P.26 (Moscow).

Pyrolysis of Hydrocarbons Catalyzed by Alkaline Earth Metal Chlorides

K.S.Minsker and S.R.Ivanova

Bashkirian State University, Ufa

Catalytic processes appeared to be the most prospective for pyrolysis of hydrocarbons. Heterogeneous catalysts allow a substantial enhancement in the conversion of the raw materials at the temperatures of thermal pyrolysis (800-850°C) or the achievement of a reasonable conversion at much lower temperatures. Metal chlorides, both simple and mixed ($LiAlCl_4$, $NaAlCl_4$, $KAlCl_4$, MgCl, $BaCl_2$, $SrCl_2$), appeared the effective catalysts for thermal degradation of low-α-highmolecular hydrocarbons. When catalyzed by the chlorides, noticeable pyrolytic transformations of hydrocarbons start at temperatures as low as 250-450°C; 60-90 wt % yields of the gaseous products can be obtained, whereas non-catalytic pyrolysis is not observed at these temperatures.

Two groups of the available catalysts may be classified upon the analysis of the temperature dependencies of catalytic activities and the compositions of the reaction gas products. The compounds of the first group ($InCl_3$, $BiCl_3$, $LiAlCl_4$, $NaAlCl_4$, etc.) with the protodonor H_2O catalyze the process proceeding with a noticeable rate at rather low temperatures only (250-300°C). Hydrocarbons dominate in the gaseous reaction products, and there are no great amount of low olefins (ethylene, propylene) there.

The second group involves anhydrous species of alkaline earth metal chlorides which reveal catalytic activities at below 400-450°C. The composition of the reaction products is rather different here, C_2-C_3 olefins being predominant.

Hence, different mechanisms of catalytic actions of various metal chlorides may be suggested. The Broensted acids involved in the first group are the eletrophilic catalysts, the carbocation mechanism is characteristic of hydrocarbon destruction over these catalysts. When the reaction is catalyzed by anhydrous earth metal chlorides (the second group), the reaction product composition is the same as that produced by non-catalytic gas phase pyrolysis of hydrocarbons (the predominate ethylene and propylene, and a small amount of C_4-olefins) following the radical mechanism.

A kinetic model for hydrocarbon destruction was developed with n-heptane as an example; the thermal pyrolysis of n-heptane proceeds through the radical mechanism, and the reaction products are well studied. Anhydrous alkaline earth metal chlorides as the catalysts were shown to promote the stage of originating the radicals during the hydrocarbon decomposition on the catalyst surface that results in a decrease in the reaction temperature by 200-400° compared to that of the thermal pyrolysis.

The sequence of elementary steps of the pyrolysis are as follows:

$$n\text{-}C_7H_6 \longrightarrow \dot{C}_3H_7\text{-first} + \dot{C}_4H_9\text{-first};$$

$$\dot{C}_3H_7\text{-first} \longrightarrow C_2H_4 + \dot{C}H_3 \xrightarrow{RH} CH_4 + \dot{R};$$

$$\dot{C}_3H_7\text{-first} \xrightarrow{RH} n\text{-}C_3H_8 + \dot{R};$$

$$\begin{tikzcd}
\dot{C}_4H_9\text{-first} \arrow[r] & C_2H_4 + \dot{C}_2H_5 \arrow[r] \arrow[dr, "RH"'] & C_2H_4 + \dot{H} - H_2 + \dot{R} \\
 & & C_2H_6
\end{tikzcd}$$

EFFICIENCY OF VITAMIN K (VIKASOL) PRODUCED VIA "VIKASIB" TECHNOLOGY AT POULTRY NUTRITION

K.Ya. Motovilov, K.I. Matveev[*], E.G. Zhizhina[*], V.F. Odyakov[*], E.V. Gusamova

Novosibirsk State Agriculture University

[*]Boreskov Institute of Catalysis

Vikasol (VS), produced via the "Vikasib" technology, was successively tested for 3 years (since 1992) at two poultry plants in the Novosibirsk region. The "Vikasib" Vikasol compares well with the best foreign samples. The tests were performed with chickens and hens intended for eggs production and poultry, and with duckling-broilers. VS was found to increase the productivity of laying hens by 11.9%, broiler chicken - by 5%, survival - by 6%, as compared with the reference groups. Vikasol increases fodder assimilation, i.e., decreases its consumption per egg produced. For instance, an average reference hen consumes 1.6 kg of fodder to lay 10 eggs, while the similar hen, fed with Vikasol, consumes 1.4 kg per 10 eggs, i.e, by 20g less per egg. The "Vikasib" Vikasol also helps eggs incubation. With Vikasol the profits from eggs and broilers production increase by 17,5%. Chickens fed with Vikasol grow faster by 8.9%, their survival rate increases by 6,4%, fodder consumption decreases by 16.4%.

The tests with duckling broilers show that Vikasol increases the product mass by 6.4%, and decreases fodder consumption by 4.4% with respect to the reference group. So, the "Vikasib" Vikasol is a valuable vitamin, enhancing poultry productivity and survival rate. It regulates blood functions, helps digestion and breathing. It is a good bactericide. The tests show that "Vikasib" Vikasol increases considerably the feasibility of poultry and cattle production.

BINUCLEAR METAL COMPLEX CATALYSTS IN POLYMERIZATION PROCESSES

E.A.Mushina, I.F.Gavrilenko, Yu.Ya.Podolsky, V.M.Frolov, B.A.Krenzel, I.N.Borodina
Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow

M.S.Gaburtdinov, C.B.Medvedeva, A.Z.Vakhbreit, S.A.Solodyankin, V.F.Cherevin
Stock Company "Kazanorgsintez", Kazan

The method and technology of preparation of binuclear heterogeneous catalytic systems for polymerization of ethylene and dienes were developed.

The essence stage of the proposed method involves anchoring of two metal complexes on the dehydrated silica gel. The first of the two complexes consists of titanium-magnesium (or chromium) compound, while the second one - of nickel- (or zirconium) aluminum organic compound. Using these systems the gas phase polymerization of ethylene and the suspension polymerization of dienes (butadiene, isoprene) were studied. The main feature of the catalysts proposed is their particularly high activity in the polymerization processes.

In case of polymerization of ethylene the developed catalytic systems display two functions, carrying out copolymerization of ethylene with its oligomers (butene, hexene), obtained in the same process "in situ". In the process of polymerization of dienes the catalysts demonstrated not only high activity, but stereospecifity as well. It is interesting to note that the consumption of Al-organic compound in a case of binuclear catalyst is reduced by an order of magnitude or greater in comparison with the known catalysts.

It was found also that the polymerization of butadiene in solution runs at a high rate already at room temperature, the composition of isomer's blend (relative contents of cis- and trans- isomers) being depended on the nature of catalyst and on the conditions of the process.

The methods for synthesis of binuclear catalysts were elaborated and the kinetic parameters of polymerization process were specified. The structure of polymers formed was investigated by means of IR-spectroscopy and X-ray analysis and the physical and mechanical properties as well as their mass-molecular characteristics were estimated. The preliminary information on the interrelation between the composition of the catalytic systems and structure and properties of polymers was obtained.

The flow chart of production on the industrial scale of the binuclear catalyst was developed and the batch of catalyst (200 kg) was produced. Test run on Ethylene gas-phase polymerization unit was successfully performed using of the synthesized catalyst.

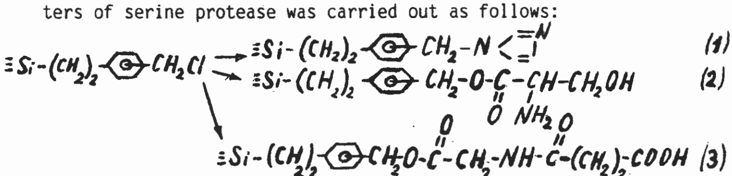
Due to unusually high activity of the catalysts proposed, the usage of them will permit to reduce substantially the scattering of metals in environment.

SYNTHESIS OF SUBSTRATUM-ORIENTED HETEROGENEOUS CATALYSTS BASED ON SILICA AND INVESTIGATION OF THEIR PROPERTIES

V.N Postnov, A.G. Novikov St.Petersburg State University,
Department of Chemistry, St.Petersburg

The use of biomimetic principles for creating heterogeneous silica-based catalysts is possible if the modification of silica surface is carried out by solid phase peptide synthesis (1,2) and molecular layering (3). These methods allow to place on the matrix surface a great variety of oxide monolayers and organic groups arranged in a specific manner thus providing the possibility to create active catalysts centers with specified structure. Additional opportunities for tuning a catalysts to a particular substratum are provided by the imprinting method based on forming the silica in the presence of the substratum molecules (4).

Synthesis of bound organic groups forming a part of active centers of serine protease was carried out as follows:



The anchor group $\equiv Si-(CH_2)_2-C_6H_4-CH_2Cl$ was produced by successive processing of the silica surface with $Cl_3Si-(CH_2)_2-C_6H_5$, CH_3-O-CH_2Cl The group (1) was synthesized by imidazole chemisorption. The groups (2),(3) containing serine remains and carboxyle groups on the silica surface were synthesized by solid phase peptide synthesis standard techniques. The catalysts were examined in the hydrolysis reaction of p-nytrophenyl-acetate, and the results showed that the catalysts activity increased when both groups (1),(2), and (1),(3) were present.

By the way of controlling the distance between these groups on the silica matrix it was possible to tune the catalyst to substratum and to increase the catalyst activity. The catalysts for the hydrolysis of p-nitrophenylacetate were obtained by combination of molecular layering and molecular imprinting methods too. For this purpose the aerosil gel was prepared with use of p-nytrophenylacetate aqueous-isopropanole solution. So produced silica was then used for the synthesis of the titanium oxide layers. Alternating $TiCl_4$ chemisorption and hydrolysis of the Cl -groups not having reacted with the surface silica groups, we obtained the samples containing from one to three titanium oxide monolayers. The investigation of the catalyst properties displayed the substantial excess of the activity of samples containing one titanium oxide monolayer on the substratum-present-formed surface over the activity of the titanium-containing sample obtained without the molecular imprinting method.

The two ways of synthesizing substratum-oriented structures proposed here could be employed for obtaining quite a number of catalysts when spatial correspondence between the substratum molecules and disposition of the active surface centers are essential.

The research described in this publication was made in part by Grant N° NXD000 from the International Science Foundation.

References:

1. Stuart D., Young D. Solid phase peptide synthesis. Moscow, Mir, 1971.
2. Postnov V.N., Makarov K.A., Aleskovsky V.B., Koltsov S.I. Doklady AN SSSR, 1977, v. 235, N° 5, p. 559-600.
3. Aleskovsky V.B. Chemistry of Solids, Moscow, 1978.
4. Dickey F.H. J. Phys. Chem., 1955, p. 695-707.

COPPER CATALYSTS FOR THE DEHYDROGENATION REACTION OF THE ETHANOL TO THE ETHYL ACETATE

I.V. Sablukova, B.S. Strelchik, E.Z. Golosman,
O.V. Lysova, V.A. Vekslina.

AO VNIIOS NK, Novokuibyshevsk
AO NIAP, Novomoskovsk
Aerocosmic University, Samara
Russia

The catalytic dehydrogenation reaction of the ethanol to the ethyl acetate has a great industrial and scientific importance.

The authors have investigated this reaction with large series of copper catalysts.

The experiment was performed in the laboratory flowing plant at 180-300°C under ordinary pressure. The catalysts were reduced before the experiments (hydrogen was used as the reducing agent).

The correlation between the activity and the selectivity of the copper catalysts and the main of the process parameters were determined on the basis of investigation.

There was examined the influence of acidic and basic centres of the carrier surface on the catalytic activity.

The analysis of the received dates let us make the supposition about the mechanism of the second stage of the reaction.

The influence of by-products of the reaction on its rate and selectivity were showed.

On the basis of the work the most active and selective catalysts of the dehydrogenation of ethanol were determined.

Complex catalytic sorptive technology for gas purification

U.M.Schindler, A.G.Sarmurzine, G.Sh.Tlepieva
Al-Pharaby Kazakh State National University
State Research-and-Production Association of Industrial Ecology, "Kazmekhanobr", Almaty

Catalytic sorptive technology for gas purification involves:

1. Optimized (based on fundamental research) technologies for preparation of sorbents, hemosorbents, ionite-catalysts for gas purification from acetic and formic acids, sulfur, nitrogen, phosphorus, hydrates, carbon mono- and dioxides, nitrogen and sulfur oxides with the utilization of valuable components;
2. Efficient reactor design (comfortable in maintenance) providing a high degree of the purification from the said compounds using dispersed sorbents, ionite-catalysts, sorbing catalytic solutions;
3. Practically wasteless technology including the preliminary (or one-phase) dust removal within the electromagnetic unit of the reactor using suspended ferromagnetic dispersed particles or liquid-phase gas treatment with circulating solutions:
   - sorptive or ion circulating (acidic and alkaline) extraction and concentration of chemical admixtures in the dusty-free gases;
   - catalytic redox transformations of hardly sorbable toxic admixture to the non-toxic or sorbable compounds;
   - electromagnetic filtering to separate the circulating liquids or solid sorbents, ionite-catalysts from the dust trapped during the gas cleaning.

This multiphase technology was implemented using only one thermoinsulated reactor with several active zones. Such a layout allows a decrease in energy and material consumption, reduction of the amount of raw materials utilized.

The waste dispersed slags of keramzit and electrophosphorus slags which are available in abundant quantities were used as the sorbent. The hemosorbent preparation procedure involved the crushing of hydromucous shale diatomite, kieselguhr (millions tons of them are currently mined), the drying and kilning, fractioning, treatment with acids and alkalines, and impregnating of the substances produced with metal salts.

The method for preparation of the magnetic ionites is covered by a patent; the distinctive features are a high magnetic permeance (more than 0.01 CGSM) and stability, the quality obtained fits the best industrial standards for ionites. The addition of non-volatile promoters (gradually transformed admixtures to the catalyst particles in order compensate the diminution of the active sites) to the ionites results in a higher stability of the catalyst produced; the metallic carrier units possess the high thermoconductivity and thermoresistance of their surface of large surface area.

There are different designs of the reactors for the low (50-350 K), moderate (350-450 K) and high temperature processes.

A low temperature reactor is a porous substance-polymer with

a) external filtering layer;

b) internal intersecting streams of gas and reactant' solutions;

c) active sites (sorptive, ion circulating, catalytic) placed regularly on the internal surfaces of channels, cavities by means of magnetic thermal dissemination.

The moderate temperature reactor looks like two cylinders (fingers) with a tangential pitch leading in of a gas. An internal pivot positioned the center is used to generate the electromagnetic field. Owing such a design there can be 3-5 different zones simultaneously within a single reactor allowing a fast automated tuning of the variable physical and chemical parameters of the gas.

The low temperature reactor was equipped with a straight angle section of two electromagnetic zones to support electromagnetic field in the layer of the magnetic ionite-catalyst; it is used to filter gas passing through the ferrite granules covered by a polymer in order to reduce the amount of heterogeneous particles carried away from the reactor.

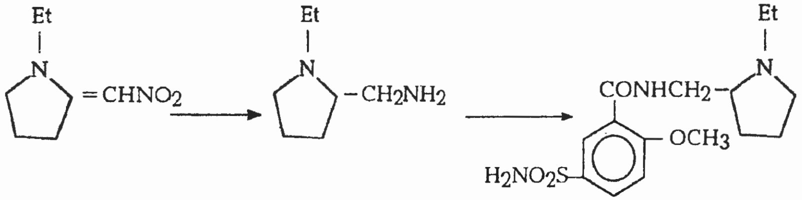
The high temperature reactor is a thermoinsulating cyclone; it was used to provide washing up the oven and the waste gas from dust, carbon, nitrogen, and sulfur within one reactor with monolythic metal catalysts which were manufactured in Kazakhstan.

CATALYTIC SYNTHESIS OF 1-ETHYL-2-AMINOMETHYLPYRROLIDINE FOR THE PRODUCTION OF PHARMACEUTICALS.

V.A. SEMIKOLENOV

Boreskov Institute of Catalysis, Prospekt Akademika Lavrentieva 5, Novosibirsk, 630090, Russia. Fax: 7(383)2 355766

1-Ethyl-2-aminomethylpyrrolidine (EAMP) is a key semi product for the synthesis of benzamides, pyrrolidylquinolines and pyrrolidylquinazolines - a new group of highly effective medicines. In particularly, one of them, «SULPYRIDE» is employed in the treatment for nervous disorders, caused by use drags and alcohol as well as stomachical diseases. The «sulpyride» can be prepared according to the general scheme:



"ENMP" "EAMP" "SULPYRIDE"

The usual methods of N-alkyl-2-aminomethylpyrrolidines synthesis are based on reduction of corresponding N-alkyl-2-nitromethylenepyrrolidines:

- by hydrogen «in situ» with an acid and metal [1].
- by electrolytic reduction under neutral to basic conditions using Cu as the cathode [2] or under hydrochloric acid conditions using Pd on carbon as the cathode [3].
- with hydrogen in the presence of metallic catalysts «Raney nickel», platinum black Rh/Al_2O_3 and Pd/C [1,4].

The starting reagent N-ethyl-2-nitromethylenepyrrolidine (ENMP) as well as partially hydrogenated intermediates are rather unstable compounds which can easy undergo the thermal decomposition, hydrolysis, dealkylation and condensation reactions under the reaction conditions. This side processes results in a decrease in the selectivity of the aimed product formation.

The purpose of the present work is to elaborate the selective catalytic method of ENMP hydrogenation and preparation of high purity EAMP for the synthesis of pharmaceuticals.

ENMP hydrogenation was performed in a slurry reactor and in a trickle flow column reactor in the presence of granulated (0.5-3.0 mm) and powdered Pd/C catalysts (Pd content 0.5-4.0%).

The influence of the solvent used on the hydrogenation rate and the selectivity of EAMP formation was studied. The high selectivity and the low hydrogenation rate were observed when process was carried out in non aqueous and aprotonic solvents. The maximum of hydrogenation rate, but minimum of selectivity were achieved in the aqueous solution. The next step of this study was focused on the elucidation of reasons of side product formation.

The side products were extracted from the reaction mixture and studied by NMR ^1H, IR and GLC methods. It has been found that the side products consists of N-ethyl-2-pyrrolidinon, methylamine and alkylamines (probably products of N-ethyl-2-pyrrolidinon hydrogenolysis).

The effect of hydrogen pressure, concentration of catalyst and reaction temperature on selectivity and rate of EAMP formation was studied. It was shown that the diminution of hydrogenation duration results in decrease the of side products yield. This phenomena can be explained in terms of ENMP hydrolysis.

The kinetic peculiarities of ENMP hydrolysis was investigated. It has been found that hydrolysis of ENMP is an acid-basic process where H_2O (a product of -NO_2 group reduction or a solvent) act as a reagent and the strong base EAMP (pKa ~ 12) - as a catalyst. Hydrolysis of ENMP gives a N-ethyl-2-pyrrolidinon and a nitromethane which can be catalyticaly reduced to methylamine.

The methods of suppressing of the side process were found out. On the basis of results obtained the new highly selective method of catalytic hydrogenation of ENMP to EAMP - semi product for the synthesis of pharmaceuticals was proposed. The method was checked in the scale of pilot plant. The EAMP samples of 98.0-99.0% purity was used for «Sulpyride» synthesis.

1. British Pat. No 1374818
2. U.S. Pat. No 4035252
3. Pat. USSR No 1421738
4. U.S. Pat No 3748341

PHYSICO-CHEMICAL AND CATALYTIC PROPERTIES OF ALUMOMOLYBDENUM CATALYSTS

Smidt F.K., Kim En Hwa and Zhdanova K.P.
Irkutsk State University, Irkutsk

Alumomolybdenum systems with various promoting additives are widely used in petrochemistry as catalysts for crude oil hydrorefining. In the present communication the results of our study on the physico-chemical and catalytic properties of alumomolybdenum catalysts (AM) carried out for many years are summarized.

AM Formation [1,2]. The effect of Mo concentration, pH, calcination temperature and aluminium oxide on the AM formation has been investigated. The largest effect is found to be produced by surface properties of aluminium oxide. At Mo concentration of 12% of MoO_3 (normal to commercial catalysts) three types of Mo oxide compounds have been found: a) individual, seemingly introduced in the near surface layers of aluminum oxide; b) Mo compounds with a structure of alkali metal dimolybdate type (AMD) and c) those with a structure of ammonium octamolybdate (IPC). In the formation of AMD and IPC OH groups of aluminum oxide are involved. A scheme for the formation of neo-crystallized Mo compounds in AM (AM model) has been offered.

AMD and IPC are Brendsted acid centers (Bc), IPC being a weaker Bc than AMD. IPC are water soluble, AMD are soluble in NH_4OH solution. The degree of sulfuration of these compounds is quite different.

AM active component dispersity [3]. Evaluation of active component dispersity can be performed with the use of two adsorbates, O_2 and CO_2. Molybdenum oxide and aluminum molybdate cannot serve as standard in dispersity evaluation.

Reduction and H_2 adsorbtion [4]. Surface Mo compounds in AM can be reduced to a different extent and contribute different deal to H_2 adsorption and desorption. Three types of adsorbed H_2 were recognized. The activation energy of H_2 adsorption in the 400-550°C range is 42-63 kJ/mol which is much lower than that of MoO_3 (105 kJ/mol).

Physical adsorption of thiophene and thiophane on AM [5]. The thermodynamic characteristics of thiophene and thiophane adsorption on AM have been determined. These values depend on the amount and ratio of Mo compounds in AM. Basing on changes in the adsorption entropy the behavior of thiophene and thiophane on the AM surface was considered.

Thiophene chemosorption on AM [6]. The compounds forming on AM during thiophene adsorption under various conditions were studied by IR spectroscopy. At 25-100°C reversible forms of thiophene bonded to AM HO-groups at thiophene C_α atoms were revealed. At high temperatures strong surface compounds of thiocarboxylate type having hydrocarbon "tails" of different composition were defined. Also, a surface compound spectrally close to butylmercaptan adsorbed at 25°C was found.

Deutero-hydrogen exchange in thiophene on AM of various composition and under different experimental conditions depends on the temperature of reduction of samples and experiment as well as on the amount and ratio of Mo compounds in AM.

Hydrogenolysis of thiophene on AM. The reactions of hydrogenation of butadiene, dehydrogenation of cyclohexane, hydrocracking of heptane, hydrogenolysis of thiophene and thiophane on AM have been studied. The activity and composition of the product obtained depend on the amount and ratio of Mo compounds in AM. The activation energies of reactions for thiophene, thiophane and butadiene are determined to be 56-68, 80-100 and 44-52 kJ/mol, respectively. Some mechanisms for the hydrogenolysis of thiophene on AM are suggested.

References

1. Kim En hwa. The nature of molybdenum surface compounds in Al-Mo catalysts and some their physico-chemical properties. Thesis (Cand.Chem.Sc.), Irkutsk, ISU, 1985, 135 p.
2. Smidt F.K., Kim En hwa, Zhdanova K.P. Catalysis and progress in chemical engineering. 1st Sov.-Indian Seminar on Catalysis. Sb.Tez., Novosibirsk, 1984, p. 189.
3. Zhdanova K.P., Rychagova O.A., Ishchenko E.D. etc., Zh.Fiz. Khim., 1992, 66, 2939.
4. Kim En hwa, Zhdanova K.P., Batashova L.P. etc., Zh.Fiz.Khim., 1994, 68, 105.
5. Borovskaya M.K., Reznikzova S.A., Kim En hwa, Smidt F.K. etc., Zh.Fiz.Khim.,1994, 68, 123.
6. Smidt F.K., Kim En Hwa and Zhdanova K.P., Vth Vses. konf. po mekhanizmu katalitich.reaktsij. Sb.Tez., Moscow, 1990, p. 207.

ANESTHESINE CATALYTIC PRODUCTION VIA LIQUID-PHASE HYDROGENATION OF ETHYL ETHER OF PARA-NITROBENZOIC ACID OVER Pd/C

E.F. Stefoglo, O.P. Zhukova

Institute of Carbon, Kemerovo, Russia

Hydrogenation of ethyl ether of para-nitrobenzoic acid (EEPNBA) to anesthesine was performed in isopropyl alcohol medium. First, we studied the temperature effect on hydrogen solubility in isopropanol and nitroether and anesthesine solutions in this solvent. Dissolved hydrogen concentration was determined at T = 40-I20°C and P = I-6 bar by chromatography. Henry constants vs temperature dependences were defined:

- for isopropyl alcohol, $He = 1.639 \cdot 10^6 \exp(6.39/RT)$ Pa·m^3/kmol, where $R = 8.3I \cdot I0^{-3}$ kJ/mol·g;
- for the initial nitroether solution in isopropyl alcohol with $C_{NE} = 0.73$ kmol/m^3, $He_{NE} = 1.708 \cdot 10^6 \exp(7.15/RT)$ Pa·m^3/kmol;
- for anesthesine (reaction product) solution with $C_{AN} = 0.64$ kmol/m^3, $He_{AN} = 1.681 \cdot 10^6 \exp(6.85/RT)$ Pa·m^3/kmol.

Based on the reduction mechanism of nitroaromatic compounds and high reagents absorption ability, the reaction rate is described by the Langmuir - Hinschelwood equation with respect to both reagents: $r = kC_{cat} \frac{K_H C_H}{1 + K_H C_H} \cdot \frac{K_L C_L}{1 + K_L C_L + K_P C_P}$. Using a specific reactor module via our procedure, we studied the kinetics of EEPNBA hydrogenation over a 5% Pd/C in a batch reactor. To do this, one should create such conditions in reactor, at which the dissolved gas equilibrium concentration corresponds to the initial catalytic rate. This allows to determine the values of the above equation parameters from the initial rate. Figure I describes the EEPNBA hydrogenation performed at the different initial conditions: with preliminary saturation of initial solution with hydrogen and without it. At a high pressure (several tens of atmospheres), the initial conditions affect greatly the process time [I]. The constant vs temperature dependences are defined:

$K_H = 5.38 \cdot 10^{-9} \exp(66.58/RT)$, $K_L = 8.186 \cdot 10^{-4} \exp(25.23/RT)$

$K_P = 0.025 \exp(19.7/RT)$, $k = 1.544 \cdot 10^{11} \exp(-81.7/RT)$

Catalytic rate vs pressure (hydrogen equilibrium concentration) dependences were obtained experimentally at a variable temperature and calculated from the rate equation at the given constants (Fig.2). Using this equation and some data on mass transfer in three-phase systems, we determined the optimal parameters for the industrial production of pharmacopeial anesthesine. The above approach to the studies on gas-liquid catalytic processes allows to control, though indirectly, the reduction medium during reaction, for instance, to hold the required saturation of reaction medium with hydrogen. This is very important since on the catalysts depleted in hydrogen proceed mainly isomerization and hydrogenolysis instead of reduction. In such conditions, a supported precious metal is removed and its losses may achieve 40% [2].

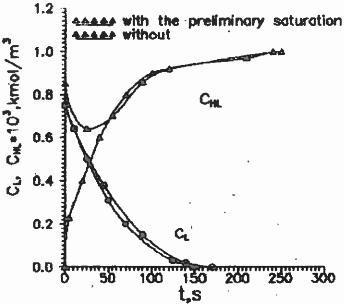


Fig.1 Hydrogenation of EEpNBA with different initial conditions ($T=100°C, P=2.5$ at, $C_{cat}=0.083$ kg$_{Pd}$/m^3)

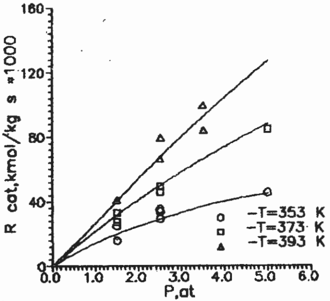


Fig.2 Dependence of $R_{o\ cat}$ on hydrogen pressure (experimental and calculated data)

References

1. In the book of papers European Symposium "Catalyst in Multiphase Reactors", Lion, 1994, p.41-48.
2. G. Leuterlitz (eds.), Increasing the profitability of gas/liquid reactions through the use of loop reactor plants. Int. Meeting for Chem. Tech., Frankfurt on Main, 1985.

HYDRODECHLORINATION OF CHLOROAROMATIC COMPOUNDS ON NICKEL CATALYSTS

Suzdorf A.R., Morozov S.V.*, Kovalev A.M., Anshits A.G.
Institute of Chemistry of Natural Organic Materials, (K.Marx str. 42, Krasnoyarsk, 660049, RUSSIA, Fax (007-3912-275384)
*Institute of Organic Chemistry, (Lavrent'ev Av., 7, Novosibirsk, 630090, RUSSIA)

INTRODUCTION

Polychlorinated organic substances (PCOS) are priority toxicants of the environment due to their high carcinogenic and mutagenic activity. The catalytic hydrodechlorination is one of the ways of the PCOS detoxification which excludes the formation of more toxic compounds such as polychlorinated dibenzodioxins and dibenzofurans.

Ni-containing systems are known to be active catalysts of a hydrogenation. Supported nickel catalysts have not been studied in the gas phase hydrodechlorination of chlorinated aromatic compounds.

The aim of this work is to study the reactivity of chlorinated aromatic compounds in the hydrodechlorination on supported Ni/γ-Al_2O_3 catalysts depending on the nature and position of substituents in a benzene ring. Data obtained will be useful both for synthetic organic chemistry and environmental protection concerning the utilization of toxic PCOS.

EXPERIMENTAL

The catalysts were prepared by impregnating pelleted γ-Al_2O_3 (0.2-0.5 mm) with an aqueous solution of salt $Ni(NO_3)_2 \cdot 6H_2O$ followed by drying and calcination at the air for 4 hours at 673 K. Ni content was varied from 1 to 100 wt.%.

Before starting experiments the catalysts were reduced in a hydrogen flow at 573 K for 2 hours. The experiments were carried out in a flow microcatalytic set-up with a fluidized-bed reactor using the reaction mixture of the following content (vol.%): $RArCl:H_2:He$ = 0.5:20:79.5. The activity of the catalysts was calculated as a sum rates of formation of organic products. The analysis of reaction mixtures was made by the GLC chromatograph equipped with the flame ionization detector.

RESULTS AND DISCUSSION

The activity of nickel catalysts with the different content of metal was studied in the reaction of the hydrodechlorination of chlorobenzene. It was shown that the $Ni/\gamma\text{-}Al_2O_3$ catalysts are not deactivated in the presence of chlorobenzene and hydrogen chloride. The properties of catalysts are determined by the metal Ni.

The reactivity of substituted chlorobenzenes RArCl (R = NH_2, OH, CH_3, Cl, CF_3, H) in hydrodechlorination was studied on $10\%Ni/\gamma\text{-}Al_2O_3$ catalyst. The hydrogenation of aromatic products did not observed. The rates of hydrodechlorination of substituted benzenes, phenols and toluenes is slightly sensitive to the ortho-, meta- and para-position of chlorine atom in respect to another substituent. However, the rates of hydrodechlorination decreases more than by the 2 order of magnitude in the row: chloroaniline > chlorophenols > chlorotoluenes > dichlorobenzenes > chloro-trifluoromethyl-benzene. Considerable difference of reactivity of substituted chlorobenzenes is testifies that the rate of hydrodechlorination on the Ni catalyst depends on donor-acceptor properties of substituents, which may be described by Hammett equation : $\lg(W/W_0)=\rho\sigma$, where: W - rate of hydrodechlorination of substituted chlorobenzenes; W_0 - rate of hydrode-chlorination of chlorobenzene; ρ - reaction parameter; σ - constant of the substituents R [1] (fig.). The electron-donor substituents increase and electron-acceptor ones decrease the reactivity of substituted chlorobenzenes in hydrode-chlorination with respect to unsubstituted chlorobenzene.

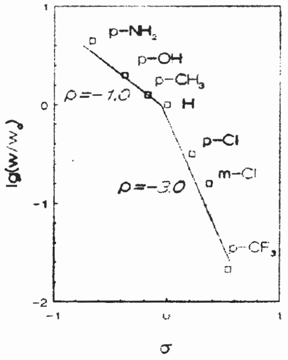


Fig. The dependens of the rates of hydrodechlorination of substituted chlorobenzenes on donor-acceptor properties of the substituents. ($10\%Ni/\gamma\text{-}Al_2O_3$. T=523 K. convertion RArCl = 10%)

The negative value of the reaction parameter ρ shows that the hydrode-chlorination of substituted chlorobenzenes on the Ni catalyst is an electrophile reaction, i.e. the transition complex of the limiting step has a partially positive charge.

REFERENCE

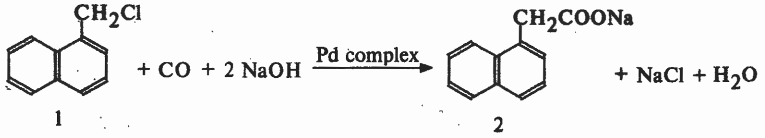
[1] C.Hansch. A. Leo, R.W. Taft, Chem.Rev.,91 (1991), 165.

CATALYTIC SYNTHESIS OF 1-NAPHTHYLACETIC ACID VIA CARBONYLATION OF 1-(CHLORMETHYL)NAPHTHALENE IN THE PRESENCE OF Pd(0)-TRIPHENYLPHOSPHINE COMPLEX

E.G. Zhizhina, A.P. Krysin[*], V.F. Odyakov, K.I. Matveev

Boreskov Institute of Catalysis, Novosibirsk
[*]*Novosibirsk Institute of Organic Chemistry*

Benzyl halides carbonylation in the presence of Pd complexes is a highly-efficient method to synthesize phenylacetic acid and some its derivatives [1], that stimulate the plants growth [2]. 1-Naphthylacetic acid (NAA) possessing higher biological activity is of great practical importance [2]. Recent Chinese papers [3,4] describe the synthesis of NAA involving the interphase catalysis. The authors carbonylate 1-(chloromethyl)naphthalene in the presence of NaOH, $PdCl_2(PPh_3)_2$ serves as a catalyst. Reaction occurs in a system n-hexanole + water, $PhCH_2NEt_3^+Cl^-$ is a catalyst of interphase transfer (CIT). The reaction product is a sodium salt of NAA and goes into water thus separating from the catalyst. No doubts, the use of two-phase system in the synthesis of NAA has many advantages.



(1)

In order to synthesize NAA via carbonylation of 1 in the presence of NaOH, we use a new and more simple catalytic system without CIT. Here carbonylation is catalysed by the complex of Pd(0) with triphenylphosphine, $Pd^0(PPh_3)_4$. The complex is obtained *in situ* via Pd-trifluoroacetate reduction by carbon oxide [5]. Reaction (1) occurs in the two-phase system water + toluene. Substrate 1 and the catalyst stay in the organic phase, while NaOH is in water. The phase volumes are almost equal. The concentration of 1 in the organic phase is 0.15 mole/l, that of catalyst is 0.001 mole/l. The NAA synthesis occurs in the organic phase only, and reaction product (Na salt of NAA (2)) easily passes to the water phase without CIT, so, we do not use the latter.

We carry our reaction under intensive stirring at 60°C and atmospheric pressure for 6 hours. Then we acidify the water solution with HCl to pH~2, and a white suspension of NAA precipitates. We extract the product with toluene and identify NAA produced with IR-spectroscopy. According to GLC, conversion attains 80%. Reaction selectivity is 89%. The yield with respect to purified product is 71% of the theoretical one. If we optimize the conditions of reaction (1) the yield of NAA can increase. Pd(0)-complex can be used repeatedly, but it should be stored in CO free of air.

References

1. Gore E.S. // Platinum Met. Rev. 1990. V.345. N.1. P.2.
2. Mel'nikov N.N., Baskakov, Ju.A. Khimiya gerbitsidov i regulyatorov rosta rastenii - Moskva: GNTIKhL, 1962. P.251.
3. Zhang S., Xiao S., Lai H., Fan J. // Shiyou Huagong. 1989. V.18. N.4. P.263. // C.A. 1989. V.111. N.24. 216257 x.
4. Huang X., Zhang Q., Sun L. // Hangzhou Daxue Xuebao Ziran Kexueban. 1990. V.17. No.4. P.499. // C.A. 1992. V.116. No.25. 254961h.
5. Likholobov V.A., Eremenko N.K., Zudin V.A. // Izv. SO AN SSSR. Ser. khim. 1976. N.3. P.102.

CONTENT

Part I

ORAL PRESENTATIONS

OP-15 Suk Bong Hong
Korea Institute of Science and Technology, Korea
LOCATION OF Tb(III) IONS IN Na-Y ZEOLITE DETERMINED BY LUMINESCENCE SPECTROSCOPY 5

OP-5 Seung-Doo Park, Ji-Hoon Jung*, Suk-In Hong
Korea University, Korea
*Hanseo University, Korea
SELECTIVE OXIDATION USING CATALYTIC ELECTRODE SUPPORTED BY SOLID ELECTROLYTE 7

OP-11 Kyung-Byung Yoon
Sogang University, Seoul, Korea
IONIC CLUSTERS OF ALKALI METALS WITHIN ZEOLITES 9

OP-18 Jeong-Kyu Lee, Ho-Taek Lee and Hyun-Ku Rhee
Seoul National University, Korea
ISOMERIZATION OF C_5/C_6 PARAFFINS OVER PLATINUM LOADED ZEOLITES 11

OP-17 Jong-Sung Yu and Larry Kevan*
Han Nam University, Taejon, Korea
*University of Houston, Houston, Texas, USA
ELECTRON SPIN RESONANCE ANALYSIS OF PARAMAGNETIC Pd (I) SPECIES IN Pd(II)-EXCHANGED H-Rho ZEOLITE 13

OP-4 Sun Hee Choi and Jae Sung Lee
Pohang University of Science and Technology, Pohang, Korea XAFS CHARACTERIZATION OF SUPPORTED $PdCl_2$-$CuCl_2$ CATALYSTS FOR CO OXIDATION 15

OP-16 Son-Ki Ihm and Jin-Ho Lee*
Korea Advanced Institute of Science and Technology, Taejon, Korea
*Chungbuk National University, Cheongju, Korea
CHARACTERISTICS OF METALLIC IRON IN Y-ZEOLITE CATALYST REDUCED BY HYDROGEN ATOM BEAMS 17

OP-25 Jong Rack Sohn and Man Young Park
Kyungpook National University, Taegu, Korea
ETHYLENE DIMERIZATION AND POLYMERIZATION OVER TRANSITION METAL-EXCHANGED MONTMORILLONITE CATALYSTS 19

OP-19 Sang-Eon Park
Korea Research Institute of Chemical Technology, Taejon, Korea

SELECTIVE CATALYTIC REDUCTION OF NO OVER METAL OXIDES INCORPERATED WITH ZEOLITES 21

OP-6 Chong Soo Han
Chonnam National University, Kwangju, Korea
I-V CHARACTERISTICS OF ZnO-ZnO CONTACT DURING OXYGEN ADSORPTION 23

OP-21 A.S. Belyi
Omsk Branch of Boreskov Institute of Catalysis SB RAS, Omsk, Russia
NEW NOTIONS OF ACTIVE SURFACE COMPOSITION OF REFORMING CATALYSTS 25

OP-7 V.A. Chumachenko, L.N. Bobrova*, A.S. Noskov*
Katalyzator Company, Novosibirsk , Russia
*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
UNSTEADY-STATE TECHNOLOGIES FOR CATALYTIC DETOXICATION OF GAS WASTES 27

OP-20 V.K. Duplyakin, G.A. Urzhuntsev
Omsk Branch of Boreskov Institute of Catalysis SB RAS, Omsk, Russia
NEW CATALYSTS FOR ENVIRONMENTALY FRIENDLY FUELS PRODUCTION 29

OP-10 K.G. Ione
Scientific Engineering Center "Zeosit", Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
THE INVESTIGATION AND DEVELOPMENT OF ENVIRONMENTALLY FREINDLY PROCESSES ON ZEOLITE CATALYSTS 31

OP-28 Z.R. Ismagilov, R.A. Shkrabina, N.A. Koryabkina
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
DEVELOPMENT OF NEW TECHNOLOGY FOR PRODUCTION OF ALUMINA SUPPORTS 33

OP-2 B.N. Kuznetsov
Institute of Chemistry of Natural Organic Materials SB RAS, Krasnoyarsk, Russia
CATALYST APPLICATION IN PRODUCING OF ORGANIC COMPOUNDS FROM PLANT BIOMASS 35

OP-30 V.A. Likholobov
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
DESIGN OF CARBON-CARBONACEOUS COMPOSITES FOR CATALYTIC AND ADSORPTIVE TECHNOLOGIES TO ABATE ENVIRONMENTAL DAMAGE 38

OP-29 I.A.Makaryan, S.M.Baturin, P.E.Matkovsky, V.I.Savchenko
Institute of Chemical Physics in Chernogolovka, Russia
NEW COMMERCIAL TECHNOLOGIES ON THE BASIS OF FUNDAMENTAL RESEARHES ON CATALYSIS WORKED OUT AT THE INSTITUTE OF CHEMICAL PHYSICS IN CHERNOGOLOVKA OF RUSSIAN ACADEMY OF SCIENCES 39

OP-8 V.A. Makhlin, B.N. Okunev

State Research Centre of Russian Federation, Karpov Institute of Physical Chemistry, Mocsow, Russia
AN AUTOTHERMAL REGIME OF CATALYTIC REACTOR FOR WASTE GAS CLEANING 41

OP-26 K.I. Matveev, E.G. Zhizhina, V.F. Odyakov, N.S. Kotsarenko, V.P. Shmachkova
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
NEW CATALYTIC METHODS FOR SYNTHESIS OF VITAMINS OF K FAMILY: VITAMINS K_3, K_4 AND VIKASOL 43

OP-22 N.M. Ostrovskii, N.M. Bukhavtsova
Omsk Branch of Boreskov Institute of Catalysis SB RAS, Omsk , Russia
CATALYTIC REACTIONS ACCOMPANIED BY CAPILLARY CONDENSATION 45

OP-1 V.N. Parmon
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
HORIZONS OF CATALYSIS IN ENERGETICS OF THE FUTURE 47

OP-9 N.M.Popova, A.K. Umbetkaliev, K. Dosumov and N.A. Antonova
Institute of Organic Catalysis and Electrochemistry, National Academy of Sciences of Republic of Kazakstan, Almaty, Kazakstan
INTERACTION OF SO_2 WITH O_2 OVER MIXED Pt, Pd, Pt-Pd and Pt-Ru CATALYSTS OF OXIDATION AND COMBINED TREATMENT OF AUTOMOBILE EXHAUST GASES 49

OP-12 B. V. Romanovsky and A. G.Gabrielov
Lomonosov Moscow State University, Moscow, Russia
ZEOLITE-ENCAPSULATED METALLOCOMPLEXES AS NANOSCALE MATERIALS 51

OP-23 A.Ya. Rozovskii
Topchiev Institite of Petrochemical Synthesis, Moscow, Russia
THE PROBLEMS OF NATURAL GAS PROCESSING INTO PETROCHEMICALS AND FUEL 53

OP-24 O.N. Temkin, L.G. Bruk
Lomonosov State Academy of Fine Chemical Technology, Moscow, Russia
NEW TRENDS AND RESULTS IN CARBONYLATION OF ALKYNES.. 54

OP-27 G.A. Tolstikov
Institute of Organic Chemistry SB RAS, Novosibirsk, Russia
METAL-COMPLEX CATALYSIS IN THE SYNTHESIS OF INSECT SEX PHEROMONES AND JUVENOIDS 56

OP-14 K. I. Zamaraev and John M. Thomas*
Boreskov Institute of Catalysis SB RAS , Novosibirsk, Russia
*Royal Institution of Great Britain
REACTION PATHWAYS, KEY INTERMEDIATES AND PORE CONFINEMENT EFFECTS IN DEHYDRATION OF BUTANOLS OVER H-ZSM-5 ZEOLITES AND AMORPHOUS ALUMOSILICATE 57

OP-13 G.M. Zhidomorov, I.V. Yudanov, N.A. Kachurovskaya
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

QUANTUM CHEMICAL TREATMENT OF ACTIVE SITES
IN ZEOLITE 59

POSTER PRESENTATIONS

ZEOLITE CATALYSIS

PP-1 A.V. Abramova, E.V. Slivinsky, B.K. Nefedov, Yu.Ya. Goldfarb,
E.K. Trusova
Topchiev Institute of Petrochemical Synthesis, Moscow
CATALYSTS ON BASE OF ULTRASTABLE ZEOLITES FOR OIL
CHEMISTRY 63

PP-2 L.Yu. Dolgikh, N.I. Ilchenko, N.V. Pavlenko
L.V. Pisarzhevskij Institute of Physical Chemistry, National Academy of
Sciences of Ukraine, Kiev
RELATIONSHIP BETWEEN PHYSICO-CHEMICAL AND CATALYTIC
PROPERTIES OF ZEOLITES OF DIFFERENT STRUCTURAL TYPES
IN THE ETHENE-TO-HIGHER HYDROCARBONS
CONVERSION 65

PP-3 V.P. Doronin, V.A. Drozdov. T.P. Sorokina, M.D. Smolikov, T.V. Kireeva
Omsk Department of Boreskov Institute of Catalysis SB RAS, Omsk
MICROPOROSITY OF KBaL ZEOLITE, Pt LOCALIZATION AND
CATALYTICAL PROPERTIES 67

PP-4 E.E. Knyazeva, G.M. Telbiz, N.F. Meged
L.V. Pisarzhevskij Institute of Physical Chemistry, National Academy of
Sciences of Ukraine, Kiev
PARAFFIN CONVERSION OVER MATALCONTAINING PENTASIL
ZEOLITES 69

PP-5 Yu.N. Kochkin, N.V. Pavlenko
L.V. Pisarzhevskij Institute of Physical Chemistry, National Academy of
Sciences of Ukraine, Kiev
EFFECT OF ACIDITY ON THE CATALYTIC ACTIVITY OF ACID
ZEOLITES FOR THE SYNTHESIS OF ETBE 71

PP-6 S.N. Orlik, V.L. Struzhko
L.V. Pisarzhevskij Institute of Physical Chemistry, National Academy of
Sciences of Ukraine, Kiev
REDUCTION OF NITROGEN OXIDES BY C_1, C_3 - C_4 -
HYDROCARBONS IN OXIDIZING ATMOSPHERE ON METAL
EXCHANGED ZEOLITES 73

PP-7 V.N. Romannikov
Boreskov Institute of Catalysis SB RAS, Novosibirsk
BASE CATALYSIS ON ZEOLITES IN THE FORMALDEHYDE-
DIMETHYLAMINE TRASFORMATIONS 75

PP-8 V.A. Sadykov, G.A. Alikina, R.V. Bunina, S.L. Baron, S.N. Pavlova , S.A.
Veniaminov, A.Ya. Rozovskii*, V.F. Tretyakov*, V.V. Lunin**, V.A. Matyshak***
Boreskov Institute of Catalysis SB RAS, Novosibirsk

*Topchiev Institute of Petrochemical Synthesis, Moscow
**Chemical Department of the Lomonosov Moscow State University
***Semenov Institite of Chemical Physics RAS, Moscow
ZEOLITE-BASED CATALYSTS FOR SELECTIVE REDUCTION OF NITROGEN OXIDES BY LIGHT HYDROCARBONS UNDER OXYGEN EXCESS 77

PP-9 E.A. Stepanova, A. Rat'ko
Institute of General and Inorganic Chemistry, Belarus Academy of Sciences, Minsk
ZEOLITE-CONTAINING CATALYSTS ON THE BASIS OF HIGH SILICA HTsVM ZEOLITE AND LAYER-PILLARED MONTMORILLONITE 80

PP-10 N.A. Zakarina, G.V. Artyukhina, L.D. Volkova
D.V. Sokolsky Institute of Organic Catalysis & Electrochemistry of National Academy of Sciences of the Republic of Kazakhstan, Almaty
HETEROPOLY ACIDS AS ZEOLITE-TYPE MODIFIERS OF CATALYSTS SURFACES 82

PP-11 G.D. Zakumbaeva, Sh.A. Gilmundinov, N.Ph. Toktabaeva, G.N. Kotova, D.T. Nurgalieva, R.I. Egizbaeva
D.V. Sokolsky Institute of Organic Catalysis & Electrochemistry of National Academy of Sciences of the Republic of Kazakhstan, Almaty
SELECTIVE REDUCTION OF NITRIC OXIDE BY PROPYLENE ON BLOCK ZEOLITE-, Pt- AND Pd-CONTAINING CATALYSTS 84

CATALYSIS FOR ENVIRONMENTAL PROTECTION

PP-12 S.N. Bukeikhanova, O.E. Lebedeva
Al-Faraby Kazakh State National University, Almaty, Republic of Kazakhstan
UTILIZATION OF ELECTROTHERMOPHOSPHORUS SLAG AS COMPONENTS OF CATALYSTS 89

PP-13 E.D. Chekurovskaya, L.G. Zubanova, R.I. Kuzmina, T.M. Tarasova and V.P. Sevostianov
Saratov State University
Scientific Research Institute of Chemistry, Saratov
METALCOMPLEX-SUPPORTED CATALYSTS FOR THE CONVERSION OF HYDROCARBONS AND THEIR DERIVATIVES 91

PP-14 R.I. Kuzmina, L.G. Zubanova, E.D. Chekurovskaya, T.M. Tarasova and V.P. Sevostianov
Scientific Research Institute of Chemistry, Saratov
Saratov State University
CATALYTIC PURIFICATION OF WASTE GASES FROM HYDROCARBONS AND THEIR O-, N-, AND CL-DERIVATIVES 93

PP-15 S.G. Shcheglova, E.V. Pletneva, R.I. Kuzmina, M.R. Kakhiani, and V.P. Sevostianov
Saratov State University
Scientific Research Institute of Chemistry, Saratov

CATALYTIC PURIFICATION OF WASTE GASES FROM CARBON AND NITROGEN OXIDES 95

PP-16 S.Y. Molina, L.P. Mukhina, and V.P. Sevostianov
Saratov State University
A CATALYST FOR NEUTRALIZING NITROGEN AND CARBON OXIDES IN WASTE GASES 97

PP-17 S.V. Borisova, E.V. Pletneva, and V.P. Sevostianov
Scientific Research Institute of Chemistry, Saratov
Saratov State University
CATALYTIC SYNTHESIS OF ACETIC ANHYDRIDE BY MEANS OF OXIDIZING ACETALDEHYDE 99

PP-18 A.V. Pletnev, N.V. Vorobiova, E.V. Pletneva, and V.P. Sevostianov
Scientific Research Institute of Chemistry, Saratov
Saratov State University
USING ULTRADISPERSE METALS IN THE ORGANIC AND ECOLOGICAL CATALYSIS 101

Part II

PP-19 Y.A. Demyanenko, A.V. Sachivco, V.P. Tverdokhlebov, V.A. Fejdorov
State Thechnology Academy, Krasnoyarsk
ISC Achinsk Refinery, Achinsk
A NEW ENVIRONMENTAL SAFE CATALYST FOR USE IN HIGH TEMPERATURE PROCESS, DERIVED FROM FERROCEN 103

PP-20 A.I. Dzhumabaeva, A.N. Sartaeva, K.A. Zhubanov
Al-Faraby Kazakh State National University, Almaty, Republic of Kazakhstan
INFLUENCE OF RARE EARTH OXIDES ON ACTIVITY OF SUPPORTED ALUMINA-CHROMIUM CATALYSTS OF SULFUR DIOXIDE OXIDATION 104

PP-21 V.N. Efremov, G.M. Tesakova, N.K. Ikonnikov, E.Z. Golosman
AOOT Novomoskovsk Institute of Nitrogen Industry, Novomoskovsk, Russia
COMBINED CATALYTIC PURIFICATION OF WASTE GASES IN NITRIC ACID PRODUCTION FROM NITRIC OXIDES, CARBON AND AMMONIA 106

PP-22 N.R. Gazimzyanov , V.I. Kvashonkin
Elektrogorsk Institute of Petroleum Refining, Elektrogorsk
SELECTIVE WATER EXTRACTION OF ACTIVE COMPONENTS FROM HYDROTREATING CATALYSTS AS AN ESTIMATION METHOD OF THEIR CATALYTIC PROPERTIES IN OXIDE FORM 108

PP-23 M.A. Kipnis, L.G. Danilova, A.Yu. Shashkov, V.F. Dovganyuk, M.A. Porublev, Yu.N. Zelentzov
Elektrogorsk Institute of Petroleum Refining, Elektrogorsk
Angarsk Petrochemical Company, Angarsk
ALUMINA AND CARBON CARRIERS FOR PALLADIUM "EGGSHELL" CATALYSTS 110

PP-24 M.A. Kipnis, V.S. Agaronov, N.R. Gazimzyanov
Elektrogorsk Institute of Petroleum Refining, Elektrogorsk
THE NEW Ni-Mo/ Al_2O_3 CATALYST FOR HYDROGENATION OF ORGANIC SULPHUR COMPOUNDS IN NATURAL AND REFINERY GASES 112

PP-25 M.A. Kipnis, A.Yu. Kalinevich, V.F. Dovganyuk, L.G. Danilova, M.A. Porublev, Yu.N. Zelentzov
Elektrogorsk Institute of Petroleum Refining, Elektrogorsk
Angarsk Petrochemical Company, Angarsk
THE NEW CATALYSTS FOR HYDROGEN, AMMONIA, AND SYNGAS PRODUCTION 114

PP-26 T.V. Turkova, M.A. Kipnis, A.Yu. Shashkov
Elektrogorsk Institute of Petroleum Refining, Elektrogorsk
LOW PALLADIUM CONTENT "EGGSHELL" CATALYSTS 116

PP-27 O.M. Ilinitch and Yu. S. Vetchinova
Boreskov Institute of Catalysis SB RAS, Novosibirsk
LIQUID PHASE OXIDATIVE DETOXICATION OF SULFIDES IN CATALYTIC MEMBRANE REACTOR 118

PP-28 N.N. Kundo, W.E. Myzlish, G.A. Faddeenkova, T.L. Stuchinskaya
Boreskov Institute of Catalysis SB RAS, Novosibirsk
POTENTIALITIES OF PHTHALOGYANINE CATALYSTS FOR DESULPHURIZATION OF GASES AND SOLUTIONS 121

PP-29 V.F. Lyakhova, N.N. Sazonova, A.V. Simakov, G.B. Barannik, T.A. Nikoro, O.V. Komova, Z.R. Ismagilov, H. Veringa*
Boreskov Institute of Catalysis SB RAS, Novosibirsk
*Energy Research Foundation, ECN, Petten, The Netherlands
THE CATALYSTS FOR DIRECT OXIDATION OF AMMONIA INTO MOLECULAR NITROGEN 123

PP-30 M.G. Martsenyuk-Kukharuk, V.A. Ostapyuk, S.N. Orlik, A.D. Tereshchenko, I.F.Mironyuk
L.V. Pisarzhevskij Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Kiev
SUPPORTED BLOCK CATALYSTS FOR SCR PROCESS OF NITROGEN OXIDES 125

PP-31 A.Y. Mil'chenko, T.A. Kremleva*, A.Y. Yuffa*
Institute of North Assimilation Problems SB RAS, Tyumen
*Tyumen State University, Tyumen
NOVEL ECOLOGICALLY PURE METHOD OF PHENOLIC ALCOHOLS PRODUCTION - ALKOXYLATION OF PHENOL WITH FORMALDEHYDE CATALYZED BY SILICA BASED SULPHOCATIONITES 127

PP-32 Z.P. Pai and A. Ermakova
Boreskov Institute of Catalysis SB RAS, Novosibirsk
CATALYTIC PROCESSING OF H_2S CONTAINING GASES OF OIL-REFINING AND COKE-CHEMISRTY 129

PP-33 Z.P. Pai and A. Yermakova

Boreskov Institute of Catalysis SB RAS, Novosibirsk
LIQUID CATALYTIC PURIFICATION OF GASES FROM SO_x AND NO_x 131

PP-34 A.N. Pestryakov, E.N. Yurchenko*, A.E. Feofilov*, O.V. Pestryakova
Tomsk State Academy of Civil Engineering, Tomsk
*Russian Scientific Center "Applied Chemistry", St. Petersburg
CATALYSTS BASED ON FOAM METALS FOR EXHAUST GAS PURIFICATION 133

PP-35 N.N. Sazonova, L.T. Tsykoza, A.V. Simakov, G.B. Barannik
Boreskov Institute of Catalysis SB RAS, Novosibirsk
WO_3 AND Nb_2O_5 ADDITIONS FOR MONITORING OF V_2O_5 - TiO_2 CATALYST RESISTANCE TO SULPHUR OXIDE POISONING 135

PP-36 R.A. Shkrabina, A.A. Kirtchanov, N.A. Koryabkina, H. Veringa*, P. Pex*, Z.R. Ismagilov
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
*ECN, Petten, The Netherlands
POROUS ALUMINA CERAMICS AS A SUPPORT OF CATALYSTS AND MEMBRANES 137

P-37 A.V. Simakov, N.N. Sazonova, E.V. Rebrov*, O.V. Komova, G.B. Barannik
Boreskov Institute of Catalysis SB RAS, Novosibirsk
*State University, Novosibirsk
REACTION KINETICS AND DYNAMICS OF NO ADSORBED FORMS ON Cu-ZSM-5 AT THE SELECTIVE REDUCTION OF NO BY PROPANE 139

PP-38 A.D. Simonov, N.A.Yasykov, E.I. Yepifantseva
Boreskov Institute of Catalysis SB RAS, Novosibirsk
CATALYTIC PROCESSING OF SEDIMENTS AND PURIFICATION OF EFFLUENTS 141

CATALYSIS FOR ORGANIC SYNTHESIS AND PETROCHEMISTRY

PP-39 V.N. Antciferov, A.M. Makarov, I.V. Filimonova, M.U. Kalashnikova
Republican Engineering -Technical Centre of Powder Metallurgy, Perm
CATALYTIC SYSTEMS FOR THE ABATEMENT OF CARBON MONOXIDE AND UNBURNED HYDROCARBONS 145

PP-40 V.N. Antciferov, A.M. Makarov, I.V. Filimonova, M.U. Kalashnikova
Republican Engineering -Technical Centre of Powder Metallurgy, Perm
CATALYSTS BASED ON HIGHLY POROUS CELLULAR MATERIALS (HPCM) 147

PP-41 M.A. Arellano, O.N. Temkin, N.Kh. Allakhverdova* and I.V. Cherepnov
Lomonosov Academy of Fine Chemical Technology, Moscow
*Azizbekov Azeri Technological University, Baku, Azerbaidzhan
HETEROGENEOUS GASE PHASE CATALYTIC OXIDATION OF ETHANOL TO ACETIC ACID OVER THE Sn-Mo OXIDE CATALYST 149

PP-42 Yu.V. Belokopytov
L.V. Pisarzhevskij Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Kiev
THE CATALYTIC TREATMENT AND DISPOSAL OF CHLOROORGANIC WASTE 151

PP-43 A.G. Dedov, M.V. Vyshneckai, M.N. Kartasheva, L.E. Tskhai, A.P. Poliokov, E.M. Rudik
I.M. Gubkin State Academy of Oil and Gaz, Moscow
THE FLUORINE-CONTAINING CATALYSTS IN OXIDATIVE-COUPLING OF METHANE 153

PP-44 Ya.A. Dorfman, G.S. Polimbetova, L.V. Levina and R.R. Abdreimova
D.V. Sokolsky Institute of Organic Catalysis & Electrochemistry of National Academy of Sciences of the Republic of Kazakhstan, Almaty
NOVEL OXIDATIVE ALKOXYLATION AND AMINATION OF PH_3 AND P_4 CATALYZED BY Cu (II) CELLULOSE ANCHORED COMPLEXES 155

PP-45 M.V. Dorogov, E.M. Alov, Y.A. Moskvichev, V.V. Plahtinskii
Yaroslavl State Technical University, Yaroslavl.
CATALYTIC HYDROGENATION OF NITRO- AND DINITROPOLYAROMATIC SUBSTANCES WITH DIFFERENT FOOT-PATH GROUPS - THE WAY OF SYNTHESIS OF MONOMERS FOR THERMOSTABLE AND THERMOPLASTIC COMPOSITIONS.......... 157

PP-46 A.V. Fionov, E.V. Lunina
Lomonosov Moscow State University, Moscow
CONTROL OF ACCEPTOR AND DONOR PROPERTIES OF ALUMINA BY MEANS OF TREATMENT BY ACIDS AND BASES 159

PP-47 S.L. Hladiy, M.K. Starchevsky, Yu.A. Pazdersky, M.N. Vargaftic* and I.I. Moiseev*
"Syntez" Research Institute, Borislav, Ukraine
*N.S. Kurnakov Instutute of General & Inorganic Chemistry RAS, Mocsow
GIANT PALLADIUM CLUSTERS IN SOFT OXIDATION OF ETHANOL 161

PP-48 O.M. Ilinitch, N.E. Kim*, B.M. Khlebnikov* and V.A. Likholobov
Boreskov Institute of Catalysis SB RAS, Novosibirsk
*Research Institute of Chemical Technology, Novosibirsk
POLY(PHENYLENE OXIDES) - CATALYTIC SYNTHESIS AND MEMBRANE APPLICATION 163

PP-49 A.S. Ivanova, E.M. Al'kaeva, T.V. Andrushkevich, V.M. Mastikhin, E.A. Paukshtis
Boreskov Institute of Catalysis SB RAS, Novosibirsk
ACIDITY EFFECT ON ALUMOSILICATE CATALYTIC PERFORMANCE AT β-PICOLINE SYNTHESIS VIA ACROLEIN CONDENSATION WITH AMMONIA 165

PP-50 S.R. Ivanova, K.S. Minsker
Bashkirian State University, Ufa

ABOUT THE CONNECTION OF THE EFFECTIVENESS OF ELECTROPHILIC CATALYSTS OF SEMIFUNCTIONAL ACTIVITY WITH THEIR ACID STRENGTH MEASURE 167

PP-51 Y.G. Kim, V.D. Stytsenko*, V.A. Khavkin*, J.S. Lee
Research Center for Catalysis and Catalytic Technology, Pohang, Korea
*Topchiev Institute of Petrochemical Synthesis RAS, Moscow
**All-Russian Research Institute of Petroleum Refining, Moscow
HYDROCONVERSION OF AROMATIC HYDROCARBONS OVER NEW TRIMETALLIC CATALYSTS.. 169

PP-52 A.V. Kondratiev, V.S. Markevich
Joint-stock company "All-Russian Research Institute of Organic Synthesis", Novokuibyshevsk
POTASSIUM ACETATE - CATALYST FOR ACID KETONIZATION... 170

PP-53 A.V. Kravtsov, E.D. Ivanchina and T.V. Kravtsova
Polytechnic University, Tomsk
COMPUTER PREDICTION OF Pt-CATALYST ACTIVITY OIL REFINING 171

PP-54 V.A. Kreuchkov, D.I. Slovetsky, V.T. Popov, A.V. Prokophjev, E.J. Bogolepova, T.S. Vinogradova, E.V. Slivinsky, G.S. Yeurjev *
Topchiev Institute of Petrochemical Synthesis RAS, Moscow
*Boreskov Institute of Catalysis SB RAS, Novosibirsk
THE NEW CATALYSTS FOR METATHESIS REACTIONS OF OLEFINS AND SUBSTITUTED OLEFINS WITH FUNCTIONALY GROUPS 173

PP-55 S.Yu. Kuz'mitskaya, N.A. Vasilyeva
Boreskov Institute of Catalysis SB RAS, Novosibirsk
EFFECT OF MODIFIED MAGNESIUM OXIDE ON N-BUTANE HIGH-TEMPERATURE DECOMPOSITION 175

PP-56 L.V. Manuilova, N.D. Parshukova and T.S. Sukhareva
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
CATALYTIC PRODUCTION OF 4-METHYLTHIAZOLE...................... 176

PP-57 A.V. Mashkina, Yu.A. Savostin*
Boreskov Institute of Catalysis SB RAS, Novosibirsk
"KATALYZATOR Ltd", Novosibirsk
CATALYTIC SYNTHESIS OF ORGANIC SULFUR COMPOUNDS 178

PP-58 S.V. Mezcheryakov, K.D. Korenev, V.A. Zavorothny
I.M. Gubkin State Academy of Oil and Gaz, Moscow
THE MINERAL-ORGANIC SULFOCATIONITES-CATALYSTS FOR THE OIL PERFORMING AND OIL CHEMISTRY PROCESSES.......... 180

PP-59 K.S. Minsker, S.R. Ivanova
Bashkirian State University, Ufa
CATALYST HYDROCARBONS PYROLISIS ON CHLORIDS OF ALKALINE EARTH METALLS 182

PP-60 K.Ya. Motovilov*, K.I. Matveev, E.G. Zhizhina, V.F. Odyakov, E.V. Gusamova*
Novosibirsk State Agriculture University, Novosibirsk
Boreskov Institute of Catalysis SB RAS, Novosibirsk

EFFICIENCY OF VITAMIN K (VIKASOL) PRODUCED VIA "VIKASIB" TECHNOLOGY AT POULTRY NUTRITION 184

PP-61 E.A. Mushina, I.F. Gavrilenko, Yu.Ya. Podolsky, V.M. Frolov, B.A. Krenzel, I.N. Borodina, M.S. Gabutdinov*, C.B. Medvedeva*, A.Z. Vakhbreit*, S.A. Solodyankin*, V.F. Cherevin*
Topchiev Institute of Petrochemical Synthesis RAS, Moscow
*Stock Company "Kazanorgsintez", Kazan
BINUCLEAR METAL COMPLEX CATALYSTS IN POLYMERIZATION PROCESSES 185

PP-62 V.N. Postnov, A.G. Novikov
St. Petersburg State University, St. Petersburg
SYNTHESIS OF SUBSTRATUM-ORIENTED HETEROGENEOUS CATALYSTS BASED ON SILICA AND INVESTIGATION OF THEIR PROPERTIES 187

PP-63 I.V. Sablukova, B.S. Strelchik, E.Z. Golosman, O.V. Lysova, V.A. Vekslina
AO VNIIOS NK, Novokuibyshevsk, Russia
AO NIAP, Novomoskovsk, Russia
Aerocosmic Iniversity, Samara, Russia
COPPER CATALYSTS FOR THE DEHYDROGENATION REACTION OF THE ETHANOL TO THE ETHYL ACETATE 189

PP-64 U.M. Schindler, A.G. Sarmuzina, G.Sh. Tlepieva
Al-Pharaby Kazakh State National University, Almaty, Republic of Kazakhstan
State Research-and-Production Association of Industrial Ecology, "Kazmekhanobr", Almaty, Republic of Kazakhstan
COMPLEX EXPLOITING OF SORBABLE CATALYTIC TECHNOLOGIES OF GAS-WATER 190

PP-65 V.A. Semikolenov
Boreskov Institute of Catalysis SB RAS, Novosibirsk
CATALYTIC SYNTHESIS OF 1-ETHYL-2-AMINOMETHYLPIRROLYDINE FOR THE PRODUCTION OF PHARMACEUTICALS 192

PP-66 F.K. Smidt, Kim En Hwa and K.P. Zhdanova
Irkutsk State University, Irkutsk
PHYSICO-CHEMICAL AND CATALYTIC PROPERTIES OF ALUMOMOLYBDENUM CATALYSTS 194

PP-67 E.F. Stefoglo, O.P. Zhukova
Institute of Carbon, Kemerovo
ANESTHESINE CATALYTIC PRODUCTION VIA LIQUID-PHASE HYDROGENATION OF ETHYL ETHER OF PARA-NITROBENZOIC ACID OVER Pd/C 196

PP-68 A.R. Suzdorf, S.V. Morozov*, A.M. Kovalev, A.G. Anshits
Institute of Chemistry of Natural Organic Materials SB RAS, Krasnoyarsk
*Institute of Organic Chemistry SB RAS , Novosibirsk

HYDRODECHLORINATION OF CHLOROAROMATIC COMPOUNDS ON NICKEL CATALYSTS 198

PP-69 E.G. Zhizhina, A.P. Krysin*, V.F. Odyakov, K.I. Matveev
Boreskov Institute of Catalysis SB RAS, Novosibirsk
*Institute of Organic Chemistry SB RAS,Novosibirsk
CATALYTIC SYNTHESIS OF 1-NAPHTHYLACETIC ACID VIA CARBONYLATION OF 1-(CHLORMETHYL)NAPHTALENE IN THE PRESENCE OF Pd(O)-TRIPHENYLPHOSPHINE COMPLEX............ 200

Russian-Korean Seminar on Catalysis

Editor: Prof. V.A. Likholobov

The present abstracts underwent a rather mild editing process.
For this reason responsibility for all presentations rests with the authors.

Technical editors: T.V. Zamulina
E.L. Mikhailenko
Cover: E.E. Razgulina

Сканирование и обработка: А.А. Спиридонов
ИК СО РАН 2019

Подписано в печать 05.05.95 Формат 60×84/16
Печ.л. 12,8 Заказ № 98 Тираж 150
Отпечатано на полиграфическом участке издательского отдела Института катализа
6300090, Новосибирск, пр. Ак. Лаврентъева. 5.