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CHRONICLE

Catalysis in the Year 2000: 12th International Congress on Catalysis Granada (Spain, July 9–14, 2000)

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INTRODUCTION

The 12th International Congress on Catalysis was held in July 9–14, 2000 in Granada (Spain). About 1300 researchers attended at congress and the amount of presented material was record-breaking. There were six plenary and seven keynote lectures to introduce each theme, 124 lectures at four parallel sections, 450 posters, and 100 posters devoted to new results.

The maximum number of oral talks were presented by US authors (27 lectures and talks, ~20%). France is in second place (17 talks) and Japan is in third place (14 talks). However, France presented the maximum number of posters (66, 14.6%). The United States presented only 37 posters. Japan and Spain held second place (45 posters each). I have an impression that a certain role belonged to piety to the United States: the organizers of the congress felt uncomfortable to reject some US oral talks. There was no difference in the scientific level between oral and poster presentations.

Russia had six oral talks (4.3%) and 26 posters (5.8%), and this fact reflects the decreased role of our country in the world science of catalysis. Some talks were accepted from other CIS countries, Bulgaria, and Romania, but they were canceled because their authors did not come.

I am unable to cover all of the information presented at the congress in a single review. Therefore, I will restrict myself to considering only plenary and keynote lectures, as well as some of oral talks.

All oral and poster presentations were published as four-volume proceedings (overall 3908 pages). This is an encyclopedia of modern catalysis in a sense.

GENERAL PROBLEMS OF CATALYSIS

The first plenary lecture devoted to catalyst characterization *in situ* was presented by H. Topsoe (Haldor Topsoe, Denmark). A systematic use of new physical methods—scanning tunneling microscopy, X-ray diffraction, and EXAFS—under conditions close to catalytic ones allows one to detect deep changes in the catalyst: recrystallization and changes in the surface area and dispersity. For instance, structural changes in the $Cu/ZnO/Al_2O_3$ catalyst under the conditions of methanol synthesis and in the V/TiO_2 catalyst in the reaction of NH_3 with NO after small changes in the ratio of reactant concentrations. On the Co–Mo–S catalyst for hydrodesulfurization, triangular nanoclusters of MoS_2 are formed near the edges of crystals. The formation and decomposition of small clusters under the conditions of O_2 and H_2S adsorption on Ni(110) were studied. Images that were demonstrated point to atomic resolution. Note, however, that data obtained *in situ* by physical methods were not compared to kinetic data as in other studies along these lines. In this respect, Russian studies are ahead of foreign ones.

L.D. Schmidt (University of Minnesota, Minneapolis, USA) talked about catalytic reactions at millisecond contact times. Similar reactions were reported earlier and even used on an industrial scale (e.g., NH_3 oxidation to NO or Andrusov's reaction $NH_3 + CH_4 + O_2$ to form HCN on Pt grids). However, Schmidt was the first to study these reactions systematically. His works are devoted to high-temperature exothermic reactions of hydrocarbon oxidation on supported and bulk metals: Pt, Rh, etc. They were actively discussed at several recent meetings. At the congress in Granada, special attention was given to the oxidative dehydrogenation of ethane to ethylene and cyclohexane oxidation to oxygenates.

Schmidt considered reactions at millisecond times on catalysts of two types: large-pore monolith blocks with supported catalysts and metallic (Pt and Rh) grids or spirals through which hydrocarbon–oxygen mixtures without oxygen excess passed. A two-zone reaction structure is formed in both cases, but differently on monolith catalysts and grids.

In the first layer of a monolith catalyst, highly exothermic hydrocarbon oxidation occurs on a 1-mm metal layer with the formation of CO_2 and H_2O accompanied by an increase in temperature to 1000°C and higher. In the case of methane oxidation, direct oxidation to syngas occurs. After that, endothermic reactions occur on the remaining monolith layer, e.g., direct C_2H_6 dehydrogenation to C_2H_4. On a Pt–Sn catalyst, the addition of hydrogen in small amounts to the $C_2H_6 + O_2$ mixture provides 85% selectivity to C_2H_4.

If grids and spirals are used, only some portion of molecules are able to contact the catalyst for milliseconds, to be heated to ~900–1000°C and oxidized. The rest of the molecules fail to react with a catalyst and appear in the postcatalytic volume without heating where they react with heated molecules to form the products at moderate temperatures. Here, peroxide radicals and hydroperoxides are probably formed. Specifically, in the course of cyclohexane oxidation, hexanol was formed.

According to Schmidt, a switch from laboratory tests to an industrial scale is not difficult. For that, one has to increase the diameter of a reactor while preserving the linear rate of the gas. He predicts that an increase in the diameter to 30 cm at a space velocity of 10^6 h^{-1} will allow the production of several tons of the product per day. If the diameter is 180 cm, the output will be 1000 ton/day.

Schmidt also considered the problems of the microtechnology of catalyst design. The catalyst should provide an optimal ratio in different phases (including the gas phase) or in spatially separated zones of exothermic and endothermic steps and mass- and heat-transfer processes. Similar microtechnologies were considered in other talks as well. Thus, M. Janicke (Karlsruhe, Germany) described a microreactor/heat exchanger with one channel filled with a Pt/Al_2O_3 catalyst for H_2 oxidation, and the other channel used for heat exchange with a gaseous or liquid flow.

M. Che (Pierre and Marie Curie University, France) in a keynote lecture considered steps for the preparation of supported oxide catalysts from aqueous solutions from the standpoint of coordination chemistry. For instance, when Ni ions are supported on SiO_2, the support can play the role of a negatively charged ligand for a supported ion. Instead of the initial $[Ni(NH_3)_6]^{2+}$ ion, a $[Ni(NH_3)_4(SiO)_2]$ complex is formed in which a chelating group $(SiO)_2$ occupies two coordination sites in the sphere of the nickel ion. The crystal-field parameter Δ measured by UV–VIS spectrometry for the SiO^- group was lower than those for the H_2O and NH_3 ligands. The following spectrochemical series of ligands in complexes and oxides was obtained.

$$\Delta_{Cl^-} < \Delta_{AlO^-} < \Delta_{SiO^-} < \Delta_{H_2O} < \Delta_{NH_3} < \Delta_{en}.$$

The keynote lecture of R. A. van Santen (Eindhoven University of Technology, Netherlands) was devoted to the theory of zeolite acidity. Quantum chemical calculations, adsorption measurements, NMR spectroscopy, and catalytic activity tests of different zeolites led him to the conclusion that the zeolite affinity to proton depends on the adsorption heat and the proper protonation energy. In its turn, the value of adsorption and the adsorption heat of hydrocarbons strongly depend on the form of zeolite pores and their sizes: the maximum corresponds to pores with a diameter of ~0.5 nm (H-mordenite). In wide-pore zeolites, adsorption is lower because of the low adsorption heat, and in narrow-pore zeolites, the adsorption is lower because of entropy loss. Using *n*-hexane hydroisomerization on zeolites with different pore sizes as an example, it was shown that the catalytic activity of zeolites is determined by the difference in adsorption to a greater degree than by the difference in their proton properties.

M. Anpo (Osaka Prefecture University, Japan) discussed the application of photocatalysts based on TiO_2 for the reduction of various environmental toxins in the atmosphere and hydrosphere under visible light irradiation.

At one of the plenary sessions, leading scientists in catalysis answered questions from the audience. E.G. Derouane (Leverhulme Centre for Innovative Catalysis, The University of Liverpool, United Kingdom) called on the audience to broadly use the methods of combinatorial chemistry in catalysis. Computers make it possible to synthesize and study in detail hundreds of catalyst samples to choose further the most active, selective, and stable of them. Some talks were devoted to this problem. For instance, K. Yajima (Tohoku University, Japan) reported on the study of many zeolite catalysts MZSM-5 with different cations M for NO_x reduction. As might be expected, the most active was CuZSM-5. In my opinion, such an approach is very similar to a method proposed 40 years ago for the statistical selection of catalysts[1]. It takes a researcher away from a scientific search and brings him or her to screening devoid of ideas.

In many reported papers, modern physical methods were used. The three-dimensional transmission electron microscopy (3D-TEM) of catalysts makes a strong impression. J.W. Geus (Utrecht University, Netherlands) demonstrated 3D images of Pt and Ag particles (~1 nm) in the NaY zeolite. Based on the analysis of 43 electron microscopic images at angles from +70° to –72°, a conclusion was drawn that Ag nanoparticles appear both on the surface of NaY and inside it.

J.T. Gleaves and G.S. Yablonskii (Washington University, St. Louis, Missouri, USA) showed that further development in the so-called TAP reactor enables minimizing the concentration gradient and obtaining information on very fast reaction steps. The use of UV resonance–laser–Raman spectroscopy allowed Can Li (Dalian University, China) to characterize the state of transition metal ions in zeolites.

K. Domen (Technological Institute, Tokyo, Japan) used picosecond IR spectroscopy to study unstable intermediate species. A change in the adsorbate state under the action of picosecond laser pulses was registered by sum frequency generation (SFG). A stable bidentate formate on the surface of Ni(111) decomposes into H_2 and CO_2 under the action of laser pulses. In this process, a short-lived (10^{-10}–10^{-11} s) monodentate formate is formed.

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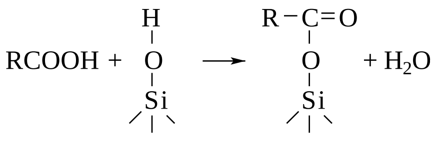
[1] See Krylov, O.V., *Catalysis by Nonmetals*, New York: Academic, 1970.

NEW CATALYSTS AND REACTIONS

M.E. Davis (California Institute of Technology, Pasadena, USA) talked in his plenary lecture about methods for the syntheses of heterogeneous nonbiological catalysts, which are close to immobilized enzymes. These syntheses are based on L. Pauling's supposition stated 50 years ago that the selectivity of enzymes is determined by the stoichiometry of a transition state and the special geometry of a cavity near the active center. Microporous materials based on SiO_2 were synthesized, which were modified by complex organic compounds with different hydrophilic and hydrophobic functional groups. The proposed systems can work as an acid or base catalyst in aqueous and hydrocarbon liquid media. In the pores of SiO_2, polymeric molecules with phenylethyl, aminopropyl, and other groups, which are responsible for stereospecific (including asymmetric) catalysis, are incorporated. Cavities had sizes and forms that were close to the sizes and forms of complex organic substrate molecules. These molecular sieves catalyzed enamine synthesis from acetylacetone and amines, retro-aldol condensation, and other reactions.

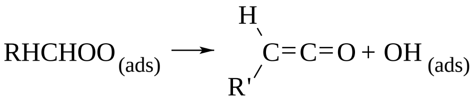
M.A. Barteau (University of Delaware, Newark, USA) delivered a plenary lecture in which he demonstrated the applications of surface science to catalyst design using two reactions as an illustration.

A search for a catalyst for ketene RR'C=C=O synthesis by the decomposition of carboxylic acids was based on adsorption data for oxide single crystals. These data suggest that ketene can selectively be formed from carboxylic acids (without hydration and decarboxylation) if the cation of an irreducible oxide has only one coordination vacancy. This condition is met in the case of the MgO(110) plane and SiO_2, which is even better. Experiments with SiO_2 single crystals showed that the coordination site is occupied by the OH group, which is a site holder. Acid adsorption leads to the formation of a carboxylate group at this site:



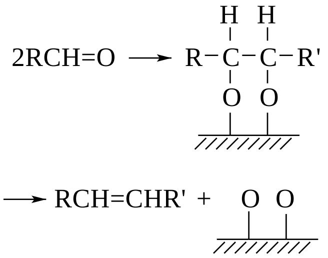
$$RCOOH + H{-}O{-}Si \longrightarrow R{-}C{=}O\,({-}O{-}Si) + H_2O$$

The reaction becomes catalytic because the active site (the OH group) is regenerated with the formation of ketene:



$$RHCHOO_{(ads)} \longrightarrow (H)(R')C{=}C{=}O + OH_{(ads)}$$

Another reaction, which was initially studied on TiO_2 single crystals is the reductive coupling of carbonyl compounds:



$$2RCH{=}O \longrightarrow R{-}CH(O{-})\,{-}\,CH(O{-}){-}R' \longrightarrow RCH{=}CHR' + O\ O$$

In this reaction, titanium atoms are oxidized. Their reduction by hydrogen with the formation of H_2O changes the charge ($Ti^{4+} \longrightarrow Ti^{<4+}$) and makes the reaction catalytic. On TiO_2 powders (anatase and rutile), the catalytic reaction of CH_3CHO with H_2 at 500°C yields butene-2, and the reaction of CH_3COCH_3 with H_2 yields 2,3-dimethylbutene-1. For his work, M.A. Barteau received the International Catalysis Award.

P.A. Jacobs (Leuven Catholic University, Belgium) delivered a keynote lecture devoted to overcoming problems associated with a synthesis carried out in a two-phase system of two immiscible liquids. For instance, it is hard to carry out a reaction between glycerol, which is soluble in water, and fatty acids, which are soluble in nonpolar solvents. Jacobs proposed to overcome these difficulties by creating a three-phase system: a catalytic functional group, such as the $-(CH_2)_3SO_3H$ group, which is grafted on to the solid support (SiO_2 or mesoporous MCM-41 zeolite). The catalyst thus obtained helped to carry out the synthesis of lauryl acid monoglyceride with a high selectivity. Experiments on enantioselective olefin epoxidation were also successful. In this case, if a grafted catalyst is absent, olefin is in the polar solvent and hypochlorite, which is an epoxidation agent, is in an aqueous solution. Another method for creating a catalyst working in a two-phase system or, to be more precise, in a three-phase system containing a catalyst and two immiscible liquids is the introduction of ions (e.g., quarternary ammonium or phosphonium salts) into cation-exchange clays (e.g., montmorillonites) or anions to anion exchangers (double lamellar hydroxides).

P. Métivier (Rhodia Chimie, Lion, France) reviewed catalysis applications for the syntheses of fine chemicals. Those are manufactures with a throughput lower than 10000 ton/year. In addition to the usual problem of lowering the product cost, there is a problem of product lifetime (5–10 years), which is usually shorter than the life time of a large-scale product (20–50 years or longer). To apply a new fine-chemical process in industry, three requirements should be fulfilled: (1) the process should be well developed to avoid additional tests when a project starts, (2) the process should be adaptable to modern technologies, and (3) the process should offer substantial advantages over existing ones. The Friedel–Krafts acylation of aromatic compounds with Lewis acids is usually carried out as a noncatalytic reaction. Sandia developed an industrial catalytic process for anisole acylation to *p*-acetoanisole over zeolite catalysts. The process of *n*-hexane hydroxycarbonylation on iridium catalysts using HCOOH is interesting because it avoids the use of toxic CO (as in the case of usual hydrocarbonylation). For the selective reduction of unsaturated acids to aldehydes with C=C bonds remaining intact, a Ru–Sn catalyst was developed. This allowed the company to obtain many useful aldehydes. Selective oxidation of alcohols to aldehydes and ketones on Pt–Bi and Pd–Bi catalysts was also carried out.

Most of the talks at the section devoted to the synthesis of fine chemicals concerned liquid-phase and gas-phase hydrogenation, including asymmetric hydrogenation. In some cases, catalysts were prepared under supercritical conditions. S. van der Hark (Chalmers Center, Göteborg, Sweden) described the hydrogenation of fats in a homogeneous supercritical solvent (propane). This enabled the creation of a homogeneous phase and solving the problems associated with diffusion.

Special interest was given to the catalytic reactions of CO_2, e.g. dimethyl carbonate and *N*,*N*-dialkyl formamide syntheses. Aldol condensation reactions were considered as a method for C–C bond formation.

At the 11th Congress on Catalysis in Baltimore, one of the plenary lectures was devoted to great changes in polymerization due to the appearance of one-center metallocene catalysts. At the 12th Congress, F. Giardelli (Pisa University, Italy) reported on advances in this area. One-center and multiple-center supported metallocene catalytic systems were developed. Metallocene (first of all, zirconocene) complexes are sewed to the surfaces of SiO_2, zeolites, and other supports using methylalumoxanes (MAO), $Cl_2Si(CH_3)_2$, and other binders. In ethylene, propylene and other olefin polymerization, polymers are formed with different properties. The Cp_2ZrCl_2 and Cp_2TiCl_2 complexes supported on zeolites Y and ZSM-5 were less active than the homogeneous complexes, but those supported on mesoporous MCM-41 are close to homogeneous catalysts in the activity. In some cases, polymers with a high molecular weight are formed.

The first attempt to study propylene polymerization on the supported Ziegler–Natta catalyst $TiCl_4$–$MgCl_2$ using *in situ* physical methods, including tunneling electron microscopy, is interesting from methodological standpoint. Fast formation (<0.03 s) of polymeric beads was detected on chaotically distributed active sites. Catalyst particles with a size of 2–5 nm are split under the action of a polymer and polymer–catalyst aggregates with different morphologies are formed on them.

New methods for catalyst preparation were discussed in many talks at the congress. Many of them considered the synthesis of nanoparticles and nanocatalysts. For that plasma methods were used, electron and molecular beams, and other exotic surface science expedients. Note that most of the catalysts with high specific surface areas have long been known to consist of nanoparticles. Often, but not always, new terminology is used just for self-advertising aimed at receiving new funds.

CATALYTIC OXIDATION

In the studies of partial oxidation, an interest in the selective oxidation of alkanes is growing. The selective oxidation of olefins by molecular oxygen, which was given the most attention earlier, was not discussed at the congress. R.K. Grasselli (Munich University, Germany) proposed a new strategy for olefin synthesis from alkanes. It was proposed to combine the catalytic dehydrogenation of alkanes with the selective oxidation of hydrogen to increase the equilibrium yield of olefins in direct dehydrogenation:

$$C_nH_{2n+2} \longrightarrow C_nH_{2n} + H_2,$$

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O.$$

A three-reactor scheme was proposed according to which the first and the third reactors are fed only with an alkane and the second reactor is fed with oxygen or air. Alternatively a one-reactor system was considered with a mixture of alkane dehydrogenation and selective H_2 oxidation catalysts. For instance, for the mixture of the propane dehydrogenation catalyst (0.7% Pt–Sn–ZSM-5) and the hydrogen oxidation catalyst (Bi_2O_3/SiO_2) at 550°C, the yield of propylene from propane was 33%, while the selectivity was 89%. To compare, the equilibrium yield in the dehydrogenation reaction is 25%.

Among the catalysts for the oxidative dehydrogenation of alkanes, supported vanadium oxide systems are the most frequent. C. Mirodatos (Institute of Catalysis, Villeurbann, France) showed that the oxidative dehydrogenation of propane on VO_x/MgO occurs via a mechanism involving the fast reduction of surface VO_3^{4-} polymers, the slow reduction of the $Mg_3V_2O_8$ phase, and slow oxygen diffusion in the bulk of the catalyst. H. Knözinger (Munich University, Germany) reported on the high selectivity of the V/Al_2O_3 catalyst promoted with potassium. D.W. Flick (Delaware, USA) reported that the selectivity of the Pt/Cr_2O_3 catalyst on a ceramic monolith in ethane and propane oxidative dehydrogenation is very high at millisecond contact times.

M.J. Ledoux (Pasteur University, Strasbourg, France) proposed a new highly active and selective V–P–O catalyst on the β-SiC support for butane oxidation to maleic anhydride.

The number of works devoted to the selective oxidation by oxidants other than molecular oxygen (especially H_2O_2) is growing. Hydroxyphosphate $Cu(OH)PO_4$ showed a high activity in phenol hydroxylation of benzene to phenol using H_2O_2 (Feng-Shou Xiao, Changchun University, China). Fe–Si–W heteropoly acid catalysts are active in selective oxidations of hydrocarbons, including methane oxidation to methanol at low conversions (M. Misono, Tokyo University, Japan).

Organic compounds can be oxidized by an $O_2 + H_2$ mixture. In this case, H_2O_2 or hydroxyl radicals $^{\bullet}OH$ are probable intermediates. I. Yamanaka (Technological University, Tokyo, Japan) carried out the direct liquid-phase hydroxylation of benzene to phenol in the $Ti(acac)_2 \cdot PtO_x/SiO_2$ system at 40°C. Oxidation by $H_2 + O_2$ mixtures is interesting and promising in the presence of gold catalysts with TiO_2 and titanium silicates. W.N. Delgass (Purdue University, West Lafayette, USA) showed that, on the $Au/TiO_2/SiO_2$ catalyst, propylene oxidation by $H_2 + O_2$ to propylene oxide can be carried out with a selectivity of up to 100% at a low conversion. He also found evidence that hydroperoxides are intermediate species in this process. M. Haruta (National Research Institute, Osaka, Japan) reported on the selective epoxidation of propylene by $H_2 + O_2$ on Au/Ti–MCM-48. The proposed mechanism involves the formation of H_2O_2 and $HO_2^{\bullet}$.

Another oxidant that is intensively studied and applied in catalysis is N_2O. The problems of purification from N_2O and its use in phenol synthesis by benzene oxidation were discussed by A.K. Uriarte (Solutia, Florida, USA). Low-temperature hydrocarbon oxidation by N_2O on FeZSM-5 was reported by G.I. Panov and co-workers (Institute of Catalysis, Novosibirsk, Russia).

K. Otsuka (Technological University, Tokyo, Japan) showed that benzene can be oxidized by molecular oxygen with a selectivity of 40% and a phenol yield of 4.3% at 550°C on the $4\%V_8Mo_4O_x/SiO_2$ catalyst in the presence of water vapor.

CATALYSIS IN OIL REFINING AND PETROCHEMISTRY

G. Martino (Institute of Oil, Malmaison, France) considered in his plenary lecture the prospects for catalysis application in oil refining and petrochemistry for the period ending in 2010. He noted that the role of catalysis is growing: catalytic processes are currently responsible for ~25% of the gross output worldwide. In 2000, expenses for catalyst manufacturing will reach \$10 billion. Oil refining uses 25% of all produced catalysts. The chemical industry's share is 42%. Gas purification, mostly car exhaust neutralization, consumes 33% catalysts. These figures are inexact; other estimates can also be found.

Currently, about 600 oil refineries are operating worldwide. Virtually all refineries use catalytic reforming and hydrotreating. Other catalytic processes are cracking, hydrogenation, paraffin isomerization, hydrocracking, polymerization, alkylation, and others. Catalysts for these processes are constantly improved. Advances in oil refining are dictated by the market demands and environmental laws. For instance, after 1998 methyl *tert*-butyl ether (MTBE), which is one of the gasoline components capable of increasing the octane number, was recognized as toxic. California and other North American states restrict its use.

From 2000 to 2010, a forecasted increase in oil consumption is from 3600 to 4300 million tons. The shares of different sectors in oil consumption are: motor fuel manufacturing, from 1870 to 2300 million ton; petrochemistry, from 250 to 300 million ton; heat, from 1265 to 1430 million ton. The forecast for 2020 is unclear because of a possible decline in oil production. A switch to the deeper refining of heavy oil residues is the most probable. New sources of energy will possibly appear.

By the year 2010, the ratio of gasoline to diesel fuel is expected to change in favor of diesel. The most serious changes in gasoline components will concern benzene (which is expected to decrease to 1% by 2005). Olefins will drop to 10% (the current ceiling is 18%). The concentration of aromatics should decrease from 42 to 35%. The concentration of sulfur should decrease from 150 to 30–50 ppm. In diesel fuel, the maximum sulfur concentration must be decreased from 350 to 30–50 ppm. Polyaromatics will drop from 11 to 1%. The cetane number should increase from 51 to 55. Forecasts for the period ending in 2010 for each refining process described below take into account that the above characteristics should be achieved.

In catalytic reforming, studies have the aim of increasing the selectivity and activity and decreasing the yields of benzene and coke. Higher aromatics is formed together with hydrogen. Reforming is now virtually the only source of H_2, which is needed in oil refining. Therefore, higher aromatics will remain in gasoline unless cheap methods for H_2 manufacture can be found.

Light paraffin isomerization is becoming more important. Improved catalysts would allow the use of lower H_2 : hydrocarbon ratios. New catalysts based on ZrO_2–SO_4 are more active than zeolites and less sensitive to poisons, but they are still worse than Al_2O_3–Cl. The studies of the isomerization of C_4 paraffins will continue.

Catalytic cracking will remain the most important method for gasoline manufacture. The refining of heavy naphtha will be improved, and the yield of olefins will increase. An important stage in the preparation of cracking feedstock is its desulfurization. Studies on diesel fuel manufacture by cracking will be continued even though it is a bad fuel.

In light olefin alkylation by isobutane, liquid acids (HF and H_2SO_4) should be replaced by solid acid catalysts. Currently, solid acids are less active, but they are preferable from the environmental standpoint.

For C_3–C_4 oligomerization, nickel-based Ziegler catalysts and supported H_3PO_4 are used. The selectivity of these catalysts is low. In connection with the MTBE manufacture decline, the problem of isobutylene dimerization to isooctene and isooctane will appear.

The most important problem in diesel fuel manufacturing remains hydrodesulfurization. Studies along these lines are toward an increase in the activity, stability, and recoverability of catalysts, as well as toward sulfur removal by alternative methods (adsorption, oxidation, and biodesulfurization).

To produce city diesel, deep hydrogenation is used. In this field, the main problem is the catalyst cost (sulfur-resistant noble metals) and the use of expensive hydrogen in large amounts.

The hydrocracking of medium distillates enables obtaining a high-quality product, but it requires substantial investment and consumes hydrogen in large amounts. The presence of naphthalenes in the feedstock requires hydrogenation and ring opening. New active catalysts capable of working at low pressures are needed to lower investment and H_2 consumption.

Turning to petrochemical processes, it is necessary to note that olefins are currently produced by the steam cracking of ethane, naphtha, and heavier fractions. The main source of aromatic hydrocarbons is catalytic reforming. The efforts are focused on lowering the product cost. Olefins for the syntheses of polymers and other chemicals should be of high purity. Olefin manufacturing growth is characterized by the following rates (% per year): ethylene, 3.5; propylene, 5; higher olefins, 8; and *p*-xylene, 6.

In 2010, worldwide ethylene production will reach 120 million tons, of which 40% will be obtained by the cracking of ethane or other hydrocarbons. The conversion of starting materials should increase to 85%. Of new methods for C_2H_4 synthesis, ethane oxidative hydrogenation is more promising than the oxidative coupling of methane. In connection with the possible rejection of MTBE and appearance of redundant plants for methanol synthesis, the Mobil methanol-to-olefins (MTO) process may become promising.

Propylene manufacture will grow to 82 million tons per year in 2010. Recently, several plants for propane dehydrogenation were constructed, but catalytic cracking on the corresponding catalysts will remain the main source of propylene. Dehydrogenation will be profitable in the regions where no catalytic cracking plants are available. An alternative method for propylene manufacture is MTO on mordenites, which gives up to 60% of C_3–C_5 olefins, and ethylene and butene-2 metathesis over rhodium catalysts.

Butene-1 is extracted from the C_4 fraction or obtained by ethylene dimerization on homogeneous catalysts. Higher α-olefins are obtained by ethylene oligomerization. Fischer–Tropsch synthesis is applicable to the manufacturing of olefins with any length of a molecule, but the separation and purification of olefins is difficult in this case.

In 2010, worldwide production of benzene, toluene, and xylenes will reach 40, 21, and 30 million ton respectively. The benzene–toluene–xylene (BTX) fraction is obtained by reforming. New catalysts are Ba/K-zeolite L (Chevron) and GaZSM-5 (UOP). In future, more stereoselective catalysts will be needed. Mobil zeolite catalysts are used in xylene isomerization and ethylbenzene dealkylation. Ni/mordenite catalysts were used for toluene transalkylation with aromatic C_9 hydrocarbons. Catalysts based on ZSM-5 are used for toluene disproportionation in the syntheses of benzene and xylenes in large amounts.

The process of styrene manufacture has two stages. It includes benzene alkylation by ethylene and further dehydrogenation. At the first stage, gas-phase processes over zeolites should be replaced by liquid-phase ones. At the second stage, limitations associated with equilibrium dehydrogenation can be removed by a decrease in pressure below atmospheric and selective hydrogen removal. Possible use of membrane technology is considered. Butadiene dimerization to vinylcyclohexane with further dehydrogenation to styrene is one of the promising processes.

S. Gembicki (UOP Research Center, Des Plaines, USA) delivered a keynote lecture with a brief historical survey of acid catalysis application in oil refining starting from process of catalytic cracking (Houdry, 1928). He mentioned that UOP developed new processes: paraffin alkylation on solid acid catalysts (the Alkylene process), paraffin isomerization on sulfated oxides (the Par–Isom process), methanol conversion to ethylene and propylene on molecular sieves SAPO-34 (the MTO process). The lecturer underlined the role of experimental physical techniques and calculation methods, as well as combinatorial methods in developing new catalysts and processes.

V.B. Kazanskii and T.V. Vasina (Institute of Organic Chemistry, Moscow, Russia) proposed a new mechanism for isoparaffin alkylation by olefins catalyzed by sulfuric acid. The mechanism implies direct alkylation of isoparaffins by alkyl sulfates.

Many talks were devoted to paraffin isomerization and hydroisomerization. L.B. Galperin (UOP Research Center, Des Plaines, USA) discovered the effect of H_2S and N_2 on *n*-decane hydroisomerization on the Pt/SAPO catalysts. L.M. Kustov and co-workers (Institute of Organic Chemistry, Moscow, Russia) studied the state of metal in bimetallic $Pt–Pd/SO_4^{2-}/ZrO_2$ catalysts.

G. Emig (Erlangen University, Germany) proposed a new method for the synthesis of ethylbenzene (an important styrene precursor) by the catalytic dimerization of butadiene-1,3. The catalyst for this process is a FAU-type zeolite, which has basic properties and contains Cs and Na ions.

CATALYSIS IN GAS CONVERSION

J.L.G. Garcia-Fierro (CSIC, Madrid, Spain) discussed the process of oxidative methanol reforming for the production of hydrogen. Methanol is currently the third product after ethylene and ammonia on the chemical market. Its production is 25 million ton/year, which exceeds demand. Garcia-Fierro proposes to convert methanol by the partial oxidation to hydrogen without toxic CO formation:

$$CH_3OH + \frac{1}{2}O_2 \longrightarrow 2H_2 + CO_2.$$

Almost 100% selectivity of methanol-to-H_2 conversion was achieved by coupling the partial oxidation of CH_3OH with its steam reforming

$$CH_3OH + H_2O \longrightarrow 3H_2 + CO_2.$$

The best catalysts for this process are $Cu_{0.4}Zn_{0.6}$ and Pd/ZnO. The optimal conditions are an O_2 pressure of 0.05 atm and 215°C.

In the catalytic C_1 chemistry, it catches the eye that an interest in the oxidative coupling has lowered considerably, although an interest in methane conversion to syngas by oxygen, carbon dioxide, and steam reforming strengthened. F. Trifiro (Bologna University, Italy) considered the problems of the optimal temperature distribution and exothermic and endothermic reactions in autothermal methane reforming on $Rh/MgO/Al_2O_3$ at low contact times. In the first catalyst layer, which is very thin, some portion of CH_4 is oxidized to CO_2 and H_2O, but the most of it is oxidized to CO + H_2. In the second layer, endothermic reactions occur. Active catalysts for carbon dioxide and steam reforming of methane are Pd/CeO_2 (R.J. Gorte, University of Pennsylvania, Philadelphia, USA), $LaNi_xFe_{1-x}O_3$ (A. Kiennemann, Strasbourg, France), Ni–La_2O_3/zeolite 5A (C.T. Au, Hong Kong University, China), and others.

A. Ya. Rozovskii and co-workers (Institute of Petrochemical Synthesis, Moscow, Russia) reported the theory of methanol synthesis on copper-containing catalysts.

ENVIRONMENTAL CATALYSIS

M. Iwamoto's plenary lecture (Hokkaido University, Japan) was devoted to catalytic cleaning of exhaust gases in industry. Iwamoto was invited as a plenary lecturer because he was first to discover in 1986 that CuZSM-5 can be used as a catalyst for cleaning oxygen-rich exhaust gases from hydrocarbons and NO_x after diesel engines. New data were not reported in the lecture, but a survey of exhaust-cleaning catalysts was useful.

One of the most important problems is desulfurization of oil fuel and exhaust gases. Sulfur transforms to SO_2 and SO_3, which bring acid rains. A new solution to this problem is the use of methane and other hydrocarbons instead of hydrogen for oil hydrodesulfurization on the Co/Al_2O_3 catalyst. Catalytic oxidation of H_2S to elementary sulfur is studied to replace H_2S oxidation to SO_2 in the Klauss process.

Studies are carried out on the removal of chlorofluorocarbons, which destroy the ozone layer, from exhaust gases. Catalytic hydrodechlorination on supported Pd is a common method. To remove dioxins selective catalytic reduction is also used.

Studies on NO_x removal are carried out along the following lines: (1) the catalytic decomposition of NO_x to N_2 and O_2; (2) NO_x adsorption with its further removal; (3) selective NO_x reduction by hydrocarbons in excess O_2; (4) the one-stage interaction of NO, O_2, and hydrocarbons; and (5) the two-stage process of NO oxidation and NO_x reduction.

As mentioned above M. Iwamoto discovered the unique activity of the CuZSM-5 catalyst in NO_x decomposition. Many researchers studied the redox mechanism of this reaction and copper forms in the zeolite, but this process has not found use in industry yet. In adsorption methods, NO_x is accumulated as nitrates and nitrites on the same zeolites or alkali-earth metal-containing adsorbents. Then, nitrates and nitrites are removed somehow. The best catalyst for the selective NO_x reduction remains CuZSM-5. A great problem related to its use is deactivation and low capacity. The FeZSM-5 catalyst, discovered more recently by W.K. Hall, is highly resistant to SO_2 and water. According to Iwamoto, the separation of NO-to-NO_2 oxidation and NO_2 reduction by hydrocarbons is used by Toyota for cleaning oxygen-rich exhaust gases. Platinum is a catalyst for NO oxidation to NO_2. In the presence of BaO/Al_2O_3, the following reaction occurs:

$$2NO + BaO + \frac{3}{2}O_2 \longrightarrow Ba(NO_3)_2.$$

Barium nitrate is then reduced by a hydrocarbon. There are substantial difficulties in using the process under the conditions of engine operation when the amount of hydrocarbon is insufficient to reduce oxygen-rich mixtures. To solve this problem, hydrocarbon can be injected between oxidation and reduction stages, although the process becomes more complicated.

To clean organics-containing exhaust gases from cars, as well as those from industry, monolith catalysts are used. New active catalysts for NO_x reduction are $Sn_{1-x}Zr_xO_2$ (Xie Youchang, Beijing University, China) and $SnO_2/\gamma\text{-}Al_2O_3$ (H.H. Kung, Northwestern University, Evanston, USA). J.C. Vedrine (Leverhulme Centre for Innovative Catalysis, The University of Liverpool, United Kingdom) summarized advances in the development of the standard V_2O_5/TiO_2 (Eurocat) catalyst for the selectie NO reduction to NH_3 and SO_2 oxidation. Many researchers from different Western European countries took part in this work. In many reports, the mechanism of NO_x reduction was considered on the basis of data obtained by various physical methods.

An important unsolved problem is soot removal from exhaust gases from diesel engines. E.E. Miro (Institute of Catalysis and Petrochemistry, Santa Fe, Argentina) reported that the activity of Co–K catalysts supported on La_2O_3 is high in this process. The presence of NO_x was found to accelerate soot oxidation.

CONCLUSION

Each congress on catalysis summarizes the main achievements for four preceding years and considers the prospects. The 12th Congress was expected to be special because it was held in 2000, at the end of the century. However, there were no sensations and many participants were disappointed. This disappointment sounds reasonable: recent development of catalysis is more quantitative than qualitative. Studies carried out at a high experimental level using modern physical methods are growing, but there are no bright theoretical ideas and even detailed kinetic analysis. The role of theory weakened due to the ease of catalyst testing using robots and computational methods for data processing. This fact also explains the lack of serious discussion after major reports: questions were asked to inquire about details. On the first congresses on catalysis the situation was quite the opposite: brisk discussions lacked serious arguments.

In this respect, the 12th Congress in Granada was similar to all recent meetings devoted to catalysis. Nevertheless, it was very useful because the talks provided a big picture of basic and applied catalysis. Positive trends are the strengthening of catalysis role in industry; the design of new active, selective, and stable catalysts; and the use of modern physical methods in catalysis research. Separateness of catalysis and surface science symposia prevents researchers from meeting each other and has a negative effect on both sciences.

At the 12th Congress, there were no reports about radically new commercial processes, such as one-center polymerization, which was discussed at the 11th Congress. However, some studies may have future in industry. In the field of selective oxidation, reactions with non-oxygen oxidants or $H_2 + O_2$ mixtures are promising. Studies of L.D. Schmidt and others on organizing complex catalytic processes at the microlevel are also promising. In connection with this, I would like to note that my paper written together with L.M. Kustov (*Ross. Khim. Zh.*, 2000, no. 2) mentions that discoveries of new catalytic processes passed through a maximum in the 1960s, and steadily decreased afterwards.

The 13th Congress of Catalysis will be held in 2004 in Paris.