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CHRONICLE

Catalytic Oxidation

(4th World Congress on Oxidation Catalysis, Potsdam, Germany, September 2001)

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Abstract—This paper presents an overview of the plenary lectures and some of the oral and poster presentations at the 4th International Congress on Oxidation Catalysis in Potsdam (Germany). The main topics were the partial oxidation of alkanes and the oxidation of olefins by H_2O_2. Considerable attention is given to the use of modern physical methods in the mechanistic studies of oxidation catalysis and in the studies of catalyst structures.

The 4th International Congress on Oxidation Catalysis was held on September 16–21, 2001 in Potsdam (Germany). Professor M. Baerns (Germany) was the Chairman of the Organizing Committee. Three previous congresses were held in Rimini (Italy), Benalmadena (Spain), and San Diego (USA). The 4th Congress gathered somewhat fewer researchers than the previous one (about 260 participants). This was partly due to the absence of American scientists (about 40) who did not arrive because of the events on September 11 in New York. Therefore, the plenary lectures of American scientists were replaced by the lectures of German participants.

There were 11 plenary and keynote lectures at the congress, 65 oral talks (at two parallel sessions), and 179 posters. Germany presented the greatest number of talks and presentations (47, 25.3% of the total). Russia presented 32 talks (17.1%), but Russian scientists were not given an opportunity to deliver plenary lectures. France presented 19 talks, and Spain and Japan presented 14 talks each. Below, I present an overview of the plenary and keynote lectures, as well as some of the oral and poster presentations.

GENERAL QUESTIONS

Several plenary lectures were devoted to the general problems of oxidation catalysis. J.C. Védrine (Leverhulme Centre, Liverpool, England) discussed redox and acid–base mechanisms in the partial oxidation of hydrocarbons on metal oxides and drew similar conclusions to those of his plenary lecture at the 3rd Congress on Oxidation Catalysis. According to him, the rate-limiting step in the partial oxidation of hydrocarbons is always the abstraction of a hydrogen atom from a C–H bond by nucleophilic oxygen, which is the O^{2-} atom of oxide lattice. Further steps, such as oxygen atom insertion into an organic molecule, the abstraction of another hydrogen atom, and product desorption, are not rate-limiting. The supply of oxygen onto the active site is due to a redox process, which is favored in binary oxide systems $M_1^{n+}M_2^{m+}O_x$ (e.g., on bismuth molybdate Bi–Mo–O in propylene oxidation to acrolein). Acidic properties of the surface favor the desorption of acidic products (e.g., acrylic acid in propylene oxidation). To support this idea, he presented a correlation of oxide activities in some oxidation reactions with their acidic properties measured by NH_3 adsorption. Carbocations are formed on acidic sites in their interaction with a hydrocarbon; for instance, the allyl cation $[C_3H_5]^+$ is formed in the reaction with propylene, and the latter gives acrolein by oxygen insertion. Basic sites are responsible for the formation of carboanions, and their further dimerization leads to the formation of diallyl CH_2CHCH_2–CH_2CHCH_2.

Adsorbed oxygen and hydrocarbons form charged species ($O^{\delta-}$ and $C_nH_m^{\sigma+}$, respectively) and local levels in the forbidden zone of the oxide. These levels stipulate a frequently seen correlation of the catalytic activity and electric conductivity of oxides. The crystalline structure of oxide also plays an important role. For instance, in the partial oxidation of *n*-butane to maleic anhydride on vanadyl phosphate $(VO)_2P_2O_7$, a crystallographic shift takes place in two–three upper monolayers of oxide under catalytic conditions. This shift leads to the formation of a thin pseudo-amorphous layer of binary oxide observed by electron microscopy and participating in the catalytic transformation.

R. van Santen (Eindhoven University of Technology, Netherlands) considered theoretical aspects of oxidative catalysis in his plenary lecture. The Sabatier principle formed the ground of his reasoning: the maximal rate of a catalytic reaction is achieved when the energy of reactant–catalyst binding is optimal. He presented the results of quantum-chemical calculations of NH_3 adsorption and oxidation on Rh(111), Rh(100), and stepped Rh(100) surfaces, the reaction $CO \longrightarrow C + O$ on Ru(0001), CH_3OH oxidation on Cu single crystals, CO oxidation on Pt(100), NH_3 oxidation to NO and N_2 on Cu/Al_2O_3, and butadiene oxidation to furan on Ag. Calculated data were supported by experimental results. The most important results mentioned in his lecture were the formation and decomposition of the islands of adsorbed CO and O molecules on metals, oscillations and the possibility of two steady states in CO oxidation, and the role of different forms of oxygen in the partial oxidation on the silver surface.

A. Zecchina (University of Turin, Italy) in his keynote lecture presented the results of his study of titanium silicalites TS-1 and FeZSM-5 using several physical methods *in situ* (XRD, UV-VIS, XANES, FTIR, and Raman spectroscopy). However, these *in situ* studies were not carried out in a kinetic variant, and he did not compare spectral and kinetic data. Using physical methods, he proved that Ti atoms in TS-1 are distributed very uniformly and hold tetrahedral positions. TS-1 is a good catalyst for oxidations by H_2O_2. When titanium interacts with H_2O_2, peroxide groups are formed, which transform into Ti–O–Si by hydrolysis. Iron atom elimination from the FeZSM-5 network on zeolite heating was studied for the FeZSM-5 catalyst, which is known to catalyze benzene oxidation to phenol by N_2O.

R. Schlögl (Fritz Haber Institute, Berlin, Germany) presented a keynote lecture with the results of studies of several oxidation catalysts using various physical methods: scanning tunneling microscopy, LEED, XPS, photoelectron emission microscopy, Auger spectroscopy, NMR, EXAFS, and TPD. Special devices made it possible to transfer a catalyst from the high-pressure reactor to an ultrahigh vacuum cell necessary for a number of physical measurements.

The most interesting data presented in the report concern ethylbenzene dehydrogenation to styrene on an iron oxide catalyst. A well-crystallized film of α-Fe_2O_3 formed in an ultrahigh vacuum is first catalytically inactive, but it becomes highly active after an induction period of 45 min because of phase transition and the formation of an ordered defect phase. The slow step in this transformation is the formation of nuclei. The active sites are vacancies on the film surface, but reduction to FeO or metallic iron leads to catalyst deactivation. The addition of water transforms the process into oxidative dehydrogenation. On the Fe_2O_3 film promoted with potassium, the induction period is much longer, but the catalytic activity is higher after this induction period. Potassium accelerates ethylbenzene polymerization, and the surface is covered with a graphite film, which catalyzes $C_6H_5C_2H_5$ dehydrogenation. The active sites contain the >C=O groups on the graphite surface. It has been shown that graphite alone (without iron) can be a catalyst. Nanotubes proved to be still more active. (In connection with this, I would like to note that the catalytic activity of coke in the oxidation of organic compounds on Al_2O_3 and other catalysts was intensively studied in the 1970s by T.G. Alkhazov and A.E. Lisovskii in Baku.)

A study of a silver catalyst by EXAFS led to finding four oxygen species on silver. The authors synthesized an $Ag_2Cu_2O_3$ catalyst in which all oxygen was very mobile. Under conditions of oxidative reactions, this catalyst was over-reduced and, therefore, is not suitable.

The phase transitions of heteropoly acids $H_4PVMo_{11}O_{40}$ were studied in detail under the conditions of oxidation catalysis. When heated to 400–450°C, they are reduced with the crystallization of MoO_3. The cesium salt of the heteropoly acid does not produce MoO_3 under these conditions and its use in catalysis is preferable. Under conditions of oxidative catalysis, a complex multiphase structure is formed, and oxygen vacancies appear in the Keggin anion.

An *in situ* study of NH_3 oxidation on copper by NEXAFS showed that the formation of Cu_2O on the copper surface leads to the partial oxidation of NH_3 to N_2, and the formation of CuO leads to the oxidation to NO. Excess amounts of NH_3 in the mixture favor the formation of CuN, which deactivates the catalyst.

The plenary lecture of F. Schüth (Max Planck Institute of Coal Research, Mülheim, Germany) was devoted to the application of combinatorial (computer) methods, which are fashionable nowadays, in the search and preparation of oxidation catalysts. According to combinatorial chemistry adherents, these methods substantially speed up the search for new catalysts. For this purpose, one chooses a catalyst property for the search. In most cases, this is a chemical composition, but it can also be a lattice parameter or atomic number. Then, a large number of solid materials are synthesized according to some program. These are potential catalysts that are submitted to fast tests. A computer program chooses the best of them and suggests the synthesis of a new group of catalysts. This procedure is repeated together with further syntheses and tests. An example is given for the combinatorial search for the catalysts of alcohol oxidation to aldehydes and ketones on supported metals and polyoxometalates.

Note that combinatorial (i.e., statistical) methods of catalyst screening are not new to catalysis. They were widely discussed in the 1960s and were described in my book *Kataliz nemetallami* (*Catalysis by Nonmetals*, Leningrad: Khimiya, 1967). However, they were not developed at that time, because the need for a scientific, rather than statistical purely empirical, search for the catalysts was generally accepted. All who have been involved in catalyst screening and preparation know that the stages of catalyst design do not take less time than the stages of their preparation and product analysis. Moreover, the same, standard methods cannot usually be used for the syntheses of materials with different crystalline structures and specific surface areas.

An advantage of these studies is the development of new fast methods for product analysis, which can be useful independently of their combinatorial applications. It was noted that gas chromatography is too slow as a method of analysis. Faster methods (laser-induced fluorescence multiphoton ionization, scanning mass spectroscopy, and others) have been already used in the studies of homogeneous gas-phase reactions. As was shown in the lecture, IR spectroscopy with spatial resolution enables the recording of up to 4096 spectra at a time.

In many reports, the use of modern physical methods was demonstrated. Their applications became much broader compared to the previous congress. Such methods as XANES and sum frequency generation (SFG), which allows obtaining vibrational spectra in the visible region, provide solutions to the pressure gap problem (a gap between the high pressure of a catalytic reaction and the low pressure of spectroscopic analyses). Note that many researchers make some excessive use of the term *in situ*. In fact, physical methods for catalyst studies are applied before or after a reaction in most cases.

Several reports were devoted to the preparation of oxidation catalysts. The use of such methods as mechanochemistry, precipitation of the active phase in a solvent under supercritical conditions, the immobilization of metal complexes on mesoporous supports (such as MCM-41, MCM-22, and others) sometimes makes it possible to increase the activity and selectivity of oxidation catalysts. G.N. Kryukova[1] *et al.* (Boreskov Institute of Catalysis, Novosibirsk, Russia) studied the genesis of the structure of a Mo–O catalyst doped with V_2O_5, which was selective in the ammoxidation of methylpyrazine. They found that, in a narrow temperature interval, a layered nanostructured phase is formed, which involves Mo, V, and O atoms on the support surface.

ALKANE OXIDATION

As at the previous congress, the selective oxidation of alkanes was given much more attention than to the selective oxidation of olefins. About forty reports on catalysts for the selective oxidation of alkanes were accepted, whereas only three reports were devoted to the catalyst for the partial oxidation of olefins.

M. Misono (Hokkaido University, Sapporo, Japan) considered the problems of alkane activation in his plenary lecture. The selective oxidation of alkanes (mostly oxidative dehydrogenation) by hydrogen peroxide on heteropoly acids of the W row and *n*-butane oxidation to maleic anhydride (MA) on $(VO)_2P_2O_7$ were studied. It was shown that the catalytic activity of heteropoly acids is due to both their redox and acid–base properties. The reaction occurs in a pseudoliquid phase, and its rate is proportional to the volume of heteropoly acid rather than to the surface area within certain limits. In the case of butane oxidation to MA, it was shown using a number of physical methods that the active sites for MA formation from butane belong to the (100) face of vanadyl phosphate, whereas side faces are responsible for complete oxidation. The redox transformations $V^{5+} \rightleftarrows V^{4+}$ occur only on the surface and do not concern the bulk of $(VO)_2P_2O_7$.

B. Meunier (Toulouse University, France) in his keynote lecture considered the role of M=O bonds in biomimetic catalytic oxidation. It is known that complex Fe-containing proteins (cytochromes) may enter biomembranes and act as organic catalysts of oxidation reactions. For instance, cytochrome P-450 is a monooxygenase capable of activating molecular oxygen. One of the oxygen atoms forms H_2O, and the other is inserted into an organic RH molecule to form ROH. Iron transfers to the Fe=O groups, where it can exist in higher oxidation states Fe(IV) and Fe(V). To model P-450, the author synthesized metal porphyrins, in which Fe, Mn, and other metal atoms are surrounded by four nitrogen atoms and form the M=O group in oxidation. Under the action of the oxidant, the hydroxylation of organic compounds may occur. B. Meunier noted that the heterogeneous FeZSM-5 catalyst, which oxidizes benzene to phenol, has similar biomimetic properties.

It is known that the oxidation of *n*-butane to maleic anhydride is the only commercialized partial oxidation process of alkane, and vanadyl pyrophosphate is the only selective catalyst for this reaction. In many talks presented at the congress, the mechanism of this reaction, the structure of the catalyst, the state of active sites on the catalyst surface, and new preparation procedures were discussed. For instance, F. Trifiro (University of Bologna, Italy) showed that the control of the oxidation state of vanadium ions on the surface of $(VO)_2P_2O_7$ leads to an increase in the process selectivity to 75%.

The oxidative dehydrogenation of alkanes to alkenes (especially propane to propylene) was discussed broadly at the congress. The main catalyst for oxidative dehydrogenation is V/MgO (and more rarely V/Al_2O_3 is used). However, high selectivities to propylene (60–70%) are achieved at low conversions (5–20%). More complex systems have also been studied. Thus, B.Y. Jibril (King Saud University, Riyadh, Saudi Arabia) showed that the selectivity to propylene in the oxidative dehydrogenation reaches 65.3% at a conversion of propane of 17.1% on a $Cr–Mo–Cs–O/Al_2O_3$ catalyst at 500°C. V.A. Sadykov *et al.* (Boreskov Institute of Catalysis, Novosibirsk, Russia) studied the oxidative dehydrogenation of propane monolith thin-wall Mn–Co–Zr–P–O catalysts supported on corundum at short contact times. These catalysts are more active than the conventional V/MgO catalyst, and the yield of C_2–C_3 olefins on them reached 34%. An increase in the yield of olefins was explained by a decrease in the contribution of cracking reactions.

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[1] Henceforth, I mention only the first or main author of a report.

Two reports were devoted to the application of combinatorial methods to the catalysts for the oxidative dehydrogenation of ethane to ethylene. For instance, I. Liu (Symyx Technologies, Santa Clara, USA) reported a $Mo_{9.72}V_{0.26}Nb_{0.03}O_x$ catalyst, on which the selectivity to C_2H_4 reached 86% at a conversion of 21% and a low temperature (300°C). A. Barama (Institute of Natural Gas, Bab Ezzouar, Algeria) obtained a selectivity of 93% at a conversion of 90% in the oxidative dehydrogenation of ethane to ethylene on a V–Mo–P–O/Al_2O_3 catalyst at 450–600°C.

Further attempts have been made to prepare a selective catalyst for the oxidation of propane to acrolein and acrylic acid. Two reports demonstrated that two-phase catalysts are promising in this process. Different phases accelerate separate steps of this reaction. According to B. Delmon (Catholic University of Louvain, Louvain-la-Neuve, Belgium), a catalyst consisting of the $NiMoO_4$ and α-Sb_2O_3 phases is characterized by a selectivity of 95% at 490°C, whereas the selectivity of $NiMoO_4$ alone is 30%, and α-Sb_2O_3 does not form acrolein at all. M.Yu. Sinev (Semenov Institute of Chemical Physics, Moscow, Russia) considered the nonadditive action of VSbBiBa/γ-Al_2O_3 and Mo–Bi–Fe–Co–O catalyst mixtures in the oxidation of propane to acrolein. The results obtained for the two-bed catalysts and their mechanical mixtures were different. He proposed that the process occurs consecutively via the oxidative dehydrogenation of propane and further oxidation of propylene. The most probable mechanism is the formation of propyl radicals and their parallel transformation into the reaction products: propylene, acrolein, and carbon oxides. New catalysts for propane ammoxidation based on the solid solutions of V_2O_5 in the Ti–Cr–Sb–O system with a rutile structure were considered in the report of F. Trifiro (University of Bologna, Italy).

Few talks were devoted to the partial oxidation of methane. This is possibly due to the fact that the reports on the partial oxidation of methane are lately considered at the conferences devoted to the processing of natural gas, whereas the complete oxidation of methane is considered at the conferences on combustion and environmental catalysis. H. Berndt, (Institute for Applied Chemistry Berlin-Adlershof, Berlin, Germany) reported the selective oxidation of methane to formaldehyde on VO/MCM-41 with a selectivity of 94% at a low conversion (3.9%). The oxidation of methane to syngas on carbides was the topic of a talk delivered by M.L.H. Green (University of Oxford, Great Britain). A high activity of Mo_2C is observed at high temperatures and pressures (above 0.8 MPa). At atmospheric pressure, Mo_2C is oxidized to oxide and loses its activity. The process occurs via the alternating carbidization and decarbidization of the carbide surface.

OXIDATION OF OLEFINS AND AROMATIC HYDROCARBONS

R.K. Grasselli (University of Delaware, Newark, USA) gave a lecture devoted to the fundamental principles of selective heterogeneous oxidation catalysis. The lecture was largely based on olefin oxidation examples. Progress in the selective oxidation of olefins was considered historically. Specifically, he spoke about the history of the development of the first selective catalyst for propylene ammoxidation to acrylonitrile C_3H_4N at Sohio. R.K. Grasselli participated actively in the development of this catalyst. The application of the Bi–Mo catalyst in a fluidized-bed reactor is most efficient.

According to R.K. Grasselli, the main properties of a catalyst that are necessary for the achievement of the high selectivity in partial oxidation are the energy of a metal–oxygen bond in an oxide catalyst and the disconnection of active sites. When the M–O bond is weak and a large amount of mobile oxygen is present, complete oxidation occurs on the catalyst. If the M–O bond is strong the hydrocarbon is not activated. Thus, partial oxidation requires a moderate strength of the M–O bond. This is typical of the transition metal–oxygen bond in the lattices of scheelite, pyrochlore, perovskite, fluorite, and rutile. Many partial oxidation catalysts have such a crystalline lattice. The separation of different steps of the process, their occurrence on different sites, and the use of a multiphase catalyst ("phase synergism") are also useful. However, the complete separation of steps (e.g., the alternating oxidation and reduction of the catalyst) is ineffective. Combining different components with different active sites is important for the design of the catalyst for the partial oxidation of alkanes.

In her keynote lecture, B. Grzybowska-Swierkosz (Institute of Catalysis and Physicochemistry, Polish Academy of Sciences, Cracow, Poland) provided a review of the effects of additives on the physicochemical and catalytic properties of the oxide catalysts for the selective oxidation of olefins and paraffins. She considered the effects of additives on the acid–base and redox properties of oxides, the arrangement of additives on oxide surfaces and in the bulk, catalyst modification, and oxygen spillover between phases. The most detailed data concerned the effect of potassium oxide on the catalytic ad physicochemical properties of a V–P–O/Al_2O_3 catalyst for butane oxidation to maleic anhydride and a V_2O_5/TiO_2 catalyst for aromatic hydrocarbon oxidation. In the plenary lecture of M. Muler (Ruhr University, Bochum, Germany), results of the study of the V_2O_5/TiO_2 catalyst for the selective oxidation of toluene to benzaldehyde and benzoic acid are presented. The studies by TPR, TPD, diffuse-reflectance IR spectroscopy, Raman spectroscopy, the TAP reactor method, XPS, and XANES led the authors to suggest a structural model of the V_2O_5/TiO_2 catalyst. Two-dimensional vanadium oxide layers are oriented on the V_2O_5/TiO_2 surface, and these layers undergo oxidation and reduction properties. The >V=O groups are responsible for the selective oxidation. Toluene is a better reducing agent for the V^{5+} layer than hydrogen, and the IR spectra of the surface show the bands of adsorbed toluene and benzoates even at 150°C, although the stationary oxidation of toluene only occurs at 500°C. Oxygen from polymeric oxygen–vanadium layers participates in partial oxidation. In the presence of gas-phase oxygen, the surface is reoxidized.

New catalysts for the partial oxidation of olefins were not reported. Only S. Rarluechai (Bangkok University, Thailand) found that the selectivity of ethylene oxidation to ethylene oxide increases to 90% when gold is added to a $Ag/\alpha\text{–}Al_2O_3$ catalyst.

Many reports were devoted to the partial oxidation of toluene to benzaldehyde. In most cases, catalysts based on V_2O_5 were studied, specifically V_2O_5/Sb_2O_3. M.V. Landau (Ben-Gurion University of the Negev, Beer-Sheva, Israel) showed that the selectivity to benzaldehyde reaches 86% on Cr_2O_3 aerogel at 270°C. A.A. Avandt (Baghdad University, Iraq) showed that toluene oxidation to benzaldehyde and benzoic acid can be a new pathway to phenol. Active catalysts for this process are copper (as well as nickel and iron) salts supported on Al_2O_3.

Studies of benzene oxidation to phenol by N_2O have been continued. G.I. Panov (Boreskov Institute of Catalysis, Novosibirsk, Russia) provided new data on the mechanism of this reaction over FeZSM-5. V.A. Zazhigalov (Institute of Sorption, National Academy of Science of Ukraine, Kiev) showed that nonstoichiometric molybdenum oxides (e.g., $\chi\text{-}Mo_8O_{23}$ modified by other oxides) can be active catalysts for benzene oxidation to phenol by molecular oxygen.

OTHER OXIDATION REACTIONS

Many talks dealt with liquid-phase oxidation. Most of them concerned the epoxidation of C=C bonds by H_2O_2. This reaction was discovered ~15 years ago and has been studied intensively since then. For oxidation by H_2O_2, catalysts of three types are used: (1) supported gold, (2) titanium silicates, and (3) heteropoly compounds. Can Li (Daliagn Institute of Chemical Physics, China) reported new data on the epoxidation of α-methylstyrene on TAPO-5 (molecular sieve prepared by the partial substitution of Ti for Si in SAPO). It was shown that the active site includes vacancies in the structure of the crystalline lattice and nanoparticles of TiO_2. I.C.M.S. Santos (University of Aveiro, Portugal) demonstrated the activity of the Keggin-type $[Mn^{(IV)}(H_2O)BW_{11}O_{39}]^{6-}$ anion in the epoxidation of natural compounds: geraniol, nerol, and α-carene by H_2O_2. It was shown by many researchers that the liquid-phase epoxidation of complex olefins by H_2O_2 can be enantioselective. In this case, mesoporous systems of the Al–MCM-41 type with metal complexes with chiral ligands immobilized in the pores are used.

B.K. Hodnett (University of Limerick, Ireland) considered factors that are favorable for selective epoxidation. Selective epoxidation by molecular oxygen is possible for olefins with C–H bond energies higher than 400 kJ/mol. Easy hydrogen abstraction leads to complete oxidation. Therefore, the epoxidation of propylene, with a weak C–H bond, to propylene oxide cannot occur, and the selectivity is almost close to zero on most catalysts. However, propylene epoxidation by H_2O_2 is possible on titanium silicates TS-1 because oxygen in the TS-1+ H_2O_2 system is more electrophilic than in the $Ag + O_2$ system.

O.A. Kholdeeva (Boreskov Institute of Catalysis, Novosibirsk, Russia) reported the selective oxidation of unsaturated and aromatic compounds by H_2O_2 mesoporous mesophase Ti–MMM catalysts and on amorphous $TiO_2\text{–}SiO_2$. For instance, 2,3,6-trimethylphenol is oxidized to 2,3,5-trimethyl-*p*-benzoquinone with a selectivity of 96% at 100% conversion.

A.M. Steele (University of Reading, Great Britain) reported the highly selective oxidation of alcohols to the corresponding aldehydes (the selectivity was >99%) with a high yield. Supported platinum catalysts were used in the supercritical medium of a CO_2 solvent. This effect of supercritical CO_2 is explained by the fact that the nonaqueous medium excludes undesirable aldehyde hydrolysis reactions.

J.A. Moulijn (Delft University of Technology, Netherlands) reported cyclohexanone oxidation to valuable dicarboxylic acids on a monolith catalyst and on a slurry catalyst. The catalyst is platinum supported on monolith carbon, but pure carbon is catalytically active as well.

No talks were given on the catalytic purification in the gas phase. Two talks were devoted to the oxidative purification of sewage. P. Gallezot (CNRS, Villeurbanne, France) reported the oxidative purification of sewage from paper manufacturing. The active catalysts are Ru/CeO_2 and Ru/ZrO_2 at 130–190°C and 5.5 MPa. D.-K. Lee (Gyeongsang National University, Kyongnam, South Korea) reported the catalytic purification of sewage containing dyes from textile industry by oxidation with Cu/Al_2O_3 on H_2O_2. In this case, the process occurs under mild conditions at 80°C and atmospheric pressure.

M.J. Ledoux (University of Strasbourg, France) presented data on the selective oxidation of H_2S to elementary sulfur on an iron oxide catalyst. The use of a new support SiC made it possible to obtain an active, selective, and stable catalyst for H_2S oxidation by oxygen.

NEW TECHNOLOGIES

New engineering concepts for an increase in the efficiency of selective oxidation catalysts were considered in the lecture of G. Emig (University Erlangen-

Nuremberg, Erlangen, Germany). New engineering ideas of the second part of the 20th century are as follows:

1. Catalytic oxidation in the pseudofluidized bed. This was put into practice by analogy with catalytic cracking in ammoxidation over a Bi–Mo catalyst.

2. A riser reactor used by Dupont in 1987 for the oxidation of butane to maleic anhydride. Catalyst is oxidized by air in a fluidized bed and reduced by *n*-butane in a mobile-bed reactor. The separation of reaction and regeneration stages enables the optimization of each of these steps, feed recycling, and elimination of explosion hazard.

3. A single-bed reactor used in propylene ammoxidation by Sohio in 1959.

4. A reactor with switched flows proposed by G.K. Boreskov and Yu.Sh. Matros for the oxidation of dilute gases. This reactor was applied by Monsanto.

5. Millisecond contact times studied in detail by L. Schmidt (Minneapolis, USA) in the oxidation of methane and other alkanes. The yield can be increased at millisecond contact times due to the integration of heat and changing the direction of a reaction.

6. A rotary reactor.

7. Microreactors with fast feed circulation. Due to an increase in the thermal conductivity, microreactors make it possible to eliminate hysteresis and light-off in oxidative mixtures. In methanol oxidation to formaldehyde on silver, the yield was increased to 95%.

8. A catalyst on the reactor walls makes it possible to couple exothermic and endothermic reactions due to heat transfer through a reactor wall.

9. A slurry process applied to hydrogenation and Fischer–Tropsch synthesis was also used for the oxidation of cyclohexanone to dicarboxylic acids.

10. Water addition partly eliminates heat and provides better isothermicity. This was applied in propylene oxidation to acrolein.

11. Membrane reactors enabled coupled reactions and heat integration.

12. Homogeneous gas-phase catalysis. Vapors of metallic sodium were fed to a reactor with methanol. The selectivity of methanol oxidation to formaldehyde reached 90% due to dehydrogenation at 350–450°C. The conversion of methanol was 10%.

Technological aspects of catalytic oxidation were considered in a separate lecture. F. Rosowski (BASF Aktiengesellschaft, Ludwigshafen, Germany) proposed a new reactor for the oxidation of *o*-xylene to phthalic anhydride. A multiple-bed reactor consists of several sections, each heated by its own salt bath. The most selective catalyst is placed at the reactor inlet, whereas further beds are less selective but more active. As a result, the overall selectivity of the process increases and the process occurs at a low temperature (340–370°C). A two-section reactor with a fluidized bed for the oxidative dehydrogenation of ethane and propane was described in the report of J.M. Lopez Nieto (Institute of Technical Chemistry, Valencia, Spain).

Studies and use of catalytic oxidation at short contact times are ongoing. F. Donsi (University of Naples, Italy) showed that the partial oxidation of ethane can be carried out at a millisecond contact time on monoliths containing noble metals and perovskite-covered monoliths. The role of the catalyst is in lowering the light-off temperature of the oxidation process compared to the purely homogeneous reaction and in making coking less intensive.

CONCLUSION

Talks presented at the 4th World Congress on Oxidation Catalysis show that the level of research has risen over the last four years. New physicochemical methods are now applied more than before and this made it possible to shed light on the mechanisms of some reactions and catalyst structures. In most cases, physicochemical methods were applied before or after a reaction, not *in situ*. However, radically new catalytic systems were not proposed. The number of studies on the partial oxidation of olefins reduced, whereas alkane oxidation (especially the oxidative dehydrogenation of C_2–C_4 alkanes) are given more attention. There were few reports where the kinetics of catalytic reactions was considered.

The 5th World Congress on Oxidation Catalysis will be held in 2005 in Sapporo (Japan). The chairman of the organizing committee will be Professor M. Misono.