

Catalysis—where science and industry meet

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SUMMARY

The role of catalysis in chemical industry as basis of modern civilization is described and mechanism of catalytic reactions is discussed. Influence of electronic structure of transition metal atoms, structure sensitivity of catalytic reactions, tailoring of acid-base and redox properties of zeolites, quantum chemical description of elementary reaction steps, dynamics of catalysts surfaces, oscillatory reactions, supramolecular and micellar catalysis and catalytic antibodies are then presented as illustration of the state of the art in science of catalysis. Main goals in sustainable increase of production at lower energy consumption and limited waste generation, removal of environmental pollution and development of new energy sources are exposed to be achieved by change of paradigm. Molecular design of integrated catalytic systems using nanotechnology and tailored to the needs of any given reaction can be envisaged.

INTRODUCTION

"When you know a thing, to hold that you know it,
and when you do not know a thing, to allow that you do not know it,
this is the true knowledge."

Confucius, 551-479 BC

Modern civilization, whose spectacular development took place in the second half of the XX century as a result of the scientific revolution, has three characteristic features: (i) - it is a mass civilization, (ii) - it is mobile, and (iii) - it is global. It is a mass civilization because the whole population has the opportunity to participate in its benefits. It is a mobile civilization, because a very large fraction of the population change places. It is a global civilization, because with the advent and later development of great multinational corporations and communications networks, whatever happens in one even remote corner of our globe, is immediately known by everybody around the world and very often has important consequences for people living in far away countries. In order to achieve these goals it was necessary to invent thousands of new materials and to find out the ways of their fast and cheap production in large quantities. This was epitomized by the dream of alchemists to transform various materials into gold which was

the exemplification of the most precious material. The unique possibility of fast and selective production of the desired chemical molecules is offered by catalysis and therefore the development of the science and practice of catalysis may be considered as the fulfilment of the alchemists' dream. Catalysis comprises technological processes of the largest scale such as cracking which is one of the greatest technological undertakings of mankind with more than one billion tons of crude oil per year being processed in this way, and smallest scale enzymatic reactions with micrograms of product formed with 100% chemo-, regio- and stereoselectivity. Increasingly important is not only the production of materials needed in our modern society, but also the destruction of undesired by-products of its activities, making application of catalysis to pollution control one of the main goals.

Catalysis is a phenomenon, in which a relatively small amount of a foreign material, called a catalyst, increases the rate of a chemical reaction. Interacting with the reactants the catalyst enters into the reaction cycle, but is regenerated in its last step and therefore is not consumed in its course, ideally remaining unchanged after its completion. Thus the amount of product obtained with the given amount of catalyst is theoretically unlimited, in practice usually very large. The accelerating effect of a catalyst is achieved by creating for the given reaction, through interaction with the substrates, a new reaction pathway, usually multistep, characterized by a lower energy barrier and an appropriate spatial arrangement of reactants facilitating the overcoming of entropy barrier.

Very often the given reactants react along several different thermodynamically possible reaction pathways and a mixture of many different products is obtained. The catalyst may create preference for the reaction along one of these pathways, very often not thermodynamically the most convenient, by modifying the potential energy surface to make reaction along the selected reaction coordinate more facile and those along other pathways more difficult. This selectivity of action is the most important and characteristic property of the catalyst, making possible the formation of products, which in the absence of the catalyst would have never been formed because of the much more rapidly proceeding competitive processes. Mechanistically this very essence of the phenomenon of catalysis may be explained in terms of the nature of the intermediate complex formed on interaction of the reacting molecules with the group of atoms of the catalyst, called the active site. Thus, by selecting the appropriate catalyst and reaction conditions it is possible to direct the reaction along only one selected pathway to obtain the desired product.


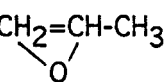
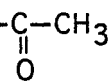

CATALYSIS IN INDUSTRY

The possibilities offered to the chemical industry by variation of the selectivity of the reaction on the change of the catalyst may be illustrated by the example of the oxidation of propene (Table 1). In the gas phase oxidation of

propene, acrolein is formed with 95% selectivity on a bismuth molybdate catalyst, whereas acrylic acid is the main product on nickel molybdate containing excess MoO_3 , acetone is obtained on cobalt or tin molybdate at lower temperatures, and dimerization to hexadiene followed by dehydrocyclization to benzene proceeds on bismuth phosphate. When cobalt oxide or copper cobaltate are used as catalysts, total oxidation of propene takes place. Supported molybdenum hexacarbonyl, in which molybdenum is in its tetravalent state, is a catalyst for dimerization of propene to ethylene and butene. By properly selecting the reaction conditions, each of these products may be obtained with high selectivity.

Table 1

PRODUCTS OF PROPENE OXIDATION ON DIFFERENT CATALYSTS

$\text{CH}_2=\text{CH}-\text{CH}_3$ + O_2		$\text{CH}_2=\text{CH}-\text{CH}_3$ 	Th_2O_3
		$\text{CH}_2=\text{CH}-\text{CHO}$	$\text{Bi}_2(\text{MoO}_4)_3$
		$\text{CH}_3=\text{CH}-\text{COOH}$	$\text{NiMoO}_4 + \text{MoO}_3$
		$\text{HCHO} + \text{CH}_3\text{CHO}$	CoTiO_3
		$\text{CH}_3-\text{C}(=\text{O})-\text{CH}_3$ 	CoMoO_4
		$\text{CH}_2=\text{CH}_2 + \text{CH}_2=\text{CHCH}_2\text{CH}_3$	$\text{Mo}(\text{CO})_6$
		$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}_2$	Bi_2O_3
			BiPO_4
		$\text{CO}_2 + \text{H}_2\text{O}$	CuCo_2O_4

A similar flexibility exists in the case of syntheses from $\text{CO} + \text{H}_2$ mixtures. Methanization takes place on Ni catalyst, methanol is formed with very high selectivity on supported copper-zinc-chromium oxide catalyst, ethanol on promoted rodium catalyst and higher alcohols appear when cobalt and molybdenum oxides are used. Higher linear hydrocarbons are the main products on promoted iron catalyst, whereas branched hydrocarbons result on thorium oxide. In liquid phase reactions, monoalcohols are formed when complexes of ruthenium are used as catalysts, whereas glycols result with cobalt salts.

Catalysis offers thus the possibility of fast and selective production of the desired chemical molecules and therefore more than 90% of the production of chemical industry is based on catalysis. The projected world-wide market for catalysts in 1994 is 7.3 billion US\$, in which production of chemicals and

Table 2

CATALYSIS IN INDUSTRY

1. FERTILIZERS

Production of hydrogen: $\text{CH}_4 + \text{H}_2\text{O} \longrightarrow 3\text{H}_2 + \text{CO}$ Ni/Al₂O₃

Ammonia synthesis: $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$ Fe

Oxidation of ammonia $\text{NH}_3 + \text{O}_2 \longrightarrow \text{NO}_2 + \text{H}_2\text{O}$ Pt, Rh

2. INORGANIC INDUSTRY

Production of sulphuric acid: $\text{SO}_2 + \text{O}_2 \longrightarrow \text{SO}_3$ V₂O₅

3. FUELS

Cracking		Al ₂ O ₃ .nSiO ₂ ,
Reforming		Pt/Al ₂ O ₃ , Pt,Re/Al ₂ O ₃
Hydrocracking		CoO-MoO ₃ /Al ₂ O ₃
Hydrodesulfurization		CoO-MoO ₃ /Al ₂ O ₃
Hydrorefining		Fe ₂ O ₃ /Al ₂ O ₃
Isomerization		Pt,Rh/Al ₂ O ₃

4. SYNTHETIC RUBBER

Production of butadiene: $\text{C}_4\text{H}_8 + \text{C}_4\text{H}_{10} \longrightarrow \text{C}_4\text{H}_6$ Cr₂O₃/Al₂O₃

Production of styrene: $\text{C}_6\text{H}_5\text{C}_2\text{H}_5 \longrightarrow \text{C}_6\text{H}_5\text{C}_2\text{H}_3$ Fe₂O₃

5. PLASTICS

Production of monomers:

ethylene oxide: $\text{C}_2\text{H}_4 + \text{O}_2 \longrightarrow \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \quad \quad \quad \diagdown \quad / \\ \quad \quad \quad \text{O} \end{array}$ Ag/Al₂O₃

vinyl chloride: $\text{C}_2\text{H}_4 + \text{O}_2 + \text{Cl}_2 \longrightarrow \text{H}_2\text{C}=\text{CHCl}$ CuCl₂,HgCl₂,carbon

phthalic anhydride from o-xylene V₂O₅/TiO₂

Polymerization:

polyethylene $\text{C}_2\text{H}_4 \longrightarrow -(\text{CH}_2\text{CH}_2)_n-$ Cr₂O₃/Al₂O₃

polystyrene $\text{CH}_2\text{CHCl} \longrightarrow -(\text{CH}_2\text{CHCl})_n-$ Al(C₂H₅)₃+TiCl₃

6. SYNTHETIC FIBRES

Production of monomers:

acrolein $\text{C}_3\text{H}_6 + \text{O}_2 \longrightarrow \text{C}_3\text{H}_4\text{O}$ Bi₂(MoO₄)₃/Al₂O₃

acrylonitrile $\text{C}_3\text{H}_6 + \text{O}_2 + \text{NH}_3 \longrightarrow \text{C}_3\text{H}_3\text{N}$ UO₃-Sb₂O₅/Al₂O₃

maleic anhydride $\text{C}_4\text{H}_8 + \text{O}_2 \longrightarrow \text{C}_2\text{H}_2(\text{CO})_2\text{O}$ V₂O₅/MoO₃

caprolactam from cyclohexane Pd/Al₂O₃

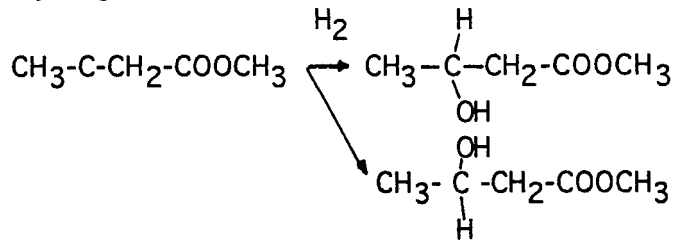
terephthalic acid from p-xylene Co-complexes

7. FINE CHEMICALS

oxo-process: $C_3H_6 + CO + H_2 \rightarrow C_4H_7OH$ Rh-complexes

Fischer-Tropsch synthesis: $CO + H_2 \rightarrow C_nH_{2n} + \text{alcohols}$ Fe, Co

enantioselective hydrogenation:



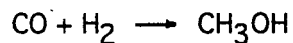
8. FOOD INDUSTRY

Hydrogenation of fatty acids

Ni/SiO₂

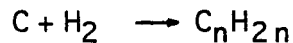
9. NEW ENERGY SOURCES

Coal gasification



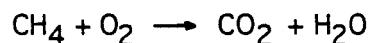
ZnO-Cr₂O₃, CuO-ZnO

Coal liquefaction



CoO-MoO₃/Al₂O₃

Fuel cells



Pt/ZrO₂

10. POLLUTION CONTROL AND ENVIRONMENTAL PROTECTION

Catalytic car mufflers

Pt/Al₂O₃

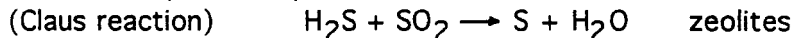
Combustion of hydrocarbons in flue gases

CuCo₂O₄

Reduction of nitrogen oxides

LaCoO₃

Removal of sulphur compounds



11. BIOTECHNOLOGY

lactose \rightarrow galactose + glucose

-galactosylase

starch \rightarrow glucose \rightarrow fructose

isomerase

penicillin G \rightarrow 6-aminopenicillanic acid

penicillin acylase

cellulose \rightarrow glucose \rightarrow C₂H₅OH

celulase

petrochemicals accounts for 4.2 billion US\$ [1]. Taking into account the long life of modern catalysts it can be assumed that the catalyst contributes usually less than 0.1% to the total value of products obtained with this catalyst. It can be thus estimated that the total value of the world production obtained by catalysis will in 1994 be a staggering sum of 4.2 trillion US\$ (4.2×10^{12} US\$) which is of the order of USA GNP in 1989. This is the measure of the financial, economic and societal impact of industrial catalysis and its criticality to our current quality of life. There is no doubt that it ranks at or near the top of the list of critical technologies for modern society. Some important catalytic processes used in different branches of chemical industry are summarized in Table 2.

FORMATION OF THE INTERMEDIATE COMPLEX

Investigation of the mechanism of formation of an intermediate complex as the result of interaction between reactants and the catalyst, description of its physical characteristics and their dependence on the properties of the catalyst, and studies of the pathways of its transformations on the potential energy hypersurface constitute the main subject of the science of catalysis. In the case of homogeneous catalysis, an organometallic complex may be described in quantum chemical language supplying data on the behaviour of the reactants of a catalytic reaction when they interact with an atom or group of atoms constituting the active centre of the catalyst. Vast amount of data on the structure and reactivity of such complexes have been published in recent years, leading to the recognition of several general classes of reactions such as oxidative addition, reductive elimination etc. [2-4]. New areas of studies have also emerged such as the chemistry of small metal clusters and metal cluster compounds containing metal-metal bonds [5,6]. Heterogeneous catalytic reactions may be discussed in terms of the formation of organometallic complexes as intermediate species, the solid playing the role of counterion or polydentate macroligand.

Thus, the elementary catalytic transformation in all types of catalytic reactions may be reduced to a model of molecules of reactants interacting with a group of atoms constituting the active centre of the catalyst [7]. This is illustrated in Fig.1. Let us consider a coordination polyhedron composed of a central cation linked by ionic bonds to five octahedrally coordinated ligands, the sixth ligand being a molecule of the reactant of the catalytic reaction, e.g. a hydrocarbon. This may be an example of an intermediate complex of a homogeneous catalytic reaction. Modification of the electronic structure of the reactant molecule, responsible for the change in its reactivity and thus for the catalytic effect, will depend on the type of bonding between this molecule and the central atom, i.e. the redox potential, spatial orientation and occupancy of metal d-orbitals, and properties of the ligands. The total number of electrons in the complex is fixed and remains constant during the course of the whole transformation, in which only

redistribution of electrons between different orbitals may take place. Let us now assume that we increase the number of polyhedra by linking them together through their ligands into an ordered arrangement of an ionic crystal. We may still discuss the bonding of the reactant molecule to the given metal cation representing an active centre on the basis of the same model, however with some important differences [8]. Firstly, now it is not the number of electrons in the complex which is fixed, but the chemical potential of electrons, determined by the position of the Fermi level of the solid. Secondly, the bonded molecule of the reactant is now under the influence of all other coordination polyhedra constituting the surface of the solid, i.e. the Madelung potential at the active centre must be taken into account.

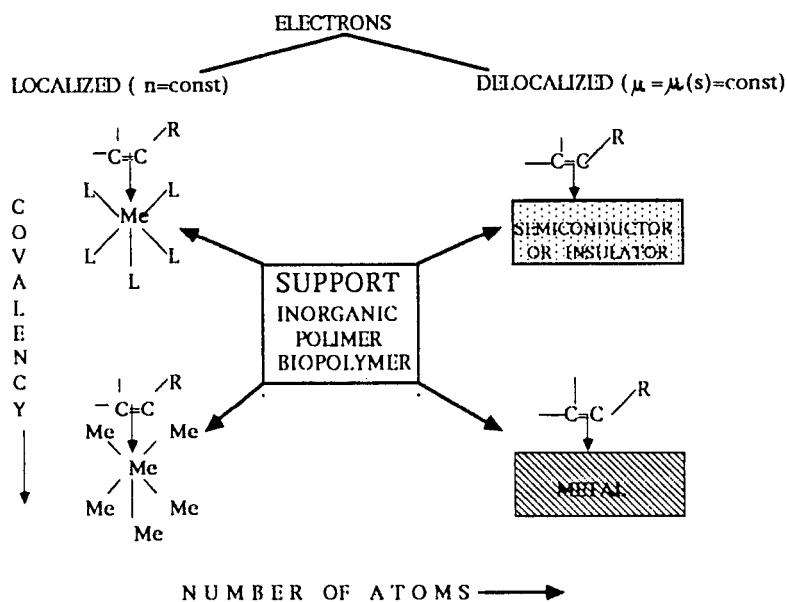


Fig.1. Intermediate complex formed on interaction with isolated metal complex, metal cluster, ionic compound and metal [8]

The discussed coordination polyhedra were composed of a central metal cation surrounded by simple or complex anions, characteristic of compounds which may be classified as salts. Let us now visualize a series of coordination polyhedra with decreasing ionicity of bonds between the central atom and the ligands. The limiting case of this series is either a coordination polyhedron composed of a central metal atom, surrounded by identical metal atoms as ligands, as shown in the lower left part of Fig.1, or a covalent organometallic molecule. In the first case it is a very small metal cluster which still exhibits molecular properties and may be examined by molecular orbital computational procedures. It is the active phase in supported metal catalysts. On increasing the number of metal atoms in the cluster, the characteristic properties of the bulk metal begin to be displayed (band structure, conductivity, cohesive energy, magnetism) which may result in drastic changes in chemisorptive and catalytic properties. In the second case it is a coordination complex which plays the role of a homogeneous catalyst in the liquid phase.

Similar approach may be used to discuss the activation of other reactants of the catalytic reaction, e.g. oxygen. Molecular oxygen may be activated by binding to a transition metal in a complex operating in solution as homogeneous catalyst [9] or at the surface of a transition metal oxide acting as heterogeneous catalyst [10,11]. In the metal complex the density of charge and hence the properties and reactivity of oxygen depend on the redox potential, spatial orientation and occupancy of metal d-orbitals, the type of ligands and the solvent. Therefore it may be varied in a broad range resulting in the change of oxygen properties from nucleophilic to electrophilic [12]. In the case of high valent transition metal cations coordinated by strong electron-accepting ligands the metal oxo group $M=O$ may behave as electrophilic showing high reactivity towards olefins to form epoxides, whereas with electrodonating ligands it should become nucleophilic, reacting with alkanes to give alcohols. This is the manifestation of the ligand effect which may operate also in the case of alloy catalysts [13]. In the solid the density of charge on oxygen is a function of chemical potential of electrons which is determined by the position of Fermi level and may be varied by shifting this position through doping with intervalent ions. The variation of charge on oxygen is however limited so that at the oxide surface terminal oxo-groups $M=O$ and μ -oxo groups $M-O-M$ have nucleophilic properties and may perform a nucleophilic attack on the C-H bond. On the other hand oxygen vacancies generate F-centres which may activate dioxygen to electrophilic molecular or atomic radicals O_2^- or O^- .

The active phase of the catalyst may be supported on a porous, high surface area support which permits a high dispersion of this phase but also enables modification of its properties. When the active phase is characterized by ionic bonds, it becomes dispersed at the surface of the support in the form of isolated polyhedra, patches of the monolayer or small crystallites. In the case of coordination compounds they may be attached to the surface through appropriate functional groups in the form of isolated complexes. The term interfacial coordination chemistry has been suggested [14]. It has become more and more apparent that the surface of the solid containing active centres interacting with adsorbed molecules may be considered as a bidimensional region in which chemical transformations occur much in analogy to the three dimensional phase of the homogeneous catalysis [15]. The interaction with adsorbed molecules may result in restructuring of the surface, and the interaction with the solid modifies the properties of the intermediate complexes. Instead of being supported on an inorganic carrier, the transition metal polyhedron playing the role of an active centre may be inside the pore system of a zeolite framework, supported on a polymer combining e.g. the catalytic properties with those of a membrane, or attached to an organic macromolecule, e.g. a protein, forming a prosthetic group of an enzyme.

The complexity of tailoring a catalyst is considerably increased by the fact that very often the reaction pathway leading from the given reactants to the desired product requires a consecutive series of elementary catalytic

transformations, in which different active sites may be involved. These centres must be then positioned at the catalyst surface in the right spatial arrangement and in proper order .

STATE OF THE ART IN SCIENCE OF CATALYSIS

The progress in understanding the structure and properties of chemical bonds combined with development of surface science, made it possible to identify the catalytically active centres on the atomic scale. As an example, Fig.2 shows the dependence of the catalytic activity of molybdenum oxides-based catalysts in different reactions of hydrocarbons as function of the oxidation state of Mo ions [16-18]. The results clearly indicate that oxidation of propene to acrolein, involving the insertion of oxygen into the hydrocarbon molecule is catalyzed by the oxide of Mo^{6+} , dismutation of propene involves Mo^{4+} ions as active centres, Mo^{3+} ions play the role of active centres for hydrogenation reaction, whereas hydrogenolysis requires the presence of Mo^0 metal atoms. A general conclusion may be thus formulated that the versatility of catalytic properties of molybdenum oxide heterogeneous catalysts is related to the ability of Mo ions to appear at the surface of an oxide support as species stabilized in different oxidation states from Mo^{6+} to Mo^0 .

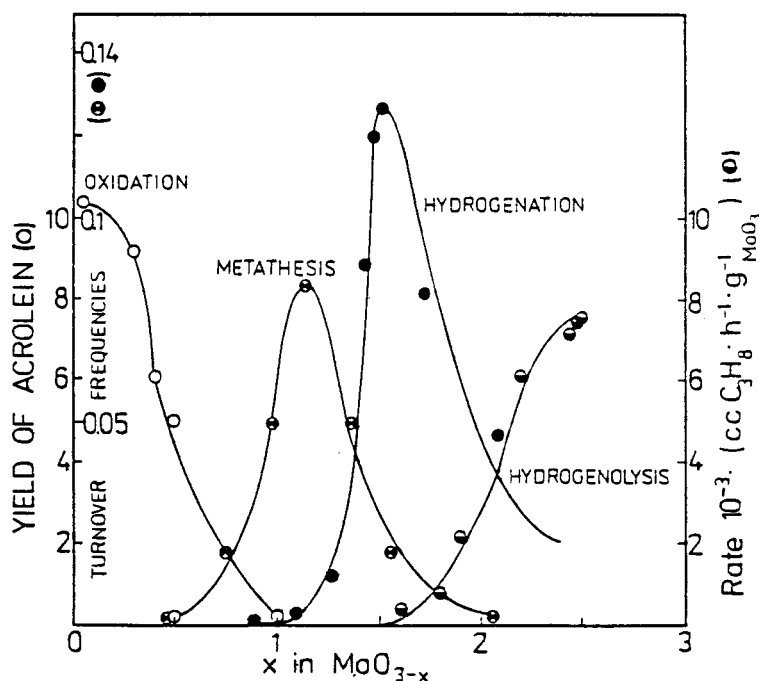


Fig.2. Catalytic activity of MoO_{3-x} -based catalysts as function of the degree of reduction x . (I)-oxidation of propene, (II)-metathesis of propene, (III)-hydrogenation of 1,3-butadiene, (IV)-propane hydrogenolysis.

In supported monolayer catalysts - an important class of catalysts more and more widely used in industry - the support plays the role of a macroligand. Thus, properties of the monolayer strongly depend on the type of support and the surface coverage. As an example, Table 3 summarizes the catalytic activity of vanadium oxides supported on a series of different oxide supports: zirconia, niobia, titania, alumina and silica, in the oxidation of methanol to formaldehyde [19]. It may be seen that catalytic activity of vanadium oxide may be dramatically modified by dispersing it on different supports, the turnover frequency varying by three orders of magnitude. It is noteworthy that coordination of vanadium ions as indicated by the position of the Raman band remains unchanged.

Table 3
REACTIVITY OF SURFACE VANADIUM OXIDE SPECIES ON DIFFERENT OXIDE SUPPORTS IN OXIDATION OF METHANOL TO FORMALDEHYDE [19]

OXIDE SUPPORT	TURNOVER FREQUENCY SEC-1	IN SITU RAMAN BAND POSITION CM-1
SiO ₂	2.0x10 ⁻³	1038
Nb ₂ O ₅	7.0x10 ⁻¹	1031
TiO ₂	3.8x10 ⁰	1030
Al ₂ O ₃	4.6x10 ⁻²	1026
ZrO ₂	2.3x10 ⁰	1026

Very early in catalytic studies attention was drawn to the importance of surface structure of the solid catalyst for its catalytic behaviour. In order to rationalize the large volume of experimental data the concept of structure sensitivity was introduced [20], the reactions of hydrocarbons and hydrogen on metal catalysts having been divided into two types: structure insensitive, whose rate depends very little on such parameters as crystalline orientation, presence of surface defects or alloying, and structure sensitive, which are strongly affected by variation of these parameters. In recent years a pronounced structure sensitivity of the oxidation reactions on oxide catalysts has been demonstrated and the general significance of this concept has been established [21,22]. A spectacular example of the strong influence of surface structure on the direction of the oxidation reaction is the behaviour of two cuprous molybdates: Cu₂Mo₃O₁₀ and Cu₆Mo₄O₁₅ in butene-1 oxidation [23]. Both are composed of the same chemical elements in the same valence state and differ only in the spatial arrangement of atoms. Yet they show entirely different catalytic properties, as shown in Fig.3: Cu₂Mo₃O₁₀ is very active in

the isomerization and dehydrogenation, but no traces of oxygenated hydrocarbon molecules are present in the products, whereas $\text{Cu}_6\text{Mo}_4\text{O}_{15}$ mainly inserts oxygen into the organic molecule to form crotonaldehyde, the most striking feature being the complete absence of isomerization.

In many complex, multistep reactions the catalyst to be active and selective must contain both redox and acid-base sites, very often located in appropriate spatial arrangement. The greatest breakthrough on the road to invent a system, in which all these parameters could be independently varied in a continuous manner, was the application of zeolites. The spectacular progress of the chemistry of molecular sieves has opened practically unlimited possibilities in this field, which only begin to be exploited. The molecular sieves can be conveniently divided into two families: derivatives of silicalite and of AlPO_4 (Fig.4). When in the silicalite framework, composed

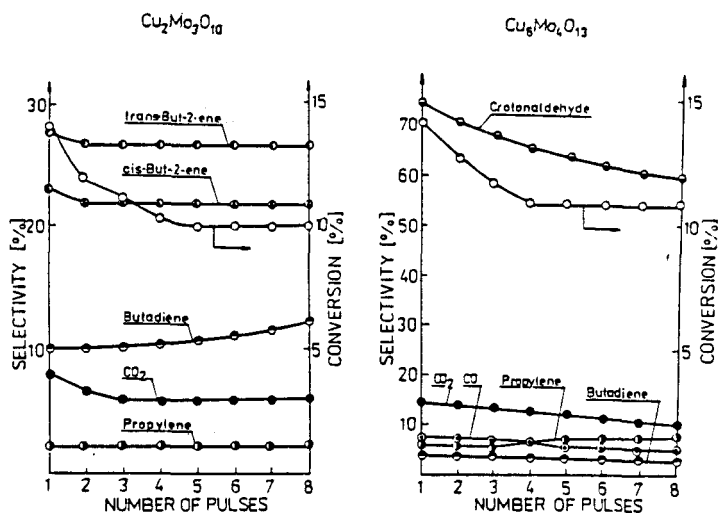


Fig.3. Conversion and selectivities to different products as a function of the number of butene-1 pulses introduced on $\text{Cu}_2\text{Mo}_3\text{O}_{10}$ and $\text{Cu}_6\text{Mo}_4\text{O}_{15}$ catalysts.

of SiO_4 tetrahedra, some of these tetrahedra are substituted by AlO_4 tetrahedra to form aluminosilicate (zeolite) framework, the framework acquires negative charge, which must be compensated by exchangeable cations or protons. Acid sites are thus generated, their number equal to the number of substituting Al^{3+} ions and their strength depending on the type of framework and number of sites. When some of SiO_4 tetrahedra are replaced by tetrahedra of other metals M^{z+}O_4 with $z \leq 4$, so called metalosilicates are formed. In the case of AlPO_4 framework, the substitution may involve either the P sites or the Al sites. Low valent metals substitute Al, whereas silicon atoms may either substitute P to form a negatively charged framework, or replace simultaneously Al and P in equal numbers to give a neutral

CHEMISTRY OF MOLECULAR SIEVES

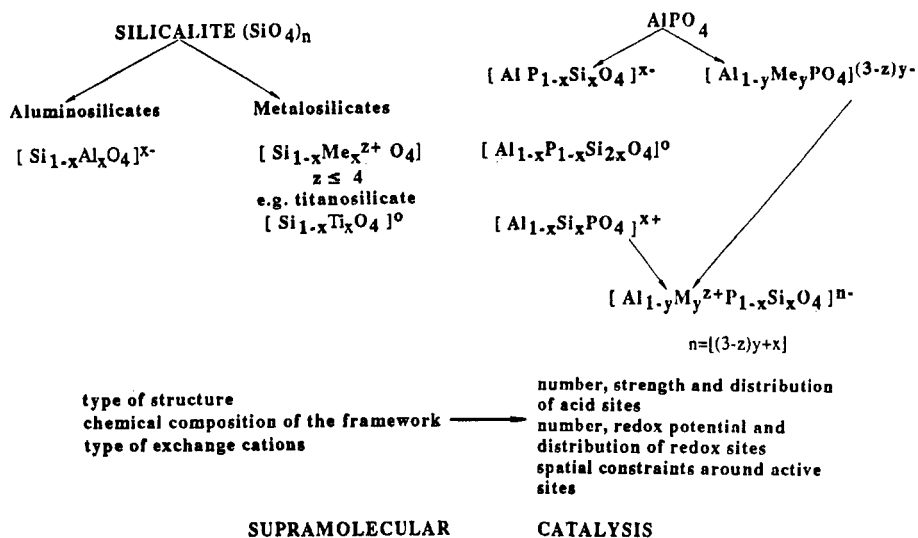


Fig.4. Chemistry of molecular sieves.

framework (the sum of Al+P valencies which amounts to 8 is equal to the sum of valencies of two Si atoms). One could envisage the substitution of Al by Si and formation of positively charged framework - a possibility which until now was not yet realized in practice. More complex situation arises when Al becomes substituted by a low valent metal and P by Si. One should remember that all these systems must also contain exchangeable protons or cations compensating the negative charge of the framework. Moreover, the tetrahedra may be linked together into frameworks of different structure, forming channels and supercages of different shape and size (see Fig.1 in ref.24).

Molecular sieves offer thus an opportunity to regulate the number, strength and distribution of both acid and redox sites by changing the chemical composition of the framework and the type of exchangeable ions. Moreover, by properly selecting the type of framework structure the shape-selectivity may be introduced and spatial constraints may be imposed around active sites, providing conditions for a stereoselective formation of the appropriate transition state. One should remember that besides the direct chemical bonding with the active site the reactant molecule is in the supercage or the channel of a molecular sieve subjected to a field of molecular interactions. In this sense catalytic transformations in molecular sieves may be thus considered as supramolecular catalysis.

The system whose unusual catalytic properties have been discovered some time ago is titanosilicate [38]. By substituting Si with Ti in ZSM-5 zeolite titanyl sites are introduced, which are able to react with hydrogen peroxide

and form a peroxide complex, shown to be active in liquid phase oxidation of phenol to hydroquinone. Other metal oxo groups like vanadyl may be incorporated into the framework, and other frameworks besides ZMS-5 may be thought of, opening many new fascinating perspectives for novel technologies in catalytic oxidation (Table 4).

Table 4
OXIDATION REACTIONS ON ZEOLITES SUBSTITUTED WITH TRANSITION METAL IONS

-
1. Hydroxylation of aromatic compounds
 2. Ammoximation of ketones
 3. Oxyfunctionalization of alkanes
 4. Epoxidation of olefins
 5. Oxidation of alcohols to aldehydes and ketones
 6. Oximdatation of sulphur compounds
 7. Oxidation of benzene and toluene to phenol and cresols
 8. Oxidation of naphthalene to naphthols and naphthaquinones
 9. Oxidation of xylenes to xylenols and trimethylbenzenes to hydroxy-TMBs
 10. Oxidation of anthracenes to antraquinone
 11. Oxidation of cymenes to hydroxycymenes
-

In recent years interesting conclusions on the molecular mechanism of the elementary steps of catalytic transformations have been made possible by quantum chemical calculations [25,26]. As an example Fig.5 [27] summarizes the changes (D,%) of the diatomic energy contributions and the energies of bond formation,calculated by a semiempirical INDO method in the adsorption complex formed when a toluene molecule is approached end-on to a bridging oxygen atom of a vanadium oxide cluster, taken as a model of vanadium oxide catalyst. C-H bonds in the methyl group become weakend to such an extent that abstraction of two hydrogen atoms and their linking to surface oxygen atoms to form OH groups with simultaneous appearance of strong interaction between the carbon atom and surface oxygen atom is energetically favourable. The formation of transition complex with the C₆H₅-CH species leads to the dramatic destabilization (more than 80%) of the bonds of oxygen, playing the role of the adsorption site, with its nearest neighbours in the cluster and desorption of a molecule of benzaldehyde takes place.

Calculations indicate that the C-H bonds in the methyl group of the toluene molecule approaching the cluster become weakened already at a fairly long distance, their strength decreasing when the molecule moves nearer and nearer to the adsorption site. During this approach the carbon interacts stronger and stronger with the oxygen atom, playing the role of adsorption site, the latter being loosened from the cluster and moved higher and higher above the basal plane. Thus, the catalytic reaction should be considered as a

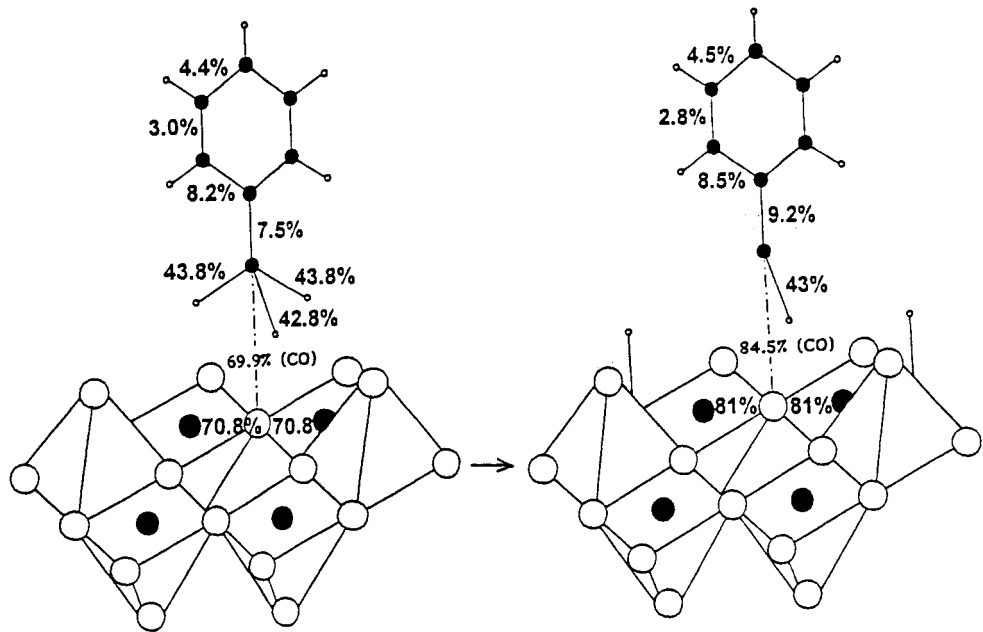


Fig.5. Changes (in %) of the diatomic contributions in adsorbate complex (non-activated and activated toluene) at bridging oxygen site of the V6O18 cluster taken as model of vanadium oxide catalyst in respect to the isolated cluster and toluene

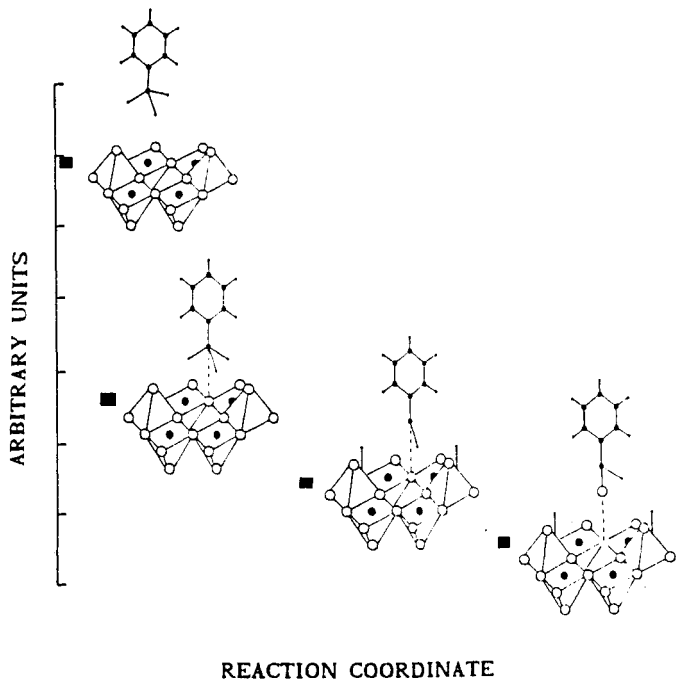


Fig.6. The sequence of elementary steps in oxidation of toluene.

dynamic process in which continuous rearrangement of atoms and redistribution of electrons take place on approach to the active site, resulting in the formation of the product desorbing from the surface. This is illustrated schematically in Fig.6.

A different picture emerges when toluene is approached to the cluster side-on. Strong interactions develop then between all carbon and hydrogen atoms of the benzene ring and oxygen atoms of the cluster, resulting in the degradation of the molecule and its total combustion. In the case of benzene the selective oxidation to maleic anhydride requires benzene and oxygen molecules to be adsorbed on vanadium atoms perpendicularly to the surface and parallel to each other. This illustrates the general conclusion that the mutual orientation of reacting molecules is one of the important factors determining selectivity of the catalytic reaction.

The catalyst surface is thus in dynamic interaction with the gas phase [28,29]. When steady state conditions of the catalytic reaction are changed, structure of the catalyst surface may also change, modifying the activity and selectivity of the catalyst itself. In certain conditions this may manifest itself in the appearance of oscillating reactions [30]. The widely investigated example is the oxidation of CO on Pt and Pd catalysts, for which the mechanism is well established [31]. Under certain external conditions the rate of this reaction varies in a periodic way. The kinetic oscillations are limited to conditions for which oxygen adsorption is rate-determining, and the oxygen sticking coefficient is considerably affected by the structure of the surface which in turn may be influenced by interaction with reactants. In this way the mechanism of periodic transitions of the surface between states of low and high reactivity may be rationalized. Development of the new technique of photoemission electron microscopy revealed the formation of spatiotemporal patterns such as propagating and standing waves as well as chemical turbulence [31,32]. This requires some kind of communication between different regions of the surface that means spatial selforganisation.

In recent years attention has been drawn to the fact that instead of accelerating the transformation of a molecule by forming few strong covalent bonds with the active centre of the catalyst, the catalytic effect may be achieved by subjecting the molecule to the field of weaker molecular interactions similar to those operating in the supramolecular systems. The term supramolecular catalysis was introduced [33] and numerous studies of different reactions have been carried out with α -cyclodextrin, macrocyclic polyethers and cyclophanes as catalysts. Supramolecular reactivity requires an appropriate fit between the molecule of the reactant and the catalyst, therefore molecular recognition step precedes the binding of the selected substrate, which is then followed by the reaction itself (Fig.7). Large and complicated molecules may be transformed into the desired products with high chemo-, regio- and enantio-selectivity.

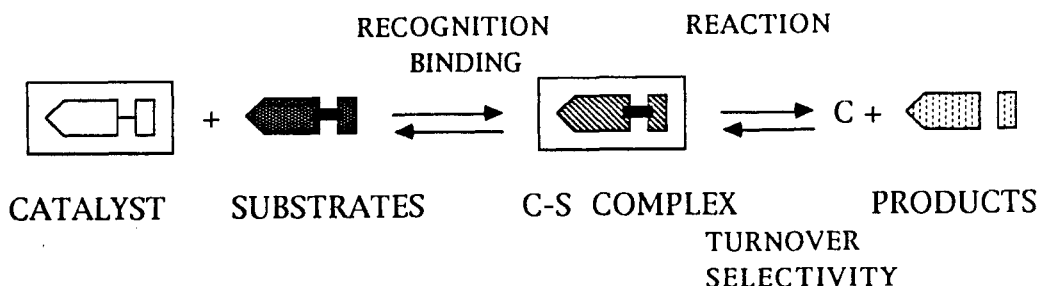


Fig.7. Scheme of supramolecular catalysis

The catalyst showing the ability to recognize a molecule to be reacted and to provide an appropriate fit to develop supramolecular interactions with this molecule, necessary for a catalytic transformation, may be obtained by exploiting the faculty of immune systems to produce superbly specific antibodies. In the past few years a new class of antibody molecules have been generated - the catalytic antibodies that not only bind but chemically transform the target molecule [34,35]. Taking into account that antibodies can be generated against the whole variety of different substances like biopolymers, natural products or synthetic molecules, catalytic antibodies offer a unique opportunity to tailor-making enzymelike catalysts. It is possible to carry out with high selectivity "disfavoured" chemical reactions along one of many reaction pathways even if the reactivity along this pathway is much smaller in comparison with others.

Fig.8 illustrates the method to produce catalytic antibodies. A hapten (the ligand against which the antibody is elicited) is being synthesized which is an analogue of the transition state of the desired reaction and antibodies are generated against this hapten. Such antibodies contain binding sites that are complementary to the rate determining transition state, that act to overcome the entropy requirements involved in orienting the reacting molecules or that contain an appropriately positioned catalytic aminoacid side chain or cofactor. There is also a possibility to introduce the required catalytic functionality into the combining site of an antibody by chemical modification and by site-directed mutagenesis. As an example Fig.9 shows some classic organic reactions which have been shown to be catalyzed by antibodies raised to stable transition-state analogues [34].

The overall activity of a catalytic system is a function of the turn-over frequency of the reaction at the active centre and the number of these centres easily accessible to the reacting molecules. Therefore one of the main objectives of the development of a catalytic system is the generation of active centres in highest, possibly molecular dispersion. This is

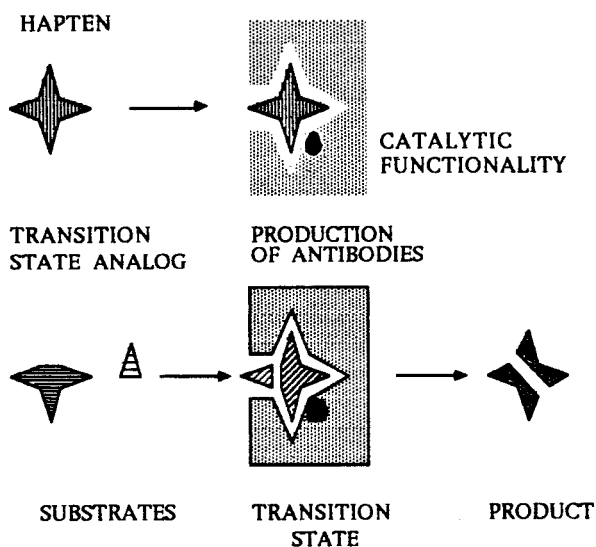


Fig.8. Generation of catalytic antibody.

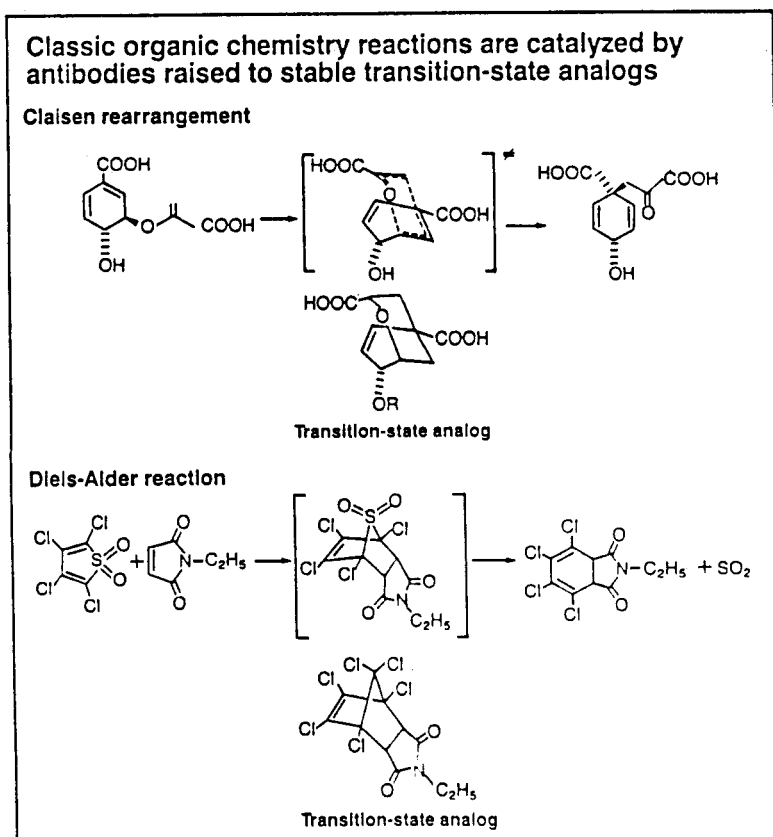


Fig.9. Examples of classic organic reactions catalyzed by antibodies raised to stable transition-state analogs.

usually achieved by supporting the active phase on a high surface area carrier. In recent years a different approach is also being adopted, based on the application of microemulsions. Many organic reactions are carried out in non-aqueous media, but many catalysts like enzymes are active only in the presence of water. In such cases encapsulation of the catalyst in reversed

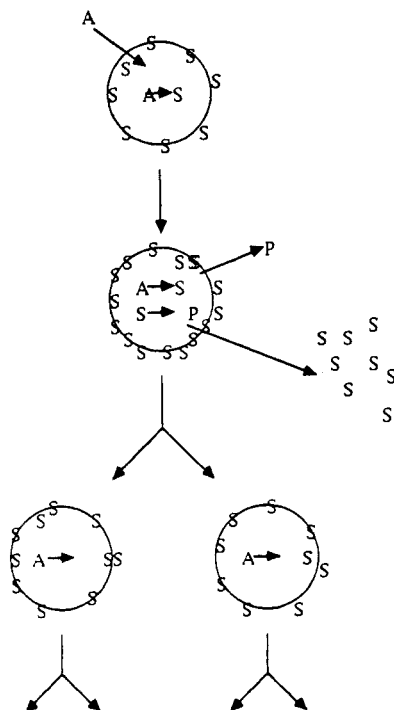


Fig.10. Self-replicating catalytic micellar system.

micelles dispersed in an organic phase provides an efficient solution [40]. A system is obtained equivalent to a very large number of identical microreactors operating with the same catalyst in the same conditions. They exemplify the principle of micro compartmentation: these structures have an interior which is chemically and physically different from the bulk solvent in which they are formed. The chemistry which takes place in the core of these structures or at the interface may have very particular features, dictated by the structure itself. It has been pointed out that micelles have the capability of spontaneous formation or self-organization, which is a thermodynamically controlled creation of order [36].

When catalytic reaction selected to proceed in the micelles produces molecules of the very surfactant which build the micelles, the micelles grow until a certain critical size at which they divide as illustrated in Fig.10. A self-replicating system is constructed in this way. The reaction may at the

same time produce another product P, which is ejected into the dispersing organic phase.

PRERSPECTIVES OF CATALYSIS

"A journey of a thousand miles must begin with a single step", Lao Tzu, 6th Cent.BC

Demographic forecasts based on the present rapid growth of the human population predict that in the year 2030, i.e. within the next 30-40 years the population of the earth will surpass 6 billion. On the other hand the rising standard of life provided by our modern civilization, coupled with a spectacular progress of different branches of chemistry bearing upon pharmacology and medicine, have brought a considerable prolongation of the average life expectancy. As a result, in the developed countries which are at the same time the main producing centres, the fraction of the population directly involved in production decreases and the fraction of those who only consume rapidly increases. The growing production results in the increase of the amount of by-products and with the rapid growth of the number of consumers increases also the amount of pollution disposed into the environment as the by-product of the civilization. In 1988 the amount of by-products of chemical industry reached 290 mln Mg and their disposal costed about 10 billion US\$, and it is forecasted that in the year 2000 this amount will rise to 510 mln Mg and the removal will cost 45 billion US\$ [37]. In this circumstances the main goals become:

- sustainable increase of production at lower energy consumption and radically limited generation of wastes;
- removal of environmental pollution;
- development of new energy sources.

Progress in science of catalysis and its industrial applications should make the fulfilment of these goals possible. In order to achieve this it is necessary to substitute the present energy consuming technologies, which produce large amounts of waste and pollution, by new, energy saving and wastefree catalytic processes of high selectivity. They must conform to five conditions:

- use very selective and active catalysts to reduce waste and consumption of energy;
- give high quality products, which must be environmentally safer;
- secure safety of technological operations by minimization of the use, transportation and storage of hazardous materials;
- emit clean exhaust gases and unpolluted waters;
- avoid the formation of by-products and salts or secure their conversion to co-products.

Development of technologies that obviate environmental problems constitute simultaneously primary measures for environmental control. Equally important are secondary methods of pollution control in which catalysis is used to convert the harmful pollutants into harmless chemicals. The best examples are

catalytic converters for automobile exhausts, which will have to be improved to catalyze the direct decomposition of NO_x to N_2 and O_2 .

One of the targets which offers the most opportunity for economic benefit is the technology of combustion of fuels [41]. The efficiency of conventional fuel combustors is still far lower than the theoretical and the gains by improvement of combustion may be enormous. World production of fuels recalculated in equivalent amount of coal was in 1990 1010 Mg. If only 1% increase in combustion efficiency were obtained by replacing high temperature flame combustors with low temperature catalytic reactors, 108 Mg of coal equivalents would be saved, worth 5 billion US\$ per year. Simultaneously a priceless advantage of considerable reduction of NO_x and particulate pollution would be gained.

The process of technology development resembles a S-curve [39]. Initially, progress is slow until a significant lead to a potentially useful application is found. Then further development proceeds more and more rapidly in the measure as the horizontal transfer of technology takes place, the invention finding its application in many different fields. However, eventually the technology evolution slows down as it becomes more and more difficult and very expensive to make significant further progress. At this point the technology has reached a state of maturity and diminishing returns and there are only limited incentives for investing in new research. The pattern of major new developments in industrial catalysis followed such an S-curve, particularly for making large volume chemicals. When a particular technology has reached its limits of technical progress, the pathway to further advances is via a technology discontinuity - a shift to an entirely new paradigm.

In the last twenty years investigations of the properties of isolated transition metal complexes and their interactions with the reactants led to the understanding of the mechanism of their catalytic action in homogeneous reactions and of their behaviour when deposited on the surface of a support. Changes of properties could be followed when these complexes were transformed into clusters composed of metal or metal and non-metal atoms which permitted the discrimination between different localized and collective properties of the system determining its behaviour in the catalytic reaction. Introduction of new more and more sophisticated spectroscopic techniques enabled the unraveling of the mechanism by which these centres transform the molecules of reactants into the desired product. The important fact has been established that interactions of adsorbed molecules with the surface of a solid not only produce the changes of the structure of the adsorbate, but may induce also reconstruction of the solid surface, the catalyst being in dynamic interaction with reactants of the catalytic reaction. The surface may adapt itself to the requirements of the reaction generating a pathway for a concerted rearrangement of electrons and atoms of reacting molecules encountering thus a much lower activation barrier. Moreover, such surface

transformations occurring in the course of the catalytic reaction as the result of the interaction of reactants with the catalyst, may lead to the appearance of new types of active centres at the catalyst surface, directing the catalytic reaction along a new pathway and thus profoundly influencing the selectivity. The concept of dynamic transformations of the system reactant-active centres as elementary steps of the catalytic reaction has been proposed. The importance of van der Waals and hydrogen bonds in the modification of the reactivity of a molecule leading to molecular recognition and catalytic transformation with chemo-, regio- and stereo-selectivity has been recognized, contributing to the understanding of the mechanism of enzymatic reactions and resulting in the spectacular development of supramolecular catalysis. The increasing potential of computational techniques has made it possible to introduce methods of quantum chemistry into the description of elementary stages of catalytic processes. The traditional branches of chemistry, such as organic chemistry, inorganic chemistry, electrochemistry, solid state, surface science, chemical kinetics, biochemistry etc. are becoming increasingly integrated into an interdisciplinary science of catalysis. This opens the prospects of the molecular design of catalysts tailored to the needs of the required reaction. Catalysis seems to be now ready for a change of the paradigm.

Synthesis of elementary molecular catalytic reactors can be envisaged, as shown in Fig.11. They may contain active centres composed of one or more transition metal atoms surrounded by appropriate ligands with one or more vacant coordinative site. Intrinsic properties of such active centre depend on

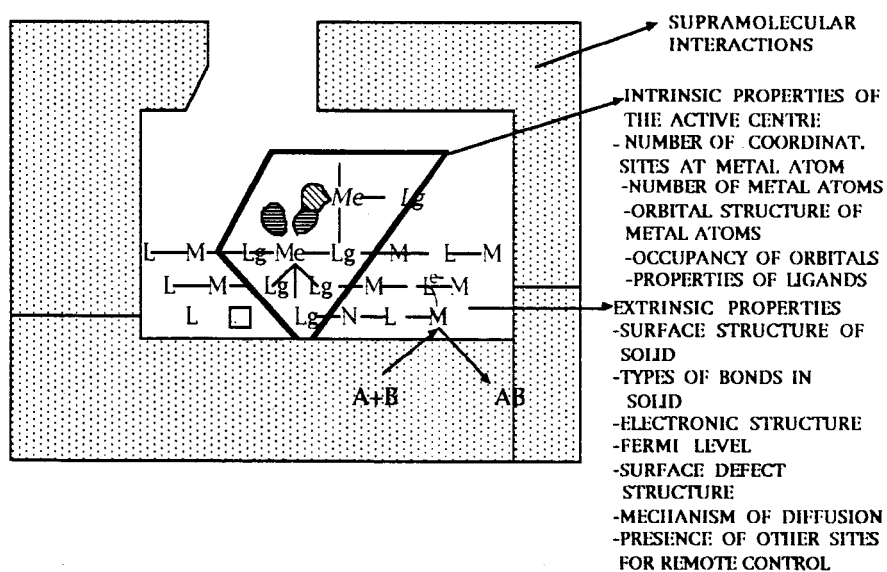


Fig.12. Elementary molecular catalytic reactor

the number and type of metal atoms, their orbital structure and occupancy, number of vacant coordination sites and properties of ligands. Its extrinsic properties are the function of the type of support, its type of bonds and electronic and defect structure, as well as structure of the surface, presence of additives etc. Elementary molecular catalytic reactor may contain other components which generate a field of molecular interactions, securing the molecular recognition deciding on the specificity of the reaction, and may be made sufficiently mobile to adapt itself to conditions for a proper mutual spatial orientation of reactants determining thus the regio- and stereoselectivity. In analogy to the semiconductor devices of highly integrated circuits, in which millions of microcircuits are located on a small silicon chip, an integrated catalytic system may be thought of, composed of millions of identical elementary molecular catalytic reactors obtained by using nanotechnology and tailored to the needs of any imaginable catalytic reaction. Active sites for other surface reactions may also be present in a certain array, permitting the density of electrons at the active centre and hence the character of frontier orbitals to be modified appropriately by remote control. This could permit switching the reaction on and off, or switching from one reaction pathway to another, making the catalyst "smart" or even "very smart".

In the fifties and sixties people were fascinated by the spectacular progress made possible by the scientific revolution of the XX century and believed that further development of science and technology is a condition sufficient to bring happiness to mankind. It was even thought that the principles of industrial mass production may be applied to art as exemplified by the ideology of pop-art. The best illustration is the lithography and silkscreen of Lichtenstein entitled "Happiness through chemistry" shown in Fig.12. When the turn of this century approaches we become more and more



Fig.13. Roy Lichtenstein. Peace through Chemistry, 1970. Litograph and silkscreen.

aware of the fact that further progress of science and technology is certainly necessary but by no means sufficient to make people happy. The eternal question arises: "quo vadis mankind?". I would like to finish by quoting the famous Chinese philosopher Chuang Tse (369-286 BC) who more than two thousand years ago said:

"I do not know whether I was then a man, dreaming I was a butterfly, or whether I am now a butterfly, dreaming I am a man".

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