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Catalysis by Heterogenized Metal Polymers: Advances and Prospects

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Abstract—The current status, trends, and a specific role for macroligands in catalysis by heterogenized metallopolymeric complexes are considered. Relations between homogeneous catalysis, enzyme catalysis, and catalysis by heterogenized metal complexes are traced. The effects of various factors on the catalysis of the main reactions used in organic synthesis—hydrogenation, polymerization (in particular, under the action of immobilized metallocene and postmetallocene catalysts), and redox processes (such as the catalysis of oxygenation, hydroperoxide oxidation, epoxidation, and hydroformylation)—are analyzed. In this review, attention is focused on the nondestructive identification of intermediates and catalytically active species in heterogenized systems. Experimental evidence is presented in support of the fact that the high activity, stability, and selectivity of immobilized catalysts are associated with a dramatic inhibition of concerted reactions in the coordination sphere of a transition metal, which result in catalyst deactivation, as well as with substrate enrichment. Prospects for the development of these highly organized hybrid systems and possibilities to consider the main requirements imposed on metal complex catalysis even at the stage of designing them are predicted.

INTRODUCTION

Since the early 1970s, outstanding advances have been made in the use of functionalized (in particular, with metal complexes) polymer materials. Of special note is advanced research in the Merrifield solid-phase peptide syntheses [1], catalysis by polymer-immobilized systems (for example, see [2, 3]), enzyme catalysis [4–6], ligand-exchange chromatography [7], and others Separation, ultrafiltration [8], membrane technologies [9], and others, should also be mentioned. The above demonstrates high potentialities and prospects for polymer-mediated synthesis. This is particularly true of immobilized metal complex catalysts for organic synthesis reactions (hydrogenation, selective oxidation, hydroformylation, polymerization, etc.); a number of competitive technologies or processes have been developed for many of these reactions. Polymer supports of two main groups are most frequently used in practice. The first group consists of rigidly crosslinked macroporous resins with high specific surface areas; their ligand groups are mainly localized at the surface, where they are exposed to substrate and reagent. These systems are functionally similar to catalysts on mineral supports [10]. The second group consists of linear or weakly crosslinked microporous network (gel-like) polymers or polymer composites. They undergo dissolution or swelling in solvents; catalytically active centers occur not only at the polymer surface but also in the bulk.

Although all the above problems have been continuously discussed, contradictory opinions on the possibility of catalysis by metal complexes (MX_n) immobilized on polymers can be encountered in the literature. Some researchers consider this technique as a panacea for all the disadvantages of traditional homogeneous catalysts, whereas others exclude the occurrence of advantages in these catalysts over typical heterogeneous catalysts. Here, an effort is made to analyze in detail the current status of the problem and the capabilities and prospects for the use of polymer-immobilized metal complex catalysts in the most commonly used organic synthesis reactions. The aim of this review was, on the one hand, to follow trends in the development of catalysis with polymer-bound metal complexes and, on the other hand, to reveal the specific role of macroligands in catalyzed processes. Note that the catalytic properties of complexes immobilized on mineral supports (essentially, inorganic polymers) are beyond the scope of this review; only complexes immobilized on synthetic or, more rarely, natural polymers will be considered. The terms *mixed-phase catalyst*, *immobilized catalyst*, or *polymer-bound* (a tailor-made polymer) *heterogenized catalyst* are used in the literature to describe these catalysts.

1. PLACE OF HETEROGENIZED METAL COMPLEXES IN CATALYSIS

Recall that a homogeneous metal complex catalyst is an individual chemical species (a complex or a combination of complexes), which occurs in the same phase as the reactants (almost always in solution). A catalytic reaction takes place in the coordination sphere of a transition metal necessarily with the electronic and steric participation of the ligands of the complex and with the formation of intermediate products [11–13]. All the cat-

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alytic centers in homogeneous catalysts are identical (at least theoretically) and equally accessible to reactants. Their activity and selectivity for a reaction product can be changed by varying the ligand environment of a transition metal.

In heterogeneous catalysis, the reaction occurs at an interface, and the reactants are activated through the step of adsorption on a catalyst surface, which exhibits collective electron properties. However, a set of centers occurs on the surface; of these centers, only one can catalyze the required reaction, the others are either inactive in the reaction or even activate side reactions [14].

The uniformity of active centers is an advantage of homogeneous catalysts in studying the nature of active species and revealing the mechanism of their catalytic effect. The opposite is true of process design; in this case, the balance of advantage lies with heterogeneous catalysts. The most important advantage consists in economic benefits: heterogeneous catalysts can be more easily separated from reaction products and often recycled in their initial form. The latter is of particular importance in many cases when metal complexes contain precious metals (such as rhodium, which is 300 times more expensive than gold) or are environmentally hazardous compounds. This is an acute problem in the manufacture of food products, pharmaceuticals, dyes, etc. In connection with the problem of catalyst separation from the reaction mixture, heterogeneous chemical processes are more widely used in industry, although considerable effort has been devoted to the development of new efficient techniques for solving this problem in homogeneous versions (such as distillation and ion exchange).

Attempts to combine the advantages and to eliminate the disadvantages of traditional homogeneous and heterogeneous catalysts resulted in the development of mixed-phase catalytic systems. The distinctive feature of these systems is that the mobility of the metal complexes is significantly restricted by chemical bonding to a polymer or mineral support. The implantation of metal complexes into strong and elastic grains, powders, fibers, or membranes, which can be easily separated from the reaction mass and, in principle, repeatedly used similarly to typical heterogeneous catalysts, appears to be the only escape from this situation. Simultaneously, a number of important problems are solved:

- The efficiency of homogeneous catalysts is increased because their concentration is not limited by solubility (it is well known that the set of appropriate solvents in homogeneous catalysis is restricted by the solubility of MX_n).

- Because of the restricted mobility of metal complexes chemically bound to a support, the state of infinite dilution is simulated.

- The process temperature can often be increased to operating ranges in this manner (as a rule, homogeneous catalysts are active at temperatures lower than 100°C). Because the rates of the majority of reactions increase with temperature, the possibility to operate at high temperatures is an advantage for a catalyst.

- Immobilized catalysts inherit the better reproducibility of homogeneous catalysts, whereas the surface structure of heterogeneous catalysts and, consequently, the number and nature of active centers strongly depend on the procedure used for catalyst preparation and the subsequent treatment.

- Mixed-phase catalysts are less sensitive to oxygen, trace moisture, and soft ligands (poisons) than their mobile analogs; this is favored by polymer surfaces of a hydrophobic character.

- When operating with these catalysts, corrosion of apparatus is often not the case (or is significantly inhibited), and reactor walls should not be coated with insulating materials. It should be remembered that many heavy metal compounds (such as OsO_4) are not only expensive but also highly toxic, although they are used for the manufacture of pharmaceuticals, fine chemicals, etc. The list of such particular advantages could be continued.

However, not only practical prospects of the problem under discussion are of interest. Considerable efforts were required for outlining the mechanism of MX_n binding to the simplest macroligands: surface functional groups of grafted polymers [15]. Experience on the development of these catalysts demonstrated that the combination of a macroligand with a metal complex could produce new unexpected results. First, note that, when MX_n is bound to a polymer, the ligands of the metal complex are partially replaced by the functional groups of a polymer chain. In this case, the catalytic properties of the metal complex are changed because of another stereochemical environment of the metal ion. The course of a catalytic process can sometimes be affected purposefully by varying these factors (the number of replaced ligands, the nature of functional groups in the macrochain, the structural organization of the macroligand [16–18], the degree of swelling, etc.). Under favorable conditions, intermediates and, occasionally, catalytically active species can be isolated and structurally characterized. Moreover, a macroligand not only serves as an inert support but also facilitates the preconcentration and preferential orientation of a substrate at the active center and thereby promotes its selectivity. These functions are performed by protein macromolecules in enzyme catalysis.

In connection with considerable progress in the simulation of enzymatic processes using homogeneous catalysis, it is reasonable to discuss relations between homogeneous catalysis, enzyme catalysis, and catalysis by heterogenized metal complexes. Metalloenzymes, which catalyze many biochemical processes, are high-molecular-weight proteinic compounds; metal ions are the constituents of their active centers. They are incorporated into the structure of biological membranes in a living organism; formally, they can be considered as immobilized complexes in a swollen (gel-like) state. Their high catalytic activity is a consequence of the combination of a number of concerted factors, in particular, a structural correspondence. Some sites of a biopolymer exhibit an enhanced affinity for a substrate and form a specific space network near the active site; the shape and size of this network correspond to the structure of the substrate. This dramatically increases the concentration of the substrate near the active sites (so-called substrate enrichment) and produces a favorable orientation of reactant molecules. In this case, multicenter catalysis plays an important role: metal ions and functional groups of a biopolymer additionally activate the substrate via a concerted mechanism. An analogous (or similar) situation can occur in heterogenized complexes based on synthetic polymers. Moreover, the Michaelis–Menten equation [19] can be applied to describe the kinetics of many reactions catalyzed by metallopolymers (such as hydrogenation and oxidation), as well as the kinetics of biological processes. Thus, for the reaction

$$\begin{tikzcd} E + S \arrow[r, shift left, "k_1"] & ES \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_2"] & E' + P, \arrow[ll, bend left] \end{tikzcd}$$

where E is the catalyst, S is the substrate, P refers to products, ES is the Michaelis–Menten complex, and E' is rapidly oxidized to E, the Michaelis constant is $K_M = (k_{-1} + k_2)/k_1$. In this case, the initial (w_0) and maximal (w_{max}) rates are related by the equation

$$\frac{1}{w_0} = \frac{K_M}{w_{max}[S]} + \frac{1}{w_{max}}.$$

The above initiated a thorough search for highly efficient catalysts that are similar to biocatalysts in operation. Thus, immobilized catalysts combine the main characteristics of homogeneous, heterogeneous, and enzyme catalysts.

The most important role of a polymer can be reduced to the stabilization of catalytically active intermediates, which are formed both in the course of MX_n binding to a macroligand (for example, because of the monomerization of dimeric complexes) and in a catalytic reaction (in particular, the generation of isolated low-valent metal ions; the prevention of their aggregation, the formation of coordinatively unsaturated metal complexes, etc.). Factors responsible for these effects can be reduced to the following:

- the structure, length, and flexibility of the macroligand chain;
- the ability of the macromolecule to contract or expand depending on solvent, temperature, and the occurrence of electric charges in the chain;
- the nature and fraction of metal-binding functional groups (the degree of chain loading) etc.

A detailed analysis of these factors is of primary interest for the development of a scientific basis for designing catalysts of this type. It provides an opportunity to take into account the main requirements imposed on metal complex catalysis even at the stage of catalyst design.

Although a great number of articles, monographs, and reviews concerning various aspects of this problem were published to date (for example, see [3, 18, 20–23]), the potentialities of this fruitful approach are by no means exhausted. In actual practice, it was much more difficult to solve this problem than it initially seemed because a number of particular difficulties appeared. For example, the test system is not always completely heterogeneous because the metal–macroligand bond is often instable under conditions of catalysis, and the catalysis can result from the simultaneous action of mobile and immobilized active centers. Moreover, it was found that uniform structurally isolated polymer-bound metal complexes are difficult to obtain: as a rule, the interaction of MX_n with a macroligand is associated with a number of parallel reactions including aggregation [24]. These phenomena are complicated by the use of solvents responsible for macrocomplex swelling in catalysis.

2. HYDROGENATION REACTIONS CATALYZED BY MACROCOMPLEXES

Macromolecular complexes based on platinum-group metals or elements from the first transition series participate in the following reactions under mild conditions [25, 26]:

- They hydrogenate alkenes, aromatics, and heteroaromatic substrates.
- They perform partial or exhaustive hydrogenation of fats and unsaturated acids.
- They reduce various (nitro, carbonyl, nitrile, etc.) functional groups.
- They are efficient in the production of polyols from sugars.
- They convert alkynes into *cis*- or *trans*-alkenes, etc.

2.1. General Kinetic Properties

Because the bond energy in the H_2 molecule is comparatively high and equal to 437 kJ/mol, the activation of hydrogen via intermediate complexes is required for reactions with the participation of hydrogen. Hydrogen activation or substrate activation can be a rate-limiting step in the hydrogenation of unsaturated compounds or functional groups depending on the substrate, catalyst, and reaction conditions. If the catalyst surface is covered with hydrogen, the rate-limiting step is substrate activation (the activation energy (E_a) of such a reaction was estimated at 20–25 kJ/mol). As the adsorption ability of the substrate increases, H_2, the substrate, and the solvent simultaneously occur at the catalyst surface (E_a = 30–40 kJ/mol). Finally, if the substrate undergoes strong adsorption and displaces the other reactants from the catalyst surface, the reaction is limited by the activation of H_2 ($E_a = 40–60$ kJ/mol). It is of importance that a change in the hydrogen–catalyst bond energy even by 4–8 kJ/mol may considerably affect the mechanism and selectivity of hydrogenation. The substrate–catalyst interaction is often strong (for example, for nitrobenzene) to an extent that it is accompanied by the formation of radical anions capable of reacting with any hydrogen species. Thus, $PdCl_2$ adsorbed on polybenzimidazole (PBI) is reduced in an atmosphere of H_2 to the polymer-bound cluster $PBI \cdot Pd^0$ [27]. Their activity in the hydrogenation of various substrates decreases in the order dienes > allyl alcohol > 1-alkene > 2-alkene > 2-methyl-2-alkene. The chemisorption ability of the substrates decreases in the same order. Evidently, the interaction of the polymer support with the surface atoms of palladium weakens the metal–substrate bond. It is of importance that, as a rule, catalyst activation processes (the formation of active centers) are not accompanied by the rupture of chemical bonds between the metal and the macroligand. This is particularly true of macrochelates: MX_n bound to macroligands in chelate units (with the groups of 2,4-pentanedione, ethylenediamine, 8-aminoquinoline, Schiff bases, etc. [28]) are more stable; the majority of them can be used in 300–1000 or more hydrogenation cycles [29]. The active centers of a high-performance catalyst for the reduction of isoprene, 1-hexyne, cyclopentadiene, and nitrobenzene are Pd^0 atoms coordinated to donor groups ($–NH_2$, –OH, –CONH–, and –COOH, including chelating groups) of Indian silk protein [30] and strongly bound to the micellar structure of silk fibroin. This catalyst can be regenerated several tens of times without a loss of activity.

Metal complexes immobilized on a macroligand with π-donor properties, in particular, on polyacetylene, are active catalysts for the hydrogenation of acetylene substrates. It is likely that the immobilization of a metal complex results in the appearance of unpaired electrons in polyacetylene, which is favorable for an increase in the concentration of free radicals and, as a consequence, for the partial reduction of transition metal ions even at the stage of binding to the polymer [31]. It is likely that, in the presence of these catalysts, the substrate is converted through dissociative chemisorption. Many examples are known in which the substrate or reaction products are irreversibly adsorbed at the active centers of a catalyst.

The most typical mechanism of hydrogenation is reduced to two steps. At the first step (it may be reversible) the substrate molecule reacts with the active center of a macrocomplex, which includes activated hydrogen (already formed catalyst):

$$]\text{–MH} + \text{S} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}}]\text{–M–SH}.$$

At the second step this intermediate irreversibly reacts with hydrogen to form the product and to regenerate the active center:

$$]\text{–MSH} + \text{H}_2 \xrightarrow{k_2}]\text{–MH} + \text{SH}_2.$$

In this case, the rate of hydrogenation is described by the general equation

$$w = -\frac{d[S]}{dt} = \frac{k_1 k_2 [S][H_2][\ ]\text{–MH}]}{k_{-1} + k_1[S] + k_2[H_2]}.$$

This equation can be easily converted into the Michaelis–Menten equation [19], which is frequently used in homogeneous and enzyme catalysis: the rate of reaction increases with substrate concentration and approaches a limiting value (w_{max}):

$$w = -d[S]/dt = k_2[H_2](K_M - [\ ]\text{–MH}]),$$

where K_M is the Michaelis constant that corresponds to a substrate concentration at which the rate of reaction is half of w_{max}.

The general rate equation describes typical experimentally observed rates of hydrogenation reactions as functions of the concentrations of a polymer-bound catalyst and various substrates and the pressure (concentration) of H_2:

- At a low pressure of H_2, the rate of reaction increases proportionally to the concentration of the catalyst.
- The dependence of the rate of hydrogenation on the concentration of H_2 may be either linear or nonlinear; the nonlinear dependence is observed at $k_1[S] \gg (k_1 + k_2[H_2])$, and it is linearized in the $1/w = f(1/P_{H_2})$ coordinates (this method is used for calculating k_1 and k_2).
- As a rule, the rate of hydrogenation is proportional to substrate concentration; however, various types of these functions are known, the zero order of reaction and a nonlinear increase in the rate of reaction (in these cases, curves are linearized in the $1/w = f(1/[S])$ coordinates, and k_1 and k_{-1} can be calculated from the plots).

Without going into detail, I can only state that the kinetics of hydrogenation in some systems is similar to homogeneous kinetics, whereas it is closer to heterogeneous kinetics in other systems.

Abundant evidence for the common effects of homogeneous and heterogeneous hydrogenation catalysts is currently available: Compounds like M–H were detected as intermediates. The stepwise addition of hydrogen, a decrease in the rate of olefin hydrogenation in the presence of acetylene or conjugated diene substrates strongly coordinated to a metal, catalyst poisoning with similar poisons, etc., were found. In other words, many processes that occur in immobilized catalysts are similar to those observed on typical heterogeneous catalysts, for example, on a 5% Rh/C standard catalyst or corresponding metal blacks. Moreover, even the additives of polystyrene (PS) or a styrene–divinylbenzene (SDVB) copolymer to rhodium or platinum black over a wide range of active phase/polymer ratios increased the rates of reduction of nitrobenzene and dimethyl ethinyl carbinol by a factor of 1.5–2 (see [3] and references therein). As will be demonstrated below, the binding of MX_n in a macrocomplex results in the further elimination of the distinction between homogeneous and heterogeneous catalysis.

2.2. Effect of the Nature of the Macrocomplex

As in heterogeneous catalysis, the effects of the specific surface area (S_{sp}, m^2/g) and porosity (pore volume V_{pore}, cm^3/g) of a catalyst on its activity were also observed in the case of immobilized metal complexes; many relevant examples are known. Thus, S_{sp} and V_{pore} in SDVB copolymers depend on the amount of a crosslinking agent; at crosslinking agent concentrations of 10, 20, 30, and 40%, the corresponding values were equal to 14 and 0.040, 182 and 0.192, 222 and 0.333, and 357 and 0.392, respectively [3]. The binding of MX_n to a porous polymer resulted in changes in its morphology and pore-size distribution [32, 33], and the grind of SDVB copolymer granules (20% divinylbenzene (DVB)) containing immobilized titanocene [34] increased its catalytic activity many times (Table 1).

Table 1. Initial rates of olefin hydrogenation (w_0) in the presence of the cyclopentadienyl (Cp) compounds of Ti^{4+}

Catalyst	Substrate		
	hexene	cyclohexene	cyclooctene
$CpTiCl_3$	2.9	2.0	0.5
SDVB copolymer–$CpTiCpCl_2$ (granules)	42.0	30.0	7.8
SDVB copolymer–$CpTiCpCl_2$ (powder)	390.0	194.0	60.5

Note: w_0 in ml H_2 (mmol Ti)$^{-1}$ min^{-1}.

An original way of increasing S_{sp} in these catalysts consists in the use of metal complexes immobilized on mixed mineral–polymer supports. They are produced in various manners: the polymerization or graft polymerization of corresponding monomers in the presence of SiO_2, MgO, TiO_2, Al_2O_3, etc., or the impregnation of oxides with polymer solutions followed by functionalization or without functionalization. Functional groups are often incorporated into the ligand environment of a metal complex, for example, of Rh [35, 36]. The specific surface area of these catalysts is 200–700 m^2/g. These methods were summarized in a review [37]. For comparison, let us exemplify the preparation of such a catalyst. The copolymerization of methacrylic acid with a mixture of *meta*-divinylbenzene and *para*-divinylbenzene in the presence of SiO_2 resulted in the formation of a crosslinked SiO_2–PMA support (PMA is polymethacrylate). Efficient catalysts for the hydrogenation of unsaturated hydrocarbons, nitro compounds, aldehydes, and ketones were formed by the interaction of the above support with $PdCl_2 \cdot 2H_2O$ or H_2PtCl_6. These catalysts are nonpyrophoric and highly stable (more than 2000 cycles, Fig. 1); they can be easily separated from the reaction mixture by decantation.

Thus, mixed-type supports combine the advantages of polymeric and mineral supports.

The functional groups of a polymer (L) play a multiple role (in terms of both nature and concentration). They participate not only in the binding of MX_n but also in a catalytic process to increase the local concentrations of active centers and a substrate (see below); they catalyze side processes or protect the active center from trace impurities and catalyst poisons. This can result in the production of catalysts significantly different in activity and selectivity. Published data [38] can be cited in support. In the hydrogenation of styrene in the presence of Pd immobilized on a functionalized SDVB copolymer (4–6% DVB), the rate of the reaction increased in the case of supports whose functional groups can form π complexes with styrene and thereby increase the lifetime of adsorbed substrate complexes (so-called substrate enrichment). At the same time, in the hydrogenation of allyl acrylate, the activity of catalysts correlated with the π-acceptor and polar properties of the functional groups of polymer matrices. The $–NO_2$ and $–OCH_3$ groups can form molecular associates with substrates, whereas the –OH, $–NH_2$, $–NR_3$, and $–CH_2OCH_2$ groups affect substrates because of polar effects. In the general case, polymers with hydrophobic surfaces decrease the rates of hydrogenation of nonpolar substrates (for example, the introduction of even 7% 2,4-dinitrophenyl groups noticeably decreased the rate of hydrogenation of 4-vinylcyclohexene).

In optimum variants, the ligand groups of a polymer perform dual functions: they exhibit electron-donor properties for coordinating a transition metal in a high oxidation state and electron-acceptor properties for stabilizing the metal in a low-valence or zero-valence state (after reduction). Note that the functional group–substrate interaction plays a particularly important role in highly crosslinked polymer supports, in which the fraction of vacant groups is often many times higher than the fraction of groups that participate in the binding of MX_n.

Let us consider an important special feature of catalysis by macrocomplexes: geometric or matrix selectivity—the dependence of the rate of hydrogenation on the geometric size of substrate molecules. This dependence manifests itself in a decrease in the rate of hydrogenation under the following conditions:

- with increasing olefin chain length;
- on going from alkenes with a terminal double bond to substrates containing a double bond within a chain or

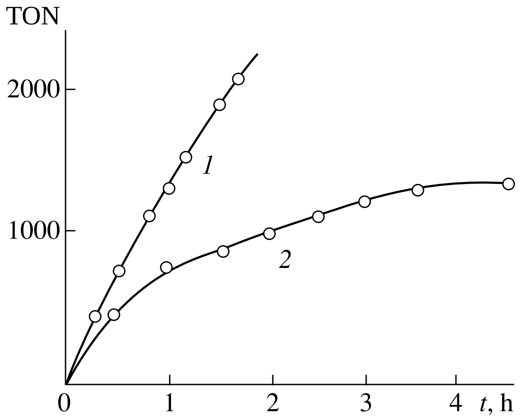


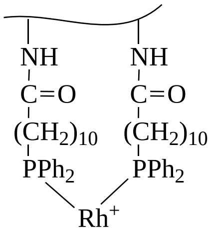
Fig. 1. The time dependence of the catalyst turnover number (TON) in the reaction of nitrobenzene hydrogenation in the presence of SiO_2–PMA catalysts with (*1*) Pd and (*2*) Pt. [COOH]/[M] = 10; [Cat] = 0.02 mmol; [substrate] = 0.05 mol.

ring (the rate of 1-hexene hydrogenation was higher than that of 2-hexene or cyclohexene by a factor of ~20);

- on going from *cis* to *trans* isomers;
- with increasing number of substituents at a double bond in linear and cyclic olefins (in this case, electron-donor or electron-acceptor substituents accelerated or inhibited the rate of reaction, respectively);
- on the introduction of heteroatoms into alkenes and aromatic substrates;
- on the introduction of bulky substituents into a benzene ring (the ratio between the rates of hydrogenation of benzene, toluene, *ortho*-xylene, *tert*-butylbenzene, and hexamethylbenzene is 1 : 0.62 : 0.27 : 0.01 : 0);
- on the introduction of substituents into nitro compounds.

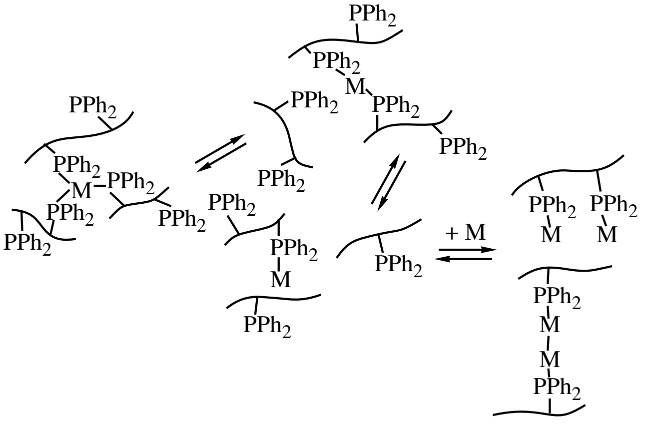
The last-named phenomenon can be exemplified in the reduction of various nitro compounds with a Pd-immobilized complex [39] (Table 2).

The effects of an increase in the length of a link between the main chain and L on both the complexation with MX_n and the activity of the catalysts formed are also of interest. These effects are due to an increase in the mobility of the metal centers, which facilitates their accessibility to a substrate. As a rule, the rate of hydrogenation increases with increasing length of an "anchor" chain and, in the limit, approaches the activity of a homogeneous analog (for example, for the structure given below).



2.3. Formation of Coordinatively Unsaturated and Isolated Metal-Containing Centers

It is well known that the monomerization of dimeric or multimeric complexes is of considerable importance in metal-complex catalysis. This is because coordination vacancies in the sphere of a transition metal should be free for the activation of a substrate or H_2. This is accomplished either at the stage of catalyst preparation (static factor) or in the course of catalysis (dynamic factor). Macrocomplexes are dynamic forms; under the action of various factors, coordination vacancies at metal centers can appear or disappear, for example, as shown in Scheme 1.



Scheme 1.

As a rule, monomeric metal complexes MX_n are formed by purposefully designing a macroligand and its functional groups (including its "intrinsic" or "framing" ligands, which enter the first coordination sphere of a transition metal: halide, carbonyl, nitrosyl, phosphines, AcAc, CH_3COO, Py, and dipy) under certain conditions of an immobilization reaction [40].

At a low degree of crosslinking (2% DVB), the polymer is sufficiently flexible, and a high mobility of the segments of a low crosslinked matrix results in the formation of dimeric structures (such as V_2Cl_8 and $[(COD)RhCl]_2$, where COD is 1,5-cyclooctadiene). Dimeric structures were almost not observed in the crosslinked polymer (20% DVB). Moreover, prerequisites to the fixation of coordinatively unsaturated structures are produced in highly crosslinked polymers. This follows from the fact that the mixing of particles with different sizes (a macroligand and a dimeric complex) is accompanied by the monomerization of associated species near the macromolecule because of an increase in the positive excess entropy of mixing as the difference in particle sizes increases. In this case, complete monomerization may take place, or dimeric and monomeric metal complexes bound to the polymer may coexist. The nature of the functional groups of a macroligand is also of considerable importance: monomeric and polymeric amines cleave the dimeric complex $[Rh(CO)_2Cl]_2$, whereas thiols form the addition products $[Rh(CO)_2RS]_2$. This is also true of the interaction of $[Ru(para\text{-}cymene)Cl_2]_2$ with phosphinated polymer matrices [41]. Dimeric complexes that are formed in the course of a catalytic reaction rather than at the stage of immobilization play a more important role; they result in an inhibition of the reaction. A classical example is the following: homogeneous titanocene systems are rapidly deactivated in the hydrogenation of olefins, dienes, or acetylenes because of the dimerization of complexes. Polystyrene modified with cyclopentadienyl (Cp) groups prevents this process; therefore, heterogenized catalysts of this type are more highly active and stable than homogeneous catalysts by a factor of 10–20 (Table 1).

A method for producing coordinatively unsaturated metal centers consists in the optimization of an M/L ratio at all the stages of catalyst operation. It is likely that the stability of process characteristics observed in catalysis by immobilized complexes is indicative of the uniformity of active species. For example, in the selective reduction of polynuclear aromatic compounds with rhodium complexes bound to a phosphinated SDVB copolymer, the P/Rh ratio decreased from 3.3 to only 2.9 even after several thousands of cycles [2, 3]. At the same time, the rate of hydrogenation of 1.5-COD, butadiene, or acetylene is a complicated function of P/Rh [42] (Table 3).

The dispersity of Rh^0 particles formed on the support surface (Rh_s) and the contribution of these particles to the total rhodium content of the catalyst also depend on the P/Rh ratio. The general trend is as follows: a maximum rate of 1,3-butadiene hydrogenation was reached at $P/Rh_s \sim 1$ and was independent of this ratio at $P/Rh_s > 2$. As the phosphorus content of the macroligand decreased, as well as at the ratio $P/Rh_s < 1$, the particle size of Rh_s increased and approached the particle size of Rh_s formed on the polymer without functional groups (unmodified SDVB copolymer) at low values of these quantities.

2.4. Solvent Effects

The nature of the solvent, which affects the flexibility of chains, is of considerable importance. For example, in *n*-hexadecane, which is a low-swelling solvent, the formation of monomeric complexes is predominant, whereas dimeric complexes are mainly formed in xylene. In sufficiently flexible polymers, complexes immobilized either at a chain or at a section between crosslinking centers can participate in dimerization. Moreover, in solvents causing no polymer swelling, macrocomplexes are localized only at the polymer surface to increase the S_{sp} of the catalysts formed. Although, as a rule, substrate diffusion into a polymer matrix is not a rate-limiting step of hydrogenation, such examples are also known (an increase in the rate of reaction on the ground particles of a macrocomplex). This is particularly manifested with increasing solvent polarity, which results in a decrease in the swelling ability of nonpolar matrices and in the size of transport routes in catalysts. An increase in the solvent polarity facilitates the diffusion of polar substrates to active centers and hinders the diffusion of nonpolar substrates. Table 4 [33] summarizes data on the effects of the solvent nature on the solubility of hydrogen, the swelling ability of various macrocomplexes, and the rate of acrylamide hydrogenation. However, the reduction of the role played by a solvent to only the above factors is a simplified approach to the problem. In the general case, the solvent effect on the rate and mechanism of liquid-phase hydrogenation with macrocomplexes is much more many-sided than in homogeneous catalysis. It depends on the following most important factors:

- the energies of substrate and hydrogen binding to the catalyst surface;
- the adsorption ability of solvent molecules and their participation as specific ligands coordinated to active centers (this interaction may be either activating or inhibiting);
- the distribution coefficients of the substrate and the product between the solution and the catalyst surface;
- the ratios between the rates of component activation (including the participation of solvents, in particular, alcohols, in the formation of transition metal hydride complexes, which occurs with or without changes in the oxidation state) and desorption from the catalyst surface;
- the solubility of hydrogen (the Henry constant) and the rate of hydrogen diffusion through a gas–liquid interface;

Table 2. Initial rates of hydrogenation (w_0) of various nitro compounds in the presence of palladium–poly(methyl methacrylate)

Substrate	w_0, ml/min	Relative rate of hydrogenation*	Substrate	w_0, ml/min	Relative rate of hydrogenation*
Nitrobenzene	46.1	1.00	*ortho*-Nitrotoluene	34.3	0.74
para-Nitroaniline	54.5	1.18	*ortho*-Nitrophenol	48.0	1.04
meta-Nitroaniline	50.0	1.08	Nitromethane	9.6	0.21
ortho-Nitroaniline	28.8	1.63	Nitroethane	4.6	0.10

* Ratio between the rates of hydrogenation of a substituted substrate and nitrobenzene.

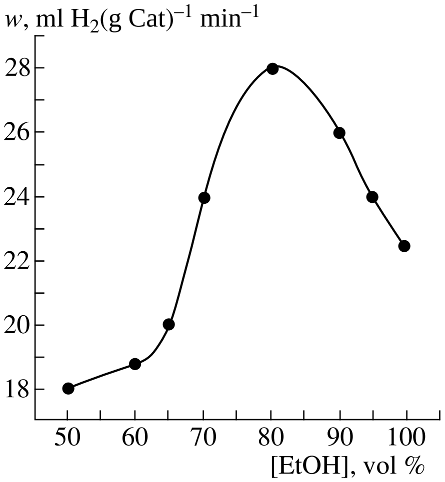


Fig. 2. Dependence of the rate of cyclohexene hydrogenation on polymer-immobilized Pd porphyrin on the concentration of EtOH in H_2O.

- the solvation of reactants, in particular, the substrate, and the use of the substrate as a solvent;
- the occurrence of polar impurities, which are capable of selective adsorption, in the solvent;
- the acid–base interactions between the solvent, the catalyst, and the functional groups of the macroligand.

The effects of the above individual factors are nonequivalent. Macroporous macroligands (having pores of size 6–75 nm) provide an opportunity to use heterogenized catalysts in the majority of organic solvents and so to overcome limitations related to choosing a solvent. Of course, the effect of a solvent mixture is much more complicated [43]. Let us cite only a single example. The rate of cyclohexene hydrogenation on polymer-bound palladium porphyrin [44] is a complicated function of the ratio ethanol/water; it reaches a maximum value at an ethanol concentration of 80 vol % (Fig. 2).

Thus, the use of homogeneous catalysts is restricted by the solubility and stability of complexes, whereas a high catalyst concentration can be produced in almost any reaction medium in hydrogenation with immobilized complexes.

2.5. Temperature Effect

The effect of temperature on the rate of hydrogenation (w) in catalysis by heterogenized metal complexes is much more complicated than that in traditional homogeneous or heterogeneous catalysis because not only the catalytic reaction but also the macroligand–MX_n system undergo the temperature effect. For this reason, the functions $w = f(T)$ are often plotted as bell-shaped curves (curves with a maximum). Detailed reasons for this phenomenon are unclear. One of them may be the occurrence of degradation processes in a polymer matrix, in particular, at elevated temperatures; these processes can be initiated or accelerated by metal complexes. In these cases, the descending branches of the curves can result from the aggregation of metal centers, which accelerates with temperature. However, the most likely explanation for this phenomenon can consist in phase transformations that occur in metallopolymeric matrices on heating. The reactions of polymers depend on the mobility of active centers and chain seg-

Table 3. Characteristics of rhodium complexes immobilized on a phosphorylated SDVB copolymer (2% DVB) and their activity in the hydrogenation of butadiene and acetylene

Component concentrations, %			Particle size of Rh, nm	P/Rh_s	$N^{**} \times 10^{-2}$	
P	Rh	Rh_s^*			1,3-butadiene	acetylene
1.6	1.1	1.0	1.5	5.8	1.3	1.0
1.7	0.6	0.5	1.7	10.7	1.0	12
1.7	1.6	1.3	1.9	4.3	0.8	–
1.2	0.5	0.5	1.2	8.4	1.4	–
1.2	1.0	0.9	1.65	4.5	1.3	0.8
2.0	2.0	1.7	1.8	2.3	1.5	–
1.2	5.0	3.3	2.9	1.2	4.2	5.0
1.7	3.0	2.4	1.9	2.3	1.1	–
0.5	0.5	0.4	1.6	4.6	3.9	–
0.5	1.0	0.7	2.9	2.4	3.8	21
0.5	2.0	1.1	4.4	1.6	6.3	–
0.5	5.0	1.7	6.7	0.9	30	–
0 (SDVB copolymer)	1.0	0.5	4.8	–	28	42

Note: Reaction conditions are P_{H_2} = 67 kPa, $P_{C_4H_6}$ = 0.11 kPa (348 K), and $P_{C_2H_2}$ = 0.11 kPa (368 K).

* Rh_s is the amount of Rh particles on the surface of the support.

** N is the number of reacted substrate molecules per surface Rh atom per second, (S molecule) (Rh_s atom)$^{-1}$ s^{-1}.

ments, which affects the catalytic properties of immobilized complexes. In particular, the defrosting of segmental mobility at a certain temperature can affect the coordinative unsaturation and valence state of a transition metal at the active center, the formation of dimeric complexes, etc. (see Scheme 1).

It is likely that the "adjustment" of a polymer matrix to produce the most favorable configuration of an active center is the property of immobilized systems that approximates them to enzyme systems. An anomalous Arrhenius equation for the rate of ethylene hydrogenation in a gas phase under the action of rhodium on phosphinated polystyrene [45] can serve as experimental evidence for the above. The reaction rate dramatically changed at the glass-transition temperature (T_g) of the polymer (341 K, Fig. 3); this phenomenon was repeatedly reproduced. The anomalous temperature behavior cannot be due to an increase in ethylene diffusion into small pores of the catalyst (which would become a rate-limiting step at T_g) or a change in the rate-limiting step at a certain temperature (because of practically equal slopes of the Arrhenius plots). A comparison of the temperature behaviors of the macroligand and the complex on its basis demonstrated that the activity decreased at temperatures equal to T_g within the limits of experimental error. The activation barrier of the reaction at $T > T_g$ remained almost the same (33 and 35 kJ/mol for higher and lower temperatures, respectively). In other words, all changes in the rate constant are due only to changes in the entropy factor; this phenomenon can be a consequence of changes in the mobility of polymer segments.

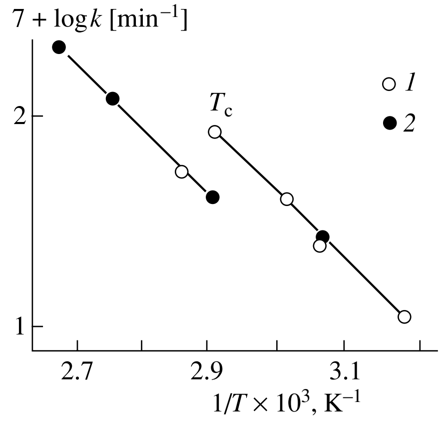


Fig. 3. Arrhenius plots for the rate constants of gas-phase ethylene hydrogenation on Rh^+ immobilized on a phosphinated SDVB copolymer (2% DVB). Before each experiment, the catalyst was evacuated at (*1*) 343 or (*2*) 363 K; $P_{\mathrm{C_2H_4}}$ = 27 kPa.

The following mechanism can be suggested for this phenomenon: On the one hand, at temperatures higher than T_g, the relaxation of the micro-Brownian motion can facilitate diffusion and increase the probability of substrate collisions with active centers. On the other hand, the motion of neighboring groups and ligands can increase steric hindrances to coordination and decrease the stability of the coordinated substrate. Moreover, a change in the character of polymer motion can also cause structural transformations in the active center due to a change in the coordination ability of functional groups. The role of olefin diffusion was supported experimentally: below T_g, both the rate and the amount of the adsorbed substrate increased with the size of olefins. Of course, the extreme temperature dependence

Table 4. Hydrogenation of acrylamide in various solvents

Solvent	Solubility[a] of H_2^1	Pd(II)[b]		Pd(0)[c]		Rh(I)[d]	
		swelling capacity, %	TON[e]	swelling capacity, %	TON[e]	swelling capacity, %	TON[e]
Methanol	0.068	12	974	16	3016	25	1928
Ethanol	0.065	13	772	13	2221	18	1217
2-Propanol	0.045	17	532	20	1801	16	1015
1-Butanol	–	10	478	15	1681	12	846
Acetone	0.053	7	558	18	2400	24	1420
DMF	0.037	19	532	15	1260	18	676
THF	–	3	551	14	1741	12	973
Water	0.015	14	109	13	540	16	372
Benzene	0.052	2	55	6	240	2	135
Dioxane	–	7	74	13	300	11	338

[Acrylamide] = 0.025 mol/l; 303 K.

[a] (ml $\mathrm{H_2}$)/(ml solvent).

[b] Support: a copolymer of 2-hydroxymethacrylate, 2,3-epoxypropyl methacrylate, and divinylbenzene.

[c] Support: functionalized poly(methacrylic acid).

[d] Support: a copolymer of 4-vinylpyridine and methylenebisacrylamide.

[e] TON is the catalyst turnover number, (mol S)/(g-atom M).

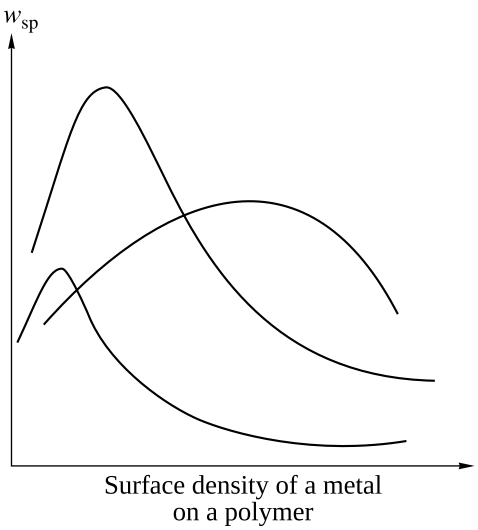


Fig. 4. Typical dependence of the specific rate of hydrogenation on the surface density of an immobilized metal for different types of immobilized systems.

affects not only the activity but also the selectivity of polymer-immobilized catalysts. This phenomenon is typical of not only hydrogenation catalysts but also other reactions (see below). Moreover, similar behavior was also observed [46] in the hydrogenation of ethylene on a mixed-type catalyst, palladium metal dispersed on Chromosorb with a polymer phase (a 1 : 1 mixture (by weight) of poly(ethylene oxide) and PS). At temperatures higher than the T_g of PS (368 K), the catalyst activity increased and became constant; this was explained by the softening of PS domains and the preferential adsorption of C_2H_4.

Thus, the temperature factor can serve as an additional tool for controlling hydrogenation processes under the action of heterogenized metal complexes. The target-oriented choice of macroligands with a certain temperature response (thermal stability) is a step toward the development of high-temperature metallopolymeric catalysts.

2.6. Effect of the Surface Density of Metal Complexes

Concentration ratios provide another opportunity to control the properties of metallopolymeric catalysts. Not only the total concentration of a polymer-bound metal complex but also the character of its distribution on a polymer matrix (its topography) are of importance. As a rule, a maximum specific rate of reaction based on the total metal content of the catalyst (w_{sp}) is observed in comparatively rare cases when all the metal particles are active and accessible to a substrate. An idealized version consists in the transfer of isolated coordinatively unsaturated metal complexes to the surface of a polymer support. This (or a similar) distribution can be constructed at the stage of the development of a catalyst or, more rarely, formed in the course of a catalytic reaction. For example, Rh-containing catalysts based on phosphinated SDVB copolymers with different concentrations of crosslinking agents (2–60%) prepared under conditions that excluded matrix swelling (and, correspondingly, metal penetration into the matrix) were found to be more active than swelling catalysts by a factor of 1.5–4 [3].

As a rule, w_{sp} is a complicated function of the concentration of a metal complex (metal density on a polymer): as this concentration is increased, w_{sp} increases, reaches a maximum value, and then decreases. Figure 4 demonstrates typical functions of this kind. Note that this character was also observed in other catalytic reactions (hydroformylation, oxidation, polymerization, etc.). A descending branch can be due to the growth of associates of low-valent or zero-valent transition metals, which decrease the efficiency of the catalyst, whereas no reasonable explanation was found for an ascending branch. Such an explanation is that the active centers of these catalysts are localized at the boundary of cluster formations and stabilized by their electron systems. As the surface density is increased, the number of these centers initially increases and then decreases. This was also supported by the fact that w_{sp} (for example, in 1-hexene hydrogenation with rhodium complexes) was higher in the case of low-percentage (0.5–1.2% metal) catalysts, all other factors being the same. In these catalysts, the main portion of the metal was localized on the surface of a polymer, whose crosslinked structure prevented the aggregation of particles both at the stages of catalyst preparation and activation and in the course of the reaction. These processes were accompanied by the deep interaction of the reduced metal with the polymer matrix. For example, in the reduction of Pd^{2+} on polyheteroarylenes (such as PBI), palladium cluster particles with average sizes of 2.0–3.5 nm were detected [27] (the particle size depended on the concentration of bound palladium); these particles included two Pd^0 species with Pd $3d_{5/2}$ binding energies of 338.0 and 336.0 eV. These small particles very strongly interacted with polymer matrices: a positive charge appeared at palladium atoms $Pd^{\delta+}$ because of electron transfer; this positive charge was favorable for coordination to substrate molecules. This process was facilitated by the occurrence of a developed π-electron system in the macroligand PBI and accompanied by the formation of an ion–radical state. Thus, the deep interaction of the metal with the support is accompanied by electron transfer and the reduction of the support to a leuco base. Evidently, all these processes are responsible for catalyst activity.

2.7. Size Effects in the Hydrogenation with Polymer-Immobilized Complexes

As mentioned above, the formation and aggregation of zero-valent metal complexes bound to a polymer matrix most frequently occur in the course of hydrogenation. This gave impetus to many studies on the dispersion of metal particles or the condensation of metal ions to form nanoparticles stabilized by polymer matrices (these studies were surveyed in [47, 48]). The main advances in this area can be summarized as described below. The colloid systems (1.8–5.6 nm) of Pd^0 bound to a polymer matrix exhibit high activity, stability, and selectivity in the reduction of dienes to monoenes. Palladium particles with an average size of 1.8 nm in a protective colloid of polyvinylpyrrolidone (PVP) are active catalysts for the hydrogenation of methyl linoleate, the partial hydrogenation of soybean oil under mild conditions, the selective hydrogenation of the triple bond in dehydolinalool (3,7-dimethyl-6-octen-1-yn-3-ol) to a double bond for preparing fragrance compounds [49], etc. It is of importance that systems of this type exhibit a narrow particle-size distribution and are stable: colloid particles did not precipitate from a gel upon a change in pH from 2 to 13. The catalyst can be easily separated from a reaction mixture by simple decantation, and it retains its activity in repeated uses. The nanoparticle size over the specified range has almost no effect on the rate of hydrogenation of linear olefins; however, the rate of cyclohexene hydrogenation decreased with the particle size of the catalyst [50]. Table 5, which summarizes data for the colloid particles of Rh with different sizes as an example, illustrates the above.

New approaches to the dispersion of noble metal nanoparticles in polymer matrices by chemical, photochemical, and radiation-chemical reduction; sputtering of metal atoms (including solvated atoms) onto various supports; etc., have been developed in recent years. Nevertheless, catalysts based on individual immobilized metal clusters exhibited a more definite and often predetermined structure. The derivatives of Os_3, Ir_4, Ru_4, Rh_4, Rh_6, etc., clusters are most frequently used for this purpose. Previously [51], it was found that the rate of ethylene hydrogenation with tetrairidium (Table 6) and tetraruthenium clusters bound to phosphinated polymers decreased with increasing number of electron-donor phosphine ligands in the cluster (that is, on going from the $–PPh_2Ir(CO)_{11}$ cluster to the $(–PPh)_2Ir(CO)_{10}$ cluster); this is a consequence of an increase in the substrate (ethylene)–catalyst bond strength.

The complete inhibition of hydrogenation by even traces of CO (however, the catalyst activity recovered upon the removal of CO) is indicative of the absence of coordination vacancies from immobilized carbonyl cluster centers. At the same time, according to physicochemical data, M–CO bond cleavage does not occur in the course of catalysis. Consequently, coordination vacancies result from L–M or, more likely, M–M (Ru–Ru, Rh–Rh, Os–Os, etc.) bond cleavage. Indeed, the results obtained in the hydrogenation of unsaturated amino acids in the presence of $Rh_4(CO)_{12}$ or $Rh_6(CO)_{16}$ clusters allowed Mutin *et al.* [52] to assume that the monomeric species $HRh(CO)_2L$, which results from the oxidative addition of H_2 and cluster segregation, is catalytically active. For the hydrogenation of styrene with nonimmobilized tetranuclear osmium complexes [53], a mechanism including cluster fragmentation with the formation of highly active species with a lower nuclearity (probably, monomeric) in low concentrations, which are true reaction catalysts was developed. Various versions of cluster immobilization were implemented in mixed-type supports for mixed-ligand and polymetallic clusters. In the latter case, in a model reaction of 1-butene hydrogenation and isomerization, the heterometallic $RhOs_3$ cluster on a phosphinated matrix (the starting cluster was $H_2RhOs_3(AcAc)(CO)_{10}$) underwent segregation to form polymer-bound triosmium clusters (responsible for stable activity in isomerization) and rhodium metal (particles 1.0 nm in diameter), which is active in the hydrogenation of 1-butene [54].

Table 5. Size of the colloid particles of Rh^0 and their activity in the hydrogenation of olefins

System	Average particle size of Rh, nm	Activity, (mol H_2) (g-atom Rh)$^{-1}$ s^{-1}	
		1-hexene	cyclo-hexene
$RhCl_3/PVAL/CH_3OH/H_2O$	4.0	15.2	3.1
$RhCl_3$/poly(methyl vinyl ether)/CH_3OH/H_2O	4.3	22.5	9.6
$RhCl_3/PVP/CH_3OH/H_2O$	3.4	15.8	5.5
$RhCl_3/PVP/C_2H_5OH$	2.2	15.5	10.3
$RhCl_3$/PVP/*iso*-C_3H_7OH	2.4	–	9.3
$RhCl_3/PVP/CH_3OH/NaOH$	0.9	16.9	19.2

Note: PVAL is poly(vinyl alcohol), and PVP is polyvinylpyrrolidone. Reaction conditions: 303 K; P_{H_2} = 0.1 MPa; the amount of an olefin was 25 mmol; and the amount of Rh was 0.01 mmol.

Table 6. Effect of the ratio P/Ir in a cluster on the rate of ethylene hydrogenation

Catalyst	P/Ir	$w \times 10^3$, (mol C_2H_4) (g-atom Ir)$^{-1}$ s^{-1}
$]-PPh_2Ir_4(CO)_{11}$	4.5	21.3
	14.3	25.3
$]-PPh_2)_2Ir_4(CO)_{10}$	3.4	3.76
	6.9	3.60

Note: Reaction conditions are $P_{C_2H_4}$ = 20 kPa, P_{H_2} = 80 kPa, and T = 313 K.

Methods for the preparation of these catalysts by the copolymerization of corresponding cluster-containing monomers with traditional monomers have been developed in recent years [55]. In these cases, a strict metal : functional group ratio is reached even at the stage of catalyst design; therefore, catalysts of this type, for example, based on the copolymers of vinylpyridine or allyldiphenyl complexes of Rh_6 or Os_3, would be expected to exhibit high activity and selectivity [56].

2.8. Selectivity Problems in Hydrogenation with Macrocomplexes

As with any catalysts, the practical importance of macrocomplexes depends on not only their high total catalytic activity but also a number of other advantages, which were considered above [57]. The reaction selectivity of hydrogenation plays an important role (frequently, the most important role); this is the possibility to direct the reaction toward the formation of one or several target products of the entire range of possible products (selectivity factor is the ratio of the concentration of a required product to the total concentration of the resulting products). The main side reactions that accompany hydrogenation and decrease its selectivity are the following: the isomerization of a substrate, an intermediate or an end product; alkylation; hydrolysis; esterification; amination with the participation of a solvent; the dimerization or cyclomerization of a substrate; reactions with the participation of vacant functional groups of a polymer; etc. The role of side reaction paths can be reduced by the optimization of reaction conditions based on the knowledge of the reaction mechanism.

Without regard to the specificity of catalysis by heterogenized complexes, the main requirements imposed on increasing selectivity can be reduced to satisfying the conditions for the selectivity of traditional heterogeneous catalysts (for example, see [58]). These are restrictions on reactant–catalyst bond strength, controlled metal coordination, controlled formation of ensembles and active groups, and template effects (“adjustment of active centers”). These characteristics depend on the electronic and geometric properties of the catalyst and the substrate. As a rule, selectivity is associated with the specific adsorption of a reactant or a product on the catalyst surface.

In essence, the selectivity of hydrogenation depends on the same factors as the activity: the nature of the matrix and its functional groups, the L : M ratio, and the conditions of the reaction. Let us consider only two of many examples. The π-acceptor properties of ligand L significantly affect the hydrogenation of 4-vinylcyclohexene: the selectivity factor for 4-vinylcyclohexene was 0.4, whereas it was as high as 0.97–0.98 when the resulting 4-ethylcyclohexene was removed from the reaction mixture [38]. Ruthenium complexes on phosphinated PS (10% degree of crosslinking) exhibited almost the same selectivity in the partial hydrogenation of cyclododecatriene (CDT) to cyclododecene (CDE) [59, 60]. Nevertheless, the attainment of an optimum selectivity at an average pore diameter of 20 nm in the support seems accidental, and the conclusion on a sieve effect in polymer-immobilized catalysis seems unconvincing: the substrate, the solvent, and high temperatures (413 K) and pressures (40 atm) make corrections to the pore-size characteristics of the initial catalyst.

Immobilized metal complexes selectively catalyze the following reactions under mild conditions:

- the reduction of aromatic and heteroaromatic hydrocarbons (for example, cyclohexanol can be obtained from phenol); selectivity particularly manifests itself in the reduction of aromatic compounds containing the functional groups $\equiv$N, $=$C$=$O, $-NO_2$, $-$C$\equiv$N, etc.;
- the reduction of sugars to polyols;
- the conversion of internal alkenes into *cis* and *trans* alkenes, whereas the hydrogenation of allylbenzene and 1,5-cyclohexadiene is often accompanied by isomerization with double-bond migration (the formation of more highly stable *cis*- and *trans*-propenylbenzenes and 1,4-cyclooctadiene);
- the selective hydrogenation of vinylacetylene to 1,3-butadiene (however, selectivity decreased with conversion) and the reduction of tetrahydrofurylacetylene alcohols with 98–99% selectivity or of other acetylene substrates (in particular, with internal triple bonds) with 76–84% selectivity;
- the partial hydrogenation of 1,5-cyclooctadiene (93–94% selectivity) and cyclododecatriene (~85% selectivity).

There are many examples of this kind; in the consideration of the phenomenon of geometric selectivity, attention was focused on many of them. In the general case, an increase in steric hindrances around the active center increases selectivity for 1-butene in the hydrogenation of 1,3-butadiene. However, the appearance of additional coordination vacancies at the active center is responsible for the isomerization of olefins etc. The topochemistry of immobilized clusters, in particular, the activity of trinuclear palladium clusters immobilized on phosphinated PS and mainly localized in a near-surface layer in the hydrogenation of 2-butyne was 35 times higher than that of clusters uniformly distributed over the diameter of granules. However, the selectivity of the latter catalyst for *cis*-2-butene was higher by a factor of ~3.

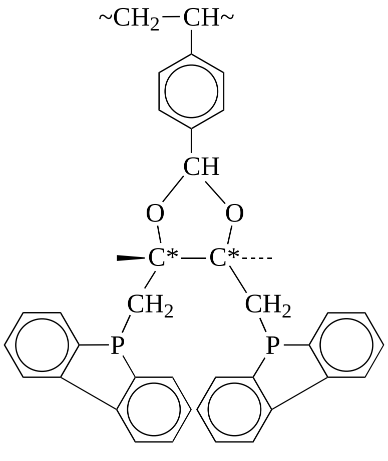
The use of the phenomenon of geometric selectivity in the hydrogenation of a substrate in the presence of one or more additional unsaturated compounds is of particular interest for improving selectivity. Thus, the macrocomplex of $PdCl_2$ with polyethyleneimine is highly selective in the hydrogenation of a mixture of dienes, for example, 1,3- and 1,4-cyclopentadienes: only the 1,3-diene reacted to 95% conversion, whereas the 1,4-diene entered into the reaction thereafter. The disproportionation of dienes in the course of hydrogenation is suppressed by the addition of acetylene substrates. This is only one of many examples.

2.9. Prospects for the Development of the Macrocomplex Catalysis of Hydrogenation Reactions

Let us focus our attention on the directions that will be developed in this area.

First, this is membrane catalysis. It is well known that membrane catalysts of Pd and its alloys have long been in use in heterogeneous catalysis for preparing products of incomplete hydrogenation, which are unstable in the presence of hydrogen [61]. So-called composite membrane catalysts—inert polymer films, which are highly permeable to hydrogen, with supported metal layers (including chemically bound metals)—have held a competition with the above catalysts in recent years. For example, thin films (0.4 μm in thickness) of cation-exchange resins, in which hydrogen cations exhibit an anomalously high mobility (the diffusion coefficient of protons in this membrane is higher than that in a palladium membrane by one order of magnitude), can be used in these catalysts [62]. The optimization of polymer membrane catalysts will make it possible to perform catalysis in thin films with a controlled rate of the passage of reactants through a membrane. One would expect (and this was supported by some examples) an increase in the selectivity of reactions due to the separation of a substrate zone and a reaction product zone. These problems remain to be solved.

It is reasonable to believe that special advances will be made in enantioselective hydrogenation under the action of immobilized metal complexes [63–66]. Interesting results were obtained with the use of metallopolymeric rhodium–phosphine catalysts containing optically active 4,5-bis(diphenylphosphino)methyl-1,3-dioxolane (**I**) or dibenzophosphine (**II**) groups and polymers based on (2*S*,4*S*)-*N*-acryloyl-4-diphenylphosphino-2-[(diphenylphosphino)methyl]pyrrolidone (**III**).



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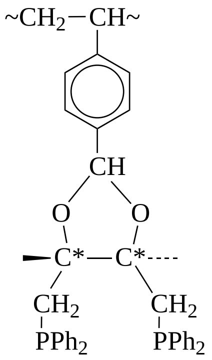

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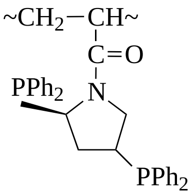
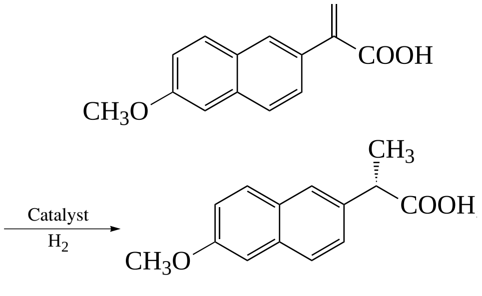


III

In the case of the best studied unsaturated amino acids (prochiral enamides) under optimum conditions (using 2-acetamidoacrylic acid as an example), the efficiency of asymmetric hydrogenation catalysis [67], which is characterized by an excess of a predominantly formed enantiomer (*R*- or *S*-configuration), was as high as 67%. This is also true of the asymmetric hydrogenation of prochiral ketones.

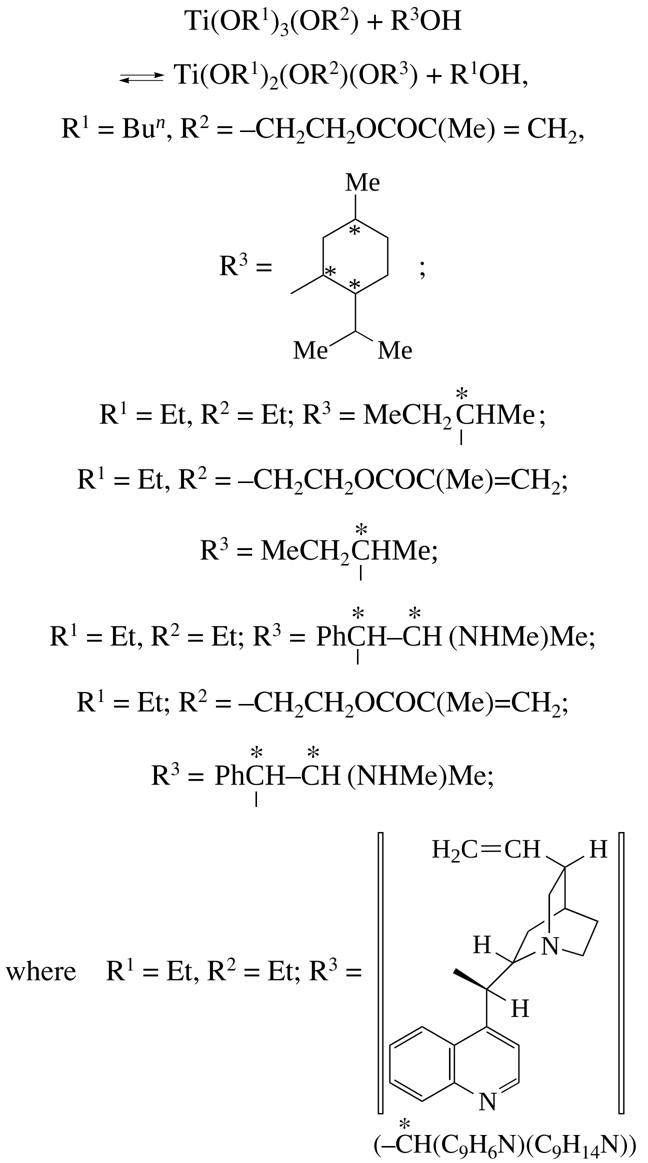
The mechanism of asymmetric induction in systems based on immobilized complexes, as well as in homogeneous catalysis, is unclear. To solve this problem, at least the following three aspects should be first comprehended: the coordination chemistry of ternary complexes (substrate–catalyst–reactant), the mechanism of catalytic reduction, and the source of enantioselectivity. A mechanism that relates the stability of mixed-ligand complexes with their asymmetric effects, that is, a correlation between asymmetric activity and constants that characterize the stability of an intermediate complex with consideration for chirodiastaltic interactions, seems most reasonable. In other words, this approach is a modification of the widespread lock and key phenomenon: enantioselectivity is determined by the initial predominant binding of a prochiral substrate to a chiral catalyst. In principle, heterogenized catalysts exhibit great capabilities for studying these intermediates. Other concepts are based on the consideration of the much higher reactivity of a smaller diastereomeric catalyst–substrate adduct and on the restriction of conformational diversity in the transition complex. The concept of the transfer of optical activity (chiral information) from a ligand to a substrate (initially through functional groups to a catalytic center and then to a substrate) is also worthy of consideration. The high efficiency of the $[Ru(cymene)Cl_2]_2$ complex bound to an optically active phosphine-containing (BINAP) polymer support in the asymmetric hydrogenation of 2-(6'-methoxy-2'-naphthyl)acrylic acid was reported [68, 69]. The product (naproxen), which is a potent anti-inflammatory drug, is formed by the reaction



(I)

It was found that even the simple microencapsulation of OsO_4 in a ternary acrylonitrile–butadiene–styrene (ABS) copolymer dissolved in THF with the addition of a chiral ligand (*N*-methylmorpholine) *N*-oxide or 1,4-di(9-*O*-dihydroquinidyl)phthalazine) resulted in a considerable increase in the rate and optical yield and in the reuse of the chiral additive in the asymmetric dihydroxylation of olefins (Table 7) [70].

Chiral rhodium or ruthenium complexes introduced in the course of a sol–gel synthesis are efficient and reusable catalysts for the enantioselective hydrogenation of itaconic acid: the yield of optically active methylsuccinic acid was as high as 78% [71]. Considerable progress in asymmetric catalysis under the action of polymer catalysts prepared by homopolymerization and copolymerization of optically active monomers would be expected [72, 73] with the use of (–)-menthol, *sec*-butyl alcohol, (–)-ephedrine hydrochloride, and (−)-cinchonidine hydrochloride as optically active alcohols (Scheme 2).



$$Ti(OR^1)_3(OR^2) + R^3OH$$

$$\rightleftharpoons Ti(OR^1)_2(OR^2)(OR^3) + R^1OH,$$

$$R^1 = Bu^n,\ R^2 = –CH_2CH_2OCOC(Me) = CH_2,$$

$$R^1 = Et,\ R^2 = Et;\ R^3 = MeCH_2\underset{|}{\overset{*}{C}}HMe;$$

$$R^1 = Et,\ R^2 = –CH_2CH_2OCOC(Me){=}CH_2;$$

$$R^3 = MeCH_2\underset{|}{\overset{*}{C}}HMe;$$

$$R^1 = Et,\ R^2 = Et;\ R^3 = Ph\underset{|}{\overset{*}{C}}H–\overset{*}{C}H\,(NHMe)Me;$$

$$R^1 = Et;\ R^2 = –CH_2CH_2OCOC(Me){=}CH_2;$$

$$R^3 = Ph\underset{|}{\overset{*}{C}}H–\overset{*}{C}H\,(NHMe)Me;$$

where $R^1 = Et,\ R^2 = Et;\ R^3 =$

$$(–\overset{*}{C}H(C_9H_6N)(C_9H_{14}N))$$

Scheme 2.

A number of other problems related to hydrogen activation and transfer in systems with the participation of immobilized metal complexes are beyond the scope of this review. These systems are promising for the activation of molecular hydrogen in exchange processes with water (especially for the preparation of heavy water) and alcohols, in the *ortho–para* conversion of hydrogen (*ortho*-H_2–*para*-H_2), and in the processes of hydrogen transfer from one substrate (most frequently, an alcohol) to another (such as a ketone)—the catalytic reduction of organic compounds with the use of chemically bound hydrogen [74]. Hydrosilylation—the reduction of alkenes, alkynes, and ketones with the use of hydrogen chemically bound in a silane molecule (like X_3SiH)—can also be assigned to the above group of reactions. Rhodium complexes bound to polyamide polymers are particularly efficient in hydrosilylation (for example, see [75, 76]). In these reactions, immobilized metal complexes fulfill the transfer of activated hydrogen by mechanisms admittedly similar to enzyme mechanisms.

3. POLYMERIZATION PROCESSES INDUCED BY MACROCOMPLEXES

Unlike hydrogenation, polymerization (including dimerization, oligomerization, and copolymerization) occurs via the activation of substrates of the same type—multiple bonds in a monomer or monomers. As a result of this, several (sometimes several tens of thousands) substrate molecules are combined to form a macromolecule, which is often a giant molecule. Strictly speaking, this is not the case. Here at least two species occur in the coordination sphere of a transition metal. These species are a growing end of the macromolecule and a coordinated monomer (or monomers in copolymerization). In any case, this is true of the anionic coordination polymerization of olefins (which is most developed in terms of the use of macrocomplexes), to a lesser degree, of the ionic polymerization of diene and acetylene monomers, and, more rarely, of the radical polymerization of vinyl monomers.

Another fundamental difference of the catalysis of polymerization processes from that of hydrogenation consists in a greater effect of macromolecular metal complexes on all the elementary steps of reactions. In hydrogenation, this effect (in optimum versions) increases activity and selectivity and provides an opportunity to regenerate the catalytic center, whereas it is incomparably more diverse in polymerization. This is the effect on the chain length, molecular-weight distribution, and stereoregularity of the resulting polymer, as well as on the composition of the copolymer in copolymerization. Moreover, the immobilization of metal complexes is an effective means of affecting all the steps of a polymerization reaction: chain initiation, chain propagation, chain termination, or chain restriction. Chain catalysis can be sometimes achieved by this means; that is, not only the active center initiates the uniform multiply repeated addition of monomer molecules to a growing chain, but also it can undergo regeneration in the course of a catalytic reaction and induce the growth of new chains.

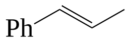
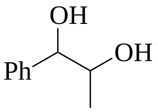
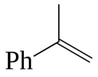
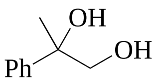
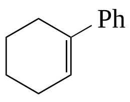
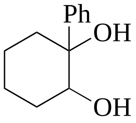
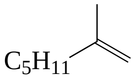
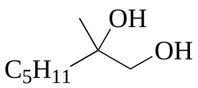
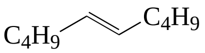
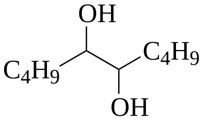
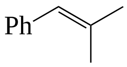
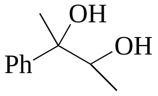
Finally, note that the application of macromolecular metal complexes to catalysis was started using polymerization catalysis as an example: as early as 1965–1966, Solvay obtained a number of patents for the production of polyolefins under the action of titanium macrocomplexes with ligands containing $>$C=O, –C≡N, and $>$N– groups. Data on these processes are yet mainly concentrated in the patent literature, whereas kinetic studies of polymerization processes under the action of macrocomplexes are scanty. Catalysts on inorganic supports are more widely used in industry; this fact only indicates that the applicability of macrocomplexes to the polymerization and copolymerization of various monomers, primarily olefins, has not been adequately studied.

3.1. Catalytic Polymerization of α-Olefins

On the one hand, the polymerization of olefins (to a greater extent, ethylene and propylene, as well as their copolymerization) is the most promising process [77]. On the other hand, this is the best studied group of polymerization processes catalyzed by macromolecular metal complexes. Previously, the mechanism of ethylene polymerization in the homogeneous and pseudohomogeneous MX_n–AlR_xCl_{3-x} Ziegler catalyst systems, where MX_n is a transition metal compound ($TiCl_4$, $TiCl_3$, $Ti(OR)_4$, $(C_5H_5)_2TiCl_2$, VCl_4, $VOCl_3$, $ZrCl_4$, and $(C_5H_5)_2ZrCl_2$), and AlR_xY_{3-x} is an organometallic compound (R is a hydrocarbon radical; $x = 1$, 1.5, or 2; and Y is a halogen or alkoxide), have been studied in detail for several decades. These studies resulted in the conclusion that the organometallic compounds of transition metals are the active centers of these systems (for simplicity, they will be designated as M–R). These compounds are formed *in situ* and stabilized by organoaluminum derivatives in a mixed bimetallic complex. Preactivated monomer molecules are repeatedly inserted into an active M–R bond; this is the step of polymer chain growth. The non-steady-state character of the action of these systems—a rapid decrease in their activity with time (particularly at elevated temperatures of 323–343 K)—is associated with the formation and degradation of a metal–carbon bond, which is active in polymerization. The reduction of an alkylated transition metal ($Ti^{4+} \longrightarrow Ti^{3+}$, $V^{5+} \longrightarrow V^{4+} \longrightarrow V^{3+}$, etc.) is one of the reasons for the deactivation of metal complex catalysts.

The process of reduction in these systems is complicated; it has been interpreted in the past decades. This process includes the bimolecular reactions of secondary alkylation, the disproportionation of alkyl groups in

Table 7. Asymmetric dihydroxylation with the use of the ABS–OsO_4 system

Olefin	Product	[ABS–MC=OsO_4], mol %	[Chiral ligand], mol %	Yield, %	Enantiomeric yield (*ee*), %
		5	10	75	91
		2.5	5	90	92
		1	2	97	86
		5	5	98	78
		5	5	64	86
		5	5	90	60
		2.5	5	85	63
		5	5	36	85

the coordination sphere of a transition metal, or the disproportionation of alkyl radicals at two coordination centers. The simplified formal schemes of these reactions can be represented as follows:

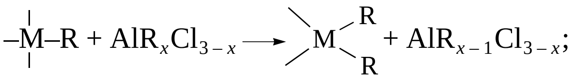
active center formation

$$-M-Cl + AlR_xCl_{3-x} \longrightarrow -M-R + AlR_{x-1}Cl_{4-x}; \quad (II)$$

chain growth

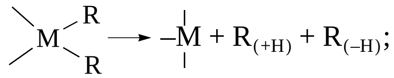
$$-M-R + n\text{-}CH_2{=}CH_2 \longrightarrow -M-(-CH_2-CH_2-)_n-R; \quad (III)$$

repeated alkylation



(IV)

unimolecular disproportionation



(V)

bimolecular disproportionation

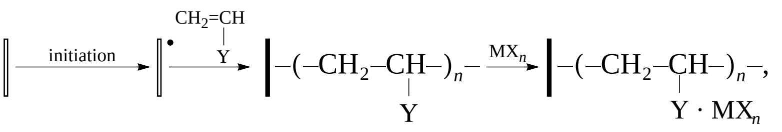
$$-M-R + -M-R \longrightarrow 2-M + R_{(+H)} + R_{(-H)}. \quad (VI)$$

The non-steady-state character of polymerization can be a consequence of both a decrease in the number of active centers (n_p) and a change in their nature in the course of polymerization (as a result of this, their reactivity is changed). Note that it seems impossible to produce a stable and high (higher than several percent) concentration of active centers because of the high reactivity of M–R, which is competitive with the reaction of chain growth.

Thus, the immobilization of active centers on supports is perhaps the only possibility to improve the efficiency of metal complex catalysts in olefin polymerization by a decrease in the contribution of side reactions, which decrease the activity of catalysts. In particular, it was expected that the spatial separation of MX_n (as is the case, for example, in enzyme immobilization, which prevents enzyme inactivation, in biology) will decrease the bimolecular deactivation of active centers and the cooperative stabilization of them by a macroligand will decrease the unimolecular deactivation. Macromolecular metal complexes for polymerization processes can be prepared based on powders, films, and fibrous materials (such as poly(vinyl acetate), polyamide, cotton, flax, and viscose fibers); MX_n or, more rarely, AlR_xCl_{3-x} is bound through the functional groups of these materials. Indeed, it was found previously (Fig. 5) [78] that heterogenized systems are stable in time.

Homogeneous or heterogeneous polymerization is a first-order reaction with respect to monomer and transition metal concentrations. The reactions of chain restriction by a monomer and an organoaluminum compound have similar kinetic parameters. The activation energies of polymerization and the temperature coefficients of changes in n_p are similar, and the rate constants of polymerization are equal to $(2–3) \times 10^8 \times \exp(-4600/RT)$. This demonstrates that active centers in the systems under comparison are of the same nature. In other words, homogeneous and heterogenized systems are different in only quantitative characteristics: n_p decreased by a factor of 45 in a standard (homogeneous) system after polymerization for 30 min, whereas it decreased by a factor of only 3–5 and then remained almost unchanged for 3 h during polymerization in a heterogenized system (Fig. 5b). As expected, a polymer matrix exerts a stabilizing effect on the active centers of polymerization and decreases the rate constant of their bimolecular activation at 313 K from 1.93×10^3 l mol^{-1} s^{-1} ($VCl_4–Al(C_2H_5)_2Cl$ system) to 0.75×10^3 l mol^{-1} s^{-1} (VCl_4 complex with poly(methyl methacrylate) (PMMA) $VCl_4 \cdot PMMA–Al(C_2H_5)_2Cl$). The polymer suppresses the unimolecular decay of active centers and decreases the constants of their unimolecular deactivation from 2.2×10^{-3} to 0.8×10^{-3} s^{-1}, that is, by a factor of ~3.

However, the reaction center should be carried to the surface of a polymer support in order to develop highly efficient catalysts by the chemical immobilization of metal complexes, which increases the activity of the systems by a factor of 50–250. In other words, because polymerization is a heterogeneous process, the active centers of a catalyst should be localized only at the surface or in a thin near-surface metallopolymeric layer, which is accessible to a monomer. Novel types of macroligands were developed for this purpose. In these macroligands, functional groups are formed only at the surface of inert polymer particles (for example, polyethylene (PE), polypropylene (PP), and polystyrene (PS)) by the graft polymerization of monomers bearing corresponding functional groups. The general procedure for the designing of these macroligands is considered below [79]. A powdered polymer support is subjected to mechanical, chemical, or radiation-chemical action in the presence of grafted monomers (allyl alcohol, acrylic acid, vinylpyridine, vinyldiphenylphosphine, etc.) (Scheme 3).



$$\| \xrightarrow{\text{initiation}} \|^{\bullet} \xrightarrow{CH_2=CH(Y)} \Big| -(-CH_2-\underset{Y}{CH}-)_n- \xrightarrow{MX_n} \Big| -(-CH_2-\underset{Y \cdot MX_n}{CH}-)_n-,$$

where ‖ – is a polymer surface, Y is a functional group.

Scheme 3.

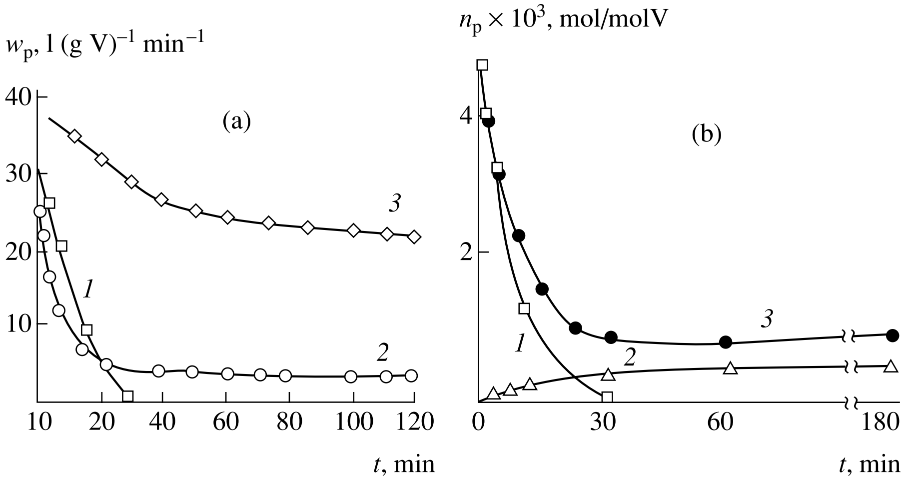


Fig. 5. Dependence of (a) the rate of reaction and (b) the number of active centers on the time of ethylene polymerization on the following catalytic systems: (a) (*1*) VCl_4–(iso-Bu)$_2$AlCl, (*2*) VCl_4–PVA(iso-Bu)$_2$AlCl, (*3*) VCl_4–hydrolyzed copolymer of styrene with VA(iso-Bu)$_2$AlCl, (b) (*1*) VCl_4–(iso-Bu)$_2$AlCl, (*2*) VCl_4–MMA(iso-Bu)$_2$AlCl, and (*3*) VCl_4–PMMA(iso-Bu)$_2$AlCl. Polymerization conditions: benzene; 313 K; [Al]/[V] = 50 (mol/mol); $[C_2H_4]$ = 0.04 mol/l. Notation: PVA is poly(vinyl acetate); VA is vinyl acetate; MMA is methyl methacrylate; and PMMA is poly(methyl methacrylate).

It was found experimentally that the grafting of small amounts (1–2%) of monomers containing functional groups (so-called functionalized monomers) is an optimum procedure. It provides the production of a loose surface cover (10–30 nm in thickness), which is accessible to reactants across the whole thickness. A transition metal compound penetrates deep into the grafted monomer up to 10 monolayers and binds to functional groups [80, 81]. Table 8 summarizes data on the catalytic properties and kinetic parameters of some of these macrocomplexes in ethylene polymerization [82]. It is likely that the binding of MX_n to the polymer surface results in the most favorable structures of active centers for catalysis; in these active centers, the energy barrier of the reaction of monomer insertion is low. Because the reaction rate constants of chain growth are practically equal (for homogeneous and immobilized complexes), by this is meant that the preexponential factor of the reaction rate constant dramatically decreases. The compensation effect observed suggests that many neighboring fragments of macroligands are affected in the reactions of active centers; this was found experimentally in a study of their temperature behavior.

The rate of polymerization increases with temperature in accordance with the Arrhenius law. However, this behavior was observed only in a certain temperature range—up to the glass-transition (or softening) temperature of the polymer support (as in the case of hydrogenation, see Section 2.5). Indeed, with the use of the $TiCl_4$P4VP–$AlEt_2Cl$ system in the gas-phase polymerization of ethylene as an example, it was found [83] that the E_a is 16 kJ/mol over the Arrhenius region (303–360 K); this value is typical of anionic coordination polymerization (Fig. 6a). The temperature coefficient of the reaction becomes negative (–130 kJ/mol) in the range of temperatures (360–423 K) at which chain segments are sufficiently mobile and relaxation due to the reorientation of the entire ligand macromolecule plays a crucial role. If this is due to only the irreversible deactivation of active centers (w_d is its specific rate) because of an increase in their mobility,

$$w_d \Delta t = 1 - w_p/w_0,$$

where w_p is the rate of polymerization, w_0 is the rate of polymerization in the absence of catalyst deactivation, and t is time.

It can be seen in Fig. 6b that curve *1* corresponds to the commonly observed dependence of the relaxation time of segmental motion: the apparent activation energy dramatically increases as the temperature of defreezing of the mobility is approached. In these cases, the temperature dependence of the rate of relaxation can be linearized on the $\log w_d - (1/\Delta T)$ ($\Delta T = T - 360$) coordinates (Fig. 6b, curve *2*). Indeed, 360 K is the temperature at which the segmental mobility of the P4VP macromolecule is unfrozen and the rate of polymerization noticeably decreases.

Thus, the restriction of the translational mobility of active centers is the most important factor for increasing the stability and activity of macrocomplexes in olefin polymerization.

3.2. Supported Titanium–Magnesium Catalysts for Olefin Polymerization

So-called titanium–magnesium and vanadium–magnesium catalysts for olefin polymerization are widely used. They are prepared by the reduction of titanium-containing compounds ($TiCl_4$ and, more rarely,

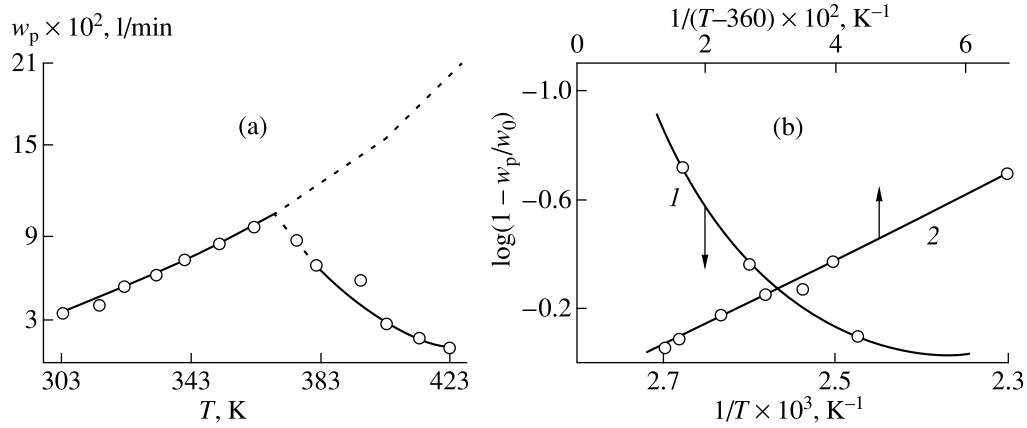
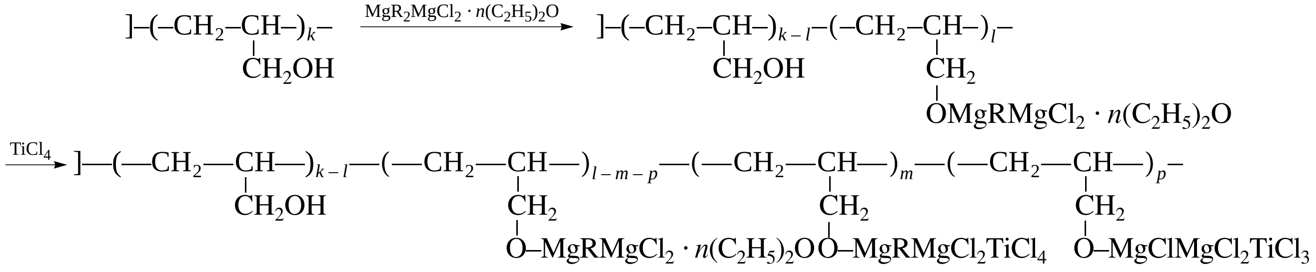


Fig. 6. (a) The temperature dependence of the rate of ethylene polymerization in a gas phase on a $TiCl_4 \cdot P4VP{-}AlEt_2Cl$ catalyst and (b) the dependence of $\log(1 - w_p/w_0)$ on (*1*) $1/T$ or (*2*) $1/(T - 360)$. Dashed and solid lines indicate calculated and experimental data, respectively.

$Ti(OR)_4$ or VCl_4) in the presence of Grignard reagents, MgO, $MgCl_2$, Mg(OH)Cl, $Mg(OR)_2$, etc. Procedures are known in which this reduction was performed in the presence of polymers or organomagnesium compounds were bound to a polymer beforehand. For example, Bochkin *et al.* [84] prepared titanium–magnesium catalysts on the PE–grafted poly(allyl alcohol) system in accordance with Scheme 4.



$$\mathrm{]\!-\!(-CH_2-\underset{\substack{|\\ CH_2OH}}{CH}-)_{\mathit{k}}-} \xrightarrow{\mathrm{MgR_2MgCl_2\cdot \mathit{n}(C_2H_5)_2O}} \mathrm{]\!-\!(-CH_2-\underset{\substack{|\\ CH_2OH}}{CH}-)_{\mathit{k-l}}-(-CH_2-\underset{\substack{|\\ CH_2\\ |\\ OMgRMgCl_2\cdot \mathit{n}(C_2H_5)_2O}}{CH}-)_{\mathit{l}}-}$$

$$\xrightarrow{\mathrm{TiCl_4}} \mathrm{]\!-\!(-CH_2-\underset{\substack{|\\ CH_2OH}}{CH}-)_{\mathit{k-l}}-(-CH_2-\underset{\substack{|\\ CH_2\\ |\\ O-MgRMgCl_2\cdot \mathit{n}(C_2H_5)_2O}}{CH}-)_{\mathit{l-m-p}}-(-CH_2-\underset{\substack{|\\ CH_2\\ |\\ O-MgRMgCl_2TiCl_4}}{CH}-)_{\mathit{m}}-(-CH_2-\underset{\substack{|\\ CH_2\\ |\\ O-MgClMgCl_2TiCl_3}}{CH}-)_{\mathit{p}}-}$$

Scheme 4.

Unreacted functional groups, residual Mg centers, and Ti^{4+} and Ti^{3+} bound to a polymer were detected in the product; the ratio between the above species depends on many factors. The fraction of isolated Ti^{3+} ions (stabilized by $TiCl_3$ or $TiCl_2$ crystallites), which are most likely responsible for polymerization, is as high as 50% of the heterogenized titanium content. These samples exhibited a maximum activity in ethylene polymerization (550 kg PE $(g\ Ti)^{-1}$ MPa^{-1} h^{-1}); the value of n_p in them was 10–20% of the total amount of titanium. A similar procedure (treatment with an organomagnesium compound) was also used for preparing titanium–magnesium catalysts (active in ethylene polymerization) based on an SDVB copolymer and its chloromethylated derivatives [85]. Of other examples of such preparation procedures, note supported $NdCl_2$ [86] and other rare earth chlorides [87], zirconium-containing polymers [88], and other components of catalysts for ethylene polymerization [89].

3.3. Gel-Immobilized Systems

Diametrically opposite principles of designing form the basis of gel-immobilized catalytic systems [90]. As distinct from the above methods for carrying the reaction center to the polymer surface, in these cases, the entire volume of the polymer with immobilized MX_n should be used productively (relevant studies were surveyed by Smetanyuk *et al.* [91]). This is accomplished by the use of polymers as “mosaic” gels under working conditions. These polymers are swelling rather than soluble in the reaction medium; however, they are permeable to reactants. Rubber resins (ethylene–propylene or ternary polymers of ethylene, propylene, and an unconjugated diene) form the basis of these polymers. Monomers with functional groups are grafted to them using radical polymerization. The crosslinking of rubber resins results in the formation of three-dimensional networks, which prevent the dispersion of catalyst particles in the reaction medium. The designing and operation of gellike catalysts and biomembranes have many common features. However, polymerization on these

Table 8. Characteristics of MX_n immobilized on polymers with a grafted functional cover and the kinetic parameters of ethylene polymerization (343 K)

Polymer support	Concentration of grafted groups $\times 10^4$, mol/g	MX_n	Metal content $\times 10^4$, g-atom/g	n_p, mmol/(mol Cat)	$k_p \times 10^{-4}$, $l\ mol^{-1}\ s^{-1}$	E_a^{eff}, kJ/mol
PE-*graft*-poly(acrylonitrile) (PE-*graft*-PAN)	11.9	VCL_4	0.70	4.0	2.8 ± 0.6	38 ± 4
PE-*graft*-poly(methyl methacrylate) (PE-*graft*-PMMA)	12.0	VCL_4	1.14	4.5	3.4 ± 0.7	38 ± 4
PE-*graft*-poly(methyl vinyl ketone) (PE-*graft*-PMVK)	6.0	VCL_4	1.50	4.5	4.0 ± 0.8	31 ± 4
PE-*graft*-poly(dibutyl vinylphosphonate) (PE-*graft*-PDBVP)	1.1	VCL_4	0.50	3.8	2.9 ± 0.6	32 ± 4
PE-*graft*-polyvinylpyrrolidone (PE-*graft*-PVP)	8.6	VCL_4	2.6	4.2	3.1 ± 0.6	29 ± 4
PE-*graft*-poly(diallylamine) (PE-*graft*-PDAA)	2.6	VCL_4	2.50	5.0	4.2 ± 0.8	27 ± 4
PE-*graft*-poly(acrylic acid) (PE-*graft*-PAA)	11.0	VCL_4	1.90	2.1	5.1 ± 1.0	38 ± 4
PE-*graft*-poly(allyl alcohol) (PE-*graft*-PAAL)	6.2	VCL_4	3.00	12.5	3.4 ± 0.7	34 ± 4
	6.2	Cp_2TiCl_2	0.10	–	–	–

systems is accompanied by pore-diffusion resistance even at superequilibrium swelling. It is most likely that these systems will be used in olefin dimerization and trimerization processes.

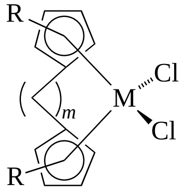
3.4. Stereospecific Polymerization of Propylene

The main line of attack on this complicated problem in classical versions consists in the production of $TiCl_3$ or VCl_3 submicrocrystals on a polymer support. For this purpose, various approaches can be used: the *in situ* precipitation of MCl_3 on a polymer; the reduction of polymer-chemisorbed MCl_4; and various procedures of the combined grinding and dispersion of MCl_3 crystals and polymers [92], including functionalized PS, SDVB copolymers, and anion-exchange (in NH_4^+ form) or cation-exchange (containing carboxyl or sulfonic acid groups) resins. It is also well known that MCl_3 salts are readily deposited on polymer surfaces, in particular, containing excess electrons, and electron donors are favorable for the grinding of MCl_3. The principal results of these studies are mainly concentrated in the patent literature. From this source, it is known that the stereoregularity of the resulting polypropylene (fraction insoluble in boiling heptane) is as high as 95–98%. It is of importance that an increase in the stereoregularity is accompanied by an increase in the catalytic activity. However, interest in these systems decreased somewhat in recent years because of the discovery of so-called zirconocene catalysts for olefin polymerization.

3.5. Heterogenization of Homogeneous Metallocene Catalysts for the Polymerization of α-Olefins

Metallocene complexes of Ti, Zr, and Hf made a revolution in the world of polyolefins. They opened a new generation of Ziegler–Natta catalysts. It will suffice to mention a fantastic record in the productivity of ethylene polymerization in the presence of the bridging bis(fluorenyl) zirconium complexes $[Zr(C_{13}H_4C_2H_4C_{13}H_8)Cl_2]$; in this case, the yield of PE was as high as 300 t PE (g Zr)$^{-1}$ h^{-1} [93]. Moreover, they provide an opportunity to control the formation of stereospecific polymers (exemplified by propylene) and short-chain or long-chain branching in the chain and to generate block copolymers (oscillating catalysts). This makes it possible to obtain polyolefins with specific properties, for example, new materials like linear low-density polyethylene (LLDPE) (see Section 3.7). They were first reported in 1980 [94].

A metallocene catalyst is the following system:



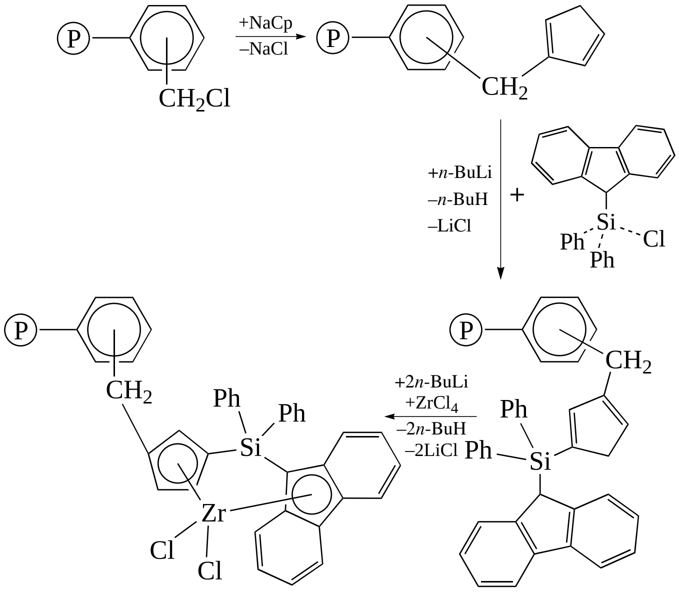
$+ [(CH_3AlO)]_n(MAO)$,

where M = Ti, Zr, or Hf; *m* is a bridge including 1–3 carbon atoms (and sometimes a silicon atom) in the main chain; R is a hydrocarbon substituent in the condensed system of indenyl and fluorenyl rings and their derivatives; and MAO is methylaluminoxane.

The aim of the immobilization of metallocene catalysts on supports is to improve the processing characteristics of these systems (which are inconvenient and unstable for industrial use) rather than to improve the activity of these highly efficient and stereospecific catalysts. The following characteristics should be improved with the retention of the above properties of the catalysts: the range of working temperatures should be extended toward higher temperatures; the commonly used aromatic solvents should be replaced by aliphatic solvents; the process technology of gas-phase or emulsion polymerization should be simplified; the polymer morphology and particle size should be regulated; the growth of polymer films on the reactor walls should be prevented; etc. Moreover, varying the nature and amount of functional groups in a polymer support frequently opens up additional opportunities for the control of the molecular structure of the polymer formed.

As with catalysts for other types of polymerization processes, these systems were first heterogenized on inorganic supports, including $MgCl_2$ and organosilanes. The heterogenization was performed by either adsorption or chemical binding of catalyst components; in particular, the fragments of a metallocene environment for zirconium were preformed on silica gel, or the surface of silica gel was treated with MAO (for example, see [95–101]). Catalysts immobilized on supports exhibited the first-order deactivation of their active centers in the gas-phase metallocene polymerization of ethylene [102–104]. The nature of active centers in supported systems for olefin polymerization was analyzed in a review [105].

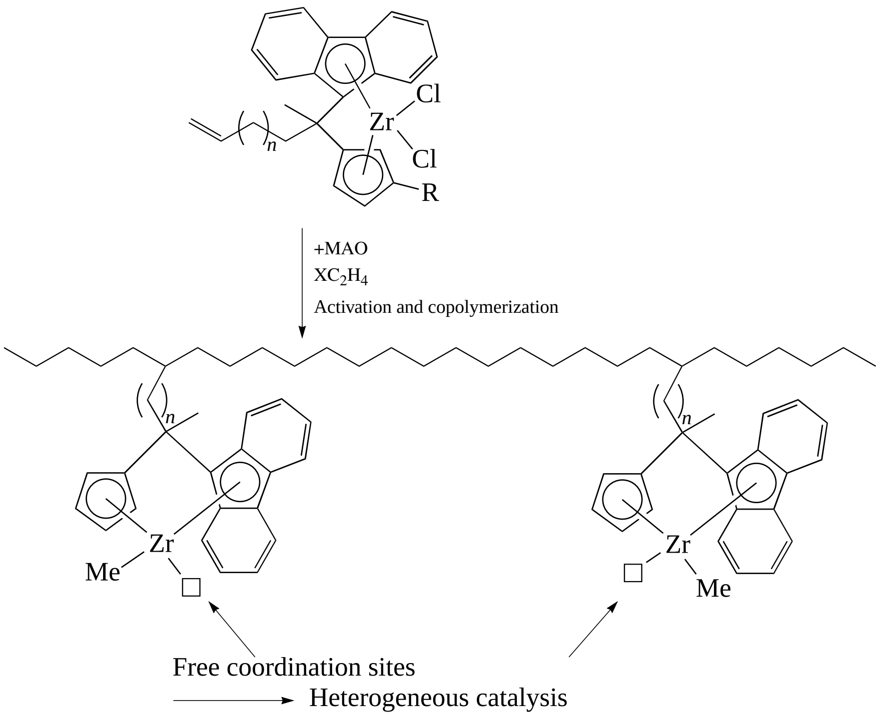
Among few polymers, materials based on PS crosslinked with DVB are most frequently used for immobilization [106, 107]. An elegant synthetic approach, which avoids the presence of polar components on a polymer (these components could decrease the catalyst activity), was exemplified [108–110] with assembling zirconocene from a polymer precursor (Scheme 5).



Scheme 5.

However, it should be remembered that η^5-cyclopentadienyl (Cp) rings were first introduced into PS for preparing polymer-immobilized dicyclopentadienyltitanium at a much earlier date [111].

The effects of various factors on ethylene polymerization under the action of Cp_2ZrCl_2 bound to crosslinked poly(styrene-*co*-4-vinylpyridine) were studied in considerable detail [112]. The polymer was preactivated with MAO or AlR_3 and then bound to the Zr compound. The main conclusion is that the concentration of 4-vinylpyridine units in the polymer and the degree of crosslinking should be increased in order to improve the activity. In this case, the catalyst treated with Al(iso-Bu)$_3$ exhibited a higher activity than MAO. Along with the retention of a high activity, these systems provide an opportunity to obtain polymers with narrow molecular-weight distributions with α-olefins (hexene) inserted into the chains. Moreover, they are more stable than homogeneous catalysts based on Cp_2ZrCl_2. Similar results were obtained with the use of a styrene and acrylamide copolymer crosslinked with DVB [113]. MAO, which activates the catalyst and coordinates to the support through the nitrogen atoms of the amido group and the oxygen atom. On the addition of α-octene to the polymerizing system no decrease in the activity was detected. The comonomer was uniformly distributed in the product; comonomer blocks were not detected in the chains.



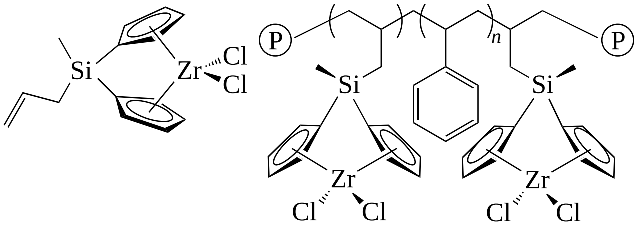
Scheme 6.

A styrene and acrylamide copolymer [114] and a saponified styrene and vinyl acetate copolymer containing different amounts (from 3 to 19 mol %) of hydroxyl groups [115] were used as polymer supports for the production of heterogenized half-titanocene catalysts for the syndiotactic polymerization of styrene. Polymer-bound $CpTiCl_3$ activated with MAO exhibited a higher activity and formed PS with a greater syndiotactic fraction. Nevertheless, it is believed that active centers of the same nature are formed in either homogeneous or heterogenized systems. Polymeric and inorganic supports have different effects on active centers; this manifests itself in different structures of the resulting polymers. One of the reasons for this difference may consist in the flexibility of a macroligand, as distinct from a mineral support. Because of this, the active center on a polymer combines several MAO molecules; this facilitates stereocontrol in the course of polymerization.

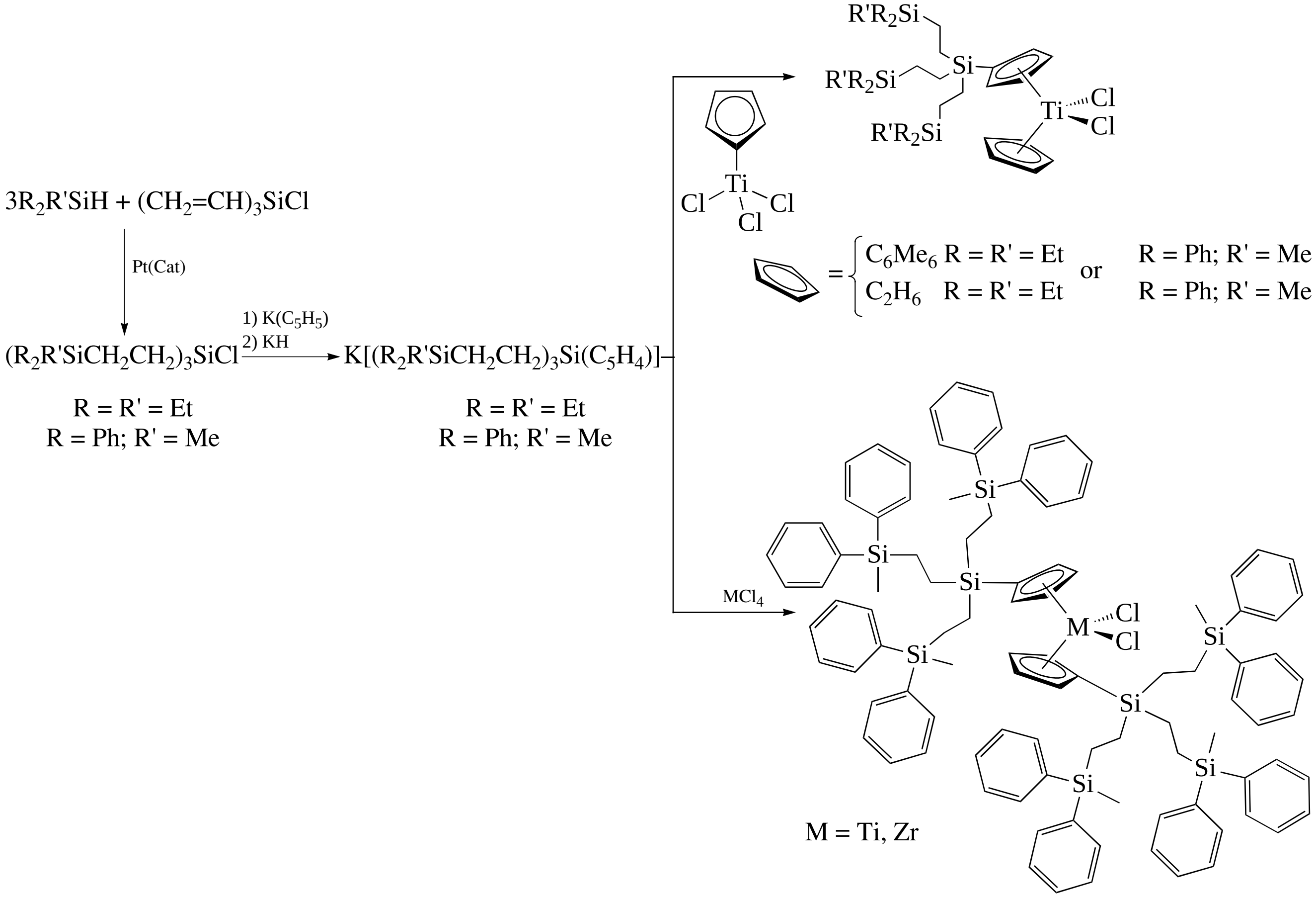
An original approach to the immobilization of Cp_2ZrCl_2 consists in its self-immobilization [108, 116–118]. It is considered below. A fluorenylidene dichloride complex of zirconium containing an ω-alkenyl substituent at the C_2 bridge or at the 3-position of the indenylidene ligand is synthesized using special methods. After the activation of these zirconocenes with MAO and the addition of ethylene, not only the polymerization of ethylene takes place but also the complex is inserted as a comonomer into the growing chain due to the ω-alkenyl substituent in the course of α-olefin polymerization. In accordance with this mechanism, the homogeneous metallocene catalyst becomes self-immobilized, and it continues olefin polymerization as a heterogeneous catalyst using the growing chain as a polymer support (Scheme 6).

In essence, this is a version of the copolymerization of a metal-containing monomer with ethylene, which was considered in detail in the monograph [119]. Note that a similar phenomenon was observed previously with the use of ethylene polymerization under the action of the following catalytic systems as an example: $MX_n \cdot VPy–AlR_2Cl$ (where VPy is 4- or 2-vinylpyridine or 2-vinyl-5-methylpyridine) [120] and $MX_n \cdot 2MMA–AlR_2Cl$ (where MMA is methyl methacrylate) [121].

An approach based on the copolymerization of *ansa*-zirconocene containing a silicon bridge with an allyl group and styrene as a means of preparing polymer-immobilized catalysts seems interesting [122]:



Finally, a unique approach to the preparation of polymer-immobilized titanocene and zirconocene catalysts was developed in recent years. This approach consists in the use of dendronized (of first or second gener-



Scheme 7.

ation) cyclopentadienyl rings as initial components (Scheme 7) [123]. Both the catalytic properties of these systems (in combination with MAO) and the molecular-weight characteristics of the resulting PE depend on the degree of generation of the dendrimer. It is of interest that a bimodal molecular-weight distribution was observed in polymers prepared with the use of immobilized second-generation titanocene.

Kinetic studies of polymerization under the action of polymer-immobilized zirconocenes are fewer in number than traditional catalytic studies. It is generally taken that homogeneous metallocene catalysts contain uniform active centers (the total zirconium is active). However, if they are immobilized on a polymer support, the molecular-weight distribution of the resulting polymers is wider than that obtained with a homogeneous catalyst [124]. As one of a few of examples, note the kinetic analysis of the gas-phase polymerization of ethylene under the action of $(CH_3)_2[Ind]_2ZrCl_2$ on a hydroxylated SDVB copolymer [125], which was pretreated with MAO (zirconium content of 0.17 wt %). The effects of temperature (333–353 K), ethylene partial pressure (2–6 atm), and MAO (MAO-to-Zr molar ratios of 2600–10700) on the process were studied. The catalyst activity in the gas-phase process varied from 5 to 32 kg PE $(g\ Zr)^{-1}\ atm^{-1}\ h^{-1}$. Based on an analysis of various conceivable mechanisms of active center deactivation in this system (unimolecular and bimolecular deactivation of uniform or different active centers), a hypothesis was proposed and supported that two types of active centers (more and less thermally stable) occurred. However, these centers underwent deactivation by the same mechanism in a first-order reaction. The temperature dependence of the reaction rate constants of chain growth on the two types of active centers was almost the same.

In recent years, new so-called postmetallocene catalysts for olefin polymerization were developed: Ni^{2+}, Ti^{4+}, and Pd^{2+} complexes containing bulky α-diimine ligands (for example, see [126, 127]) and Fe^{2+} and Co^{2+} complexes with 2,6-di(imino)pyridyl ligands [128, 129]. However, there is no data on the immobilization of macromolecular ligands, except for self-immobilized catalysts for ethylene polymerization based on the complexes of salicylaldiiminatophenylnickel(2+) with allyl substituents [130].

3.6. Polymerization of Vinyl Monomers Initiated by Macrocomplexes

Metal complexes most frequently induce radical polymerization of vinyl monomers and more rarely induce ionic polymerization. For example, metal chelates with activators (most often, halogenated hydrocarbons) initiate the homopolymerization and copolymerization of vinyl acetate. Similar variants with metallopolymeric systems are also known [3]. The mechanisms of these processes are unclear; it is well known that these cannot be true radical or common cationic mechanisms because polymerization takes place in water. At the same time, a Cu^{2+} macrochelate bound to a polymeric ester of acetoacetic acid is active in the polymerization of acrylonitrile (a test monomer for radical polymerization), and mixed-ligand manganese complexes with carboxyl-containing polymers are active in the emulsion polymerization of vinyl monomers. The macrocomplexes of $Cu(NO_3)_2$ and $Fe(NO_3)_3$ immobilized on diaminocellulose in combination with CCl_4 initiate the radical polymerization of MMA etc.

Many examples of redox systems based on the polymer-bound complexes of Cu^{2+}, Fe^{3+}, V^{5+}, etc., as the main constituents, which initiate the polymerization of vinyl monomers, are known. Among them are the vanadyl polycarboxylate–thiourea–HNO_3 system, which initiates acrylonitrile polymerization, and a complex of Cu^{2+} with poly(vinyl alcohol), which is an initiator of the (co)polymerization of allyl and acrylic monomers (the process is noticeably accelerated on the addition of carbon tetrahalides). The redox polymerization of acrylamide was performed [131] with V^{5+} complexes bound in the chelate unit of a glycol methacrylate–ethylene glycol dimethacrylate copolymer in combination with cyclohexanone at 303 K. The distinctive features of these polymer-bound initiators consist in an increase in the molecular weights of the resulting polymers (for example, in the last-named case, up to $(6.3–13.3) \times 10^5$, as compared with 3.5×10^5 for a homogeneous system), the possibility of repeated use, and the prevention of metal ions from entering the polymer formed.

Considerable progress was made toward ionic polymerization under the action of macrocomplexes, in particular, macromolecular Lewis acids, so-called solid superacids. Various forms of cationic catalysts (proton and Lewis acids, their combinations, and complexes with various supports) were summarized in a review [132] (Table 9). A polymer, which is a base or bears functional groups of different basicity, enters into acid–base reactions with MX_n to stabilize the resulting ionic species. All types of acids (individual Lewis and Brønsted acids and complex acids including the Gustavson complexes ($HCl \cdot 2AlCl_3 \cdot 3C_6H_5CH_3$) on PS) were immobilized on polymer matrices. These catalysts are effective in the polymerization of olefins (isobutylene) and in the carbonium-ion polymerization of styrene, α-methylstyrene, and β-pinene. As a rule, depending on the strength of the Lewis acid, the cationic polymerization of styrene decreases in the order $SbF_5 > AlCl_3 > ZnCl_2$.

N-Vinylcarbazole undergoes polymerization by a cationic mechanism under the action of dimethylglyoximate chelates of various metals immobilized on poly(vinyl chloride), whereas Lewis acids in a polymer gel polymerize and oligomerize vinyl ethers etc. The cationic complexes of Pd^{2+} bound to modified PS catalyze the alternant copolymerization of fluorinated olefins $(C_nF_{2n+1})(CH_2)_mCH{=}CH_2$ with carbon monoxide [133, 134]. In this case, polyspiroketals rather than polyketones are formed.

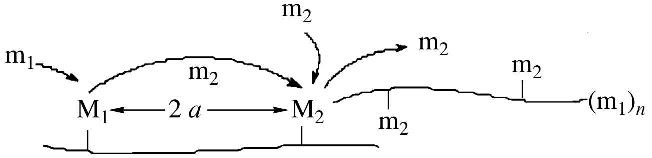
Table 9. Main types of immobilized cationic systems [132]

Acid types	Support types
Brønsted acids	
(H_2O, HCl, HF, H_2SO_4, H_3PO_4, $HClO_4$, FSO_3H, and the heteropoly acids $H_4SiW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$)	Oxides, silica gel, aluminosilicates, zeolites, salts, styrene–divinylbenzene copolymers, poly(phenyl ketones), perfluoroolefins and their copolymers, and network copolymers of alkoxy- and akoxyorganosilanes
Lewis acids	
(R_nAlCl_{3-n}, $AlCl_3$, $AlBr_3$, BF_3, BCl_3, BBr_3, $ZnCl_2$, $CuCl_2$, $FeCl_3$, $TiCl_4$, TiF_4, $SnCl_4$, $SbCl_5$, NbF_5)	Oxides, aluminosilicates, silica gel, mixed oxides, metals, polystyrene, styrene–divinylbenzene copolymers, styrene–4-vinylpyridine copolymers, copolymers of acrylic monomers, coal, and graphite
Complex acids	
(HX (H_2O, HCl, HF)–MeX_n(R_nAlCl_{3-n}, $AlCl_3$, $FeCl_3$, BF_3)	Oxides, aluminosilicates, polystyrene, styrene–divinylbenzene copolymers, copolymers of acrylic monomers, and sulfonated styrene–divinylbenzene copolymers
Carbene ions, MX_n–R_nAlCl_{3-n}, $AlCl_3$, $TiCl_4$, VCl_4, $SnCl_4$, $AgClO_4$	Poly(vinyl chloride), chlorinated (brominated) butyl rubber resins, and polychloroprene

3.7. Other Promising Directions in Polymerization Catalysis under the Action of Macromolecular Metal Complexes

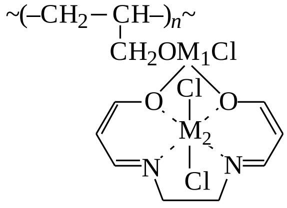
Let us summarize briefly the status of studies in the polymerization reactions of other classes of monomers under the action of immobilized metal complexes. First, considerable advances were made in the polymerization of diene monomers (primarily, butadiene and isoprene) catalyzed by macrocomplexes based on rare metal halides [135]. Studies on the cooligomerization of 1,3-butadiene and CO_2 under the action of palladium macrocomplexes (macroligand: phosphorylated PS) [136] and on the polymerization of acetylene monomers (particularly, on immobilized Mo^{5+} [137], W^{6+}, and Pd^{2+} [78] complexes) are in progress, although they are not very intensive. A comparison between the kinetics of polymerization and the properties of polymers formed under the action of homogeneous and heterogenized metal complexes suggests that the nature of active components was the same in almost all cases. In other words, as noted above, the effect of the binding of MX_n in a macrocomplex on catalysis is quantitative rather than qualitative, although it affects all the steps of a polymerization process. The active role of a macroligand as a support is reduced to the regulation of the reactions of active center formation and deactivation and, sometimes, to the regeneration of active centers. Under optimum conditions, the mechanisms of rate-limiting steps can be revealed, and intermediates in the formation of active centers can be isolated and characterized (see Section 6).

The development and characterization of bifunctional catalysts, in the presence of which various concerted reactions occur simultaneously, are of importance for polymerization processes. The product of one of these processes serves as a substrate for another process; that is, a conveyor of sorts is formed. Of known examples for the traditional catalytic systems of this type, note the monomer-isomerization polymerization of 2- and 3-heptenes or 4-methyl-2-pentene, the combination of propylene disproportionation with oligomerization, etc. In the context of the above problem of the production of LLDPE by the *in situ* copolymerization of ethylene with α-butene, bifunctional catalysts have received wide acceptance in the practice of polymerization. The production of LLDPE is based on the introduction of short-chain branches into a PE chain by the catalytic copolymerization of ethylene with C_3–C_{10} α-olefins. Macroligands are of unlimited capabilities for combining active centers of different types within a single matrix (see also Section 5.2). The “relay-race” copolymerization consists in the use of bifunctional catalysts, in which active centers of two types are localized within a macroligand (a center for ethylene dimerization (Ni^{2+}) and a center for the copolymerization of the resulting butene with ethylene) [138]:



m_1 is ethylene; m_2 is butene; and M_1 and M_2 are the active centers.

In the general case, the initial monomer m_1 is converted into the monomer m_2 at the active center M_1 because of simple dimerization, trimerization, oligomerization, or isomerization reactions, and m_1 undergoes copolymerization with m_2 at the active center M_2. A microcell containing active centers of the two types is about half the average distance between the centers of M_1 and M_2 in the bifunctional catalyst, and it can be regulated at the stage of synthesis [139]. This design significantly decreases diffusion limitations and increases the frequency of embedding m_2 in a copolymer chain (in other words, increases its effective concentration in the cell or the constant of the relative reactivity of the comonomer r). This approach is sometimes referred to as tandem catalysis [140]. Note that the synthetic capabilities of macrocomplexes provide an opportunity to design bimetallic systems with the controlled arrangements of M_1 and M_2 metals. This was demonstrated with the use of the completion method: the macrocomplexes of Ti^{4+} or V^{4+} (M_1) were coupled [141] with tricyclic azomethine chelates of Ni^{2+} (M_2) to form strictly localized bimetallic macrocomplexes like



Finally, let us consider another interesting aspect of this problem. If a macrocomplex in ingredient rather than catalytic (or initiating) concentrations is used for the polymerization of a monomer, polymer–polymer compositions of ingredients that are incompatible under ordinary conditions (mechanical mixing of ingredients) can be produced at the stage of polymerization. This approach was implemented using new composites (polyolefin–polyvinyl compositions, chemical hybrids of polyolefins and polydienes, conducting polymer–polymer compositions, etc.) [142]. A considerable additional effort should be made in order to solve many of these problems.

4. OXIDATION CATALYSIS BY MACROCOMPLEXES

Oxygenation and hydroperoxide oxidation occupy a special place in catalysts because they are the most important reactions of organic synthesis and the main constituents of complex enzyme reactions in living systems. This process makes it possible to perform the single-step introduction of an oxygen function into almost any compound, to prepare purposefully substances with a homogeneous functional composition, and to prevent their subsequent degradation. The problem of selectivity should be considered as the most important problem of partial oxidation. Advances in this area of catalysis are closely related to extending our knowledge of the kinetics and mechanism of catalytic oxidation of various substrates, as well as to the development of new and, what is most important, highly selective catalytic systems, including polymer-immobilized systems.

4.1. On the Role of Metal Ions in Oxidation

The oxidation process consists of many consecutive and parallel reactions with the participation of starting substances, intermediate products, and free radicals, which carry a chain process. The main elementary steps of oxidation (using the chain reactions of hydrocarbon (RH) oxidation as an example) are the following [143]:

- the reactions of chain initiation, chain propagation, and degenerate chain branching accompanied by the formation of hydroxides;
- the chain decomposition of a hydroperoxide;
- the molecular degradation of a hydroperoxide;
- chain termination with the formation of molecular products.

The rate of chain initiation is very low (10^{-9}–10^{-7} mol l^{-1} s^{-1}); this fact is responsible for an induction period in the uncatalyzed low-temperature oxidation of *RH*. The oxidizability parameter, which characterizes the ability of hydrocarbons to undergo oxidation, is determined from the ratio between the reaction rate constants of chain propagation and termination $k_2/k_6^{1/2}$. In this case, chain radical oxidation can be catalyzed. Metal ions M^{n+} can affect (promote or inhibit) the direction of any step of the oxidation process; however, the importance of these ions for each particular step can be determined only in very rare cases [144–146]. The key role of M^{n+} consists in the acceleration of a rate-limiting step (the initiation of a radical chain process) to result in both the disappearance of the induction period of reaction and a change in the kinetic characteristics (the one-half and first orders of reaction with respect to the catalyst and *RH*, respectively). This acceleration is due to the following factors:

- The catalytic decomposition of negligibly small impurities in RH (which cannot undergo decomposition under mild conditions), which is described by the Haber–Weiss cycle [147]

$$\begin{array}{l} ROOH + M^{n+} \longrightarrow RO^{\bullet} + {}^{\bullet}OH + M^{(n+1)+}, \\ ROOH + M^{(n+1)+} \longrightarrow ROO^{\bullet} + H^{+} + M^{n+} \end{array} \qquad (VII)$$

These reactions are preceded by the complexation of ROOH with M^{n+} or $M^{(n+1)+}$; the main mechanism of their decomposition in the radical chain process developed consists in a radical reaction path.

- The step of initiation can also be accelerated because of the activation of molecular O_2 by a metal ion with the subsequent reaction of the resulting complex with *RH*

$$M^{(n+1)+} + O_2 \longrightarrow M^{(n+1+\delta)+}\ldots O_2^{\delta-} \xrightarrow{RH} \left\langle \begin{array}{l} MOOH + R^{\bullet} \\ M^{(n+1)} + {}^{\bullet}OH + RO^{\bullet} \end{array} \right. \qquad (VIII)$$

It is of importance that this reaction path (initiation due to molecular oxygen) is most promising in terms of selectivity; in principle, the direct insertion of O_2 into a C–H bond of the substrate molecule to be oxidized can be accomplished.

- Transition metal peroxides are active intermediates, and they can catalyze homolytic (with M–O bond cleavage in a peroxo complex) or heterolytic (in the presence of a free coordination site at the transition metal ion in a peroxo complex) oxidation of alkenes, aromatic hydrocarbons, and alkanes.
- Acceleration due to substrate activation on coordination to a catalyst by the mechanism of electron transfer from the substrate to the metal ion (through the formation of a radical cation). Ions with d^7 (Co^{2+}) and d^5 (Mn^{2+}) configurations exhibit a particularly high activity in selective oxidation. On this basis, a conclusion can be made that ions with odd numbers of *d* electrons more easily form a σ bond with the substrate by pairing their valence electrons. It makes a crucial contribution to the total energy of the coordination bond. This participation of unpaired *d* electrons facilitates the formation of the substrate–catalyst (especially olefin–catalyst) activated complex and intermediate radicals with a high degree of delocalization.

At the same time, the majority of salts, including transition metal acetates, which are most frequently used in the liquid-phase oxidation of hydrocarbons, are poorly compatible with a medium (sparingly soluble); this restricts their application in required concentrations. Attempts to incorporate MX_n into the inverse micelles of ionogenic or nonionic surfactants, although they gave positive results, did not solve the problem.

The situation is complicated by the fact that, in the research practice, it is believed that metallopolymeric systems are extremely highly sensitive to oxidation reaction (sometimes this is really the case). For example, in the course of the hydroperoxide oxidation of 2,3,6-trimethylphenol in the presence of polymeric Cu^{2+} chelates, the oxidation of a polymer support occurs in parallel with the reaction of substrate oxidation. The oxidation of the polymer support is accompanied by the reactions of its functional groups [148]. In other words, the system becomes chemically fragile and degradable.[1] Because of this, oxidation catalysis by metal-containing polymers was developed at a slow pace (for example, see [2]), although many metallopolymeric catalysts are stable in an oxygen atmosphere even at temperatures higher than 393 K [149]. At the same time, the chemical binding of MX_n with a polymer provides an opportunity to obtain structures that have no soluble analogs and to improve the activity and selectivity of an oxidation process because of the specific mechanistic features considered below.

First, it becomes possible to regenerate reduced transition metal species, that is, to change from stoichiometric to catalytic oxidation. In this case, the nature of the macroligand and its functional groups affects the dynamics of a redox process [150]. Ligands should be considerably mobile because oxidation is accompanied by the displacement of a portion of ligands by a substrate or oxygen. The strong binding of reaction mixture components can result in the inhibition of the reaction.

Another advantage of metallopolymers consists in the acceleration of hydroperoxide degradation, which occurs by a heterogeneous–homogeneous mechanism (the formation of radicals on a metallopolymeric surface with the subsequent chain reactions in the bulk of the liquid phase) or via a heterogeneous reaction path (without the exit of radicals into the bulk). In the latter case, all the steps of oxidation occur at the catalyst surface, although a mixed mechanism most frequently occurs—the simultaneous development of reactions both at the surface and in the bulk of a liquid phase. Polymer-immobilized catalysts often facilitate the occurrence of only heterogeneous oxidation (in a surface cage); this creates prerequisites to the activation of only one of the reacting species and allows one to expect that the main problem, selectivity, will be solved. This is also favored by the immobilization of oxidants (perbenzoic acid and other peracids), the hypochlorite anion, periodates, etc., on polymers.

4.2. Catalytic Oxygenation Reactions of Hydrocarbons

On the one hand, these reactions make it possible to reveal special features of oxidation catalysis under the action of polymer-immobilized complexes. On the other hand, they have much in common with enzyme catalysis because they occur at low temperatures, require small catalyst amounts, and exhibit high selectivity [151]. The catalytic liquid-phase oxidation of paraffins was practically not studied, and available data are spread in the patent literature.[2]

Analyzing these spread data, note [3] that the oxidation of *n*-paraffins in the presence of manganese macrocomplexes is accompanied by a significant increase in the yield of acids, compared with homogeneous catalysts. Although Co^{3+} complexes are highly active, they are characterized by a low selectivity: the ratio between fatty acids, esters, ketones, and alcohols is 3 : 3 : 3 : 1. The liquid-phase oxidation of paraffins was performed [153] with the use of Cu^{2+} and Mn^{2+} complexes bound to the copolymers of vinyl ether, β-pinene, and maleic anhydride (Amberlite IRS-50).

The oxidation of both linear and cyclic olefins was better studied. As a rule, it occurs by a free-radical mechanism; the accumulation of epoxides, acids, aldehydes, and ketones along with hydroperoxides is indicative of a chain character. The main goal of these processes is to considerably increase the reaction selectivity. For comparison, let us cite a typical example. The uncatalyzed oxidation of propylene at 423 K was accompanied by the formation of more than 20 products, whereas the catalytic oxidation mainly resulted in the formation of acrolein at the first step and then acrylic acid with almost 90% selectivity. Of the most important products of catalytic oxidation, the following compounds should be noted: methyl methacrylate, ethylene oxide (ethylene oxygenation in an acetic acid solution at 383 K catalyzed by macrocomplexes), methacrolein (low-temperature isobutylene oxidation on Cu^{2+} macrocomplexes at 360 K with 100% selectivity), etc. Polymer-immobilized metal clusters were also used for the oxidation of olefins. For example, a mixture of $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ clusters in a molar ratio of (1–3) : 1 immobilized on an amine-containing ion-exchange resin selectively oxidized 2-olefins to the corresponding alcohols [154].

In due time, the oxygenation of cycloolefins, primarily cyclohexene, served as a model reaction for studying the mechanism of uncatalyzed olefin oxidation. It also plays an important role in studying catalytic oxidation; moreover, this role went to heterogenized catalysts.

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[1] This process results in the degradation of an aromatic ring with the formation of carboxylic acids and the products of trimethylphenol oxidative coupling to 2,2',3,3',5,5'-hexamethyl-4,4'-dihydroxyphenyl.

[2] Palladium complexes immobilized on ion-exchange resins are also highly active in the oxidation of hydrogen with air; for example, see [152].

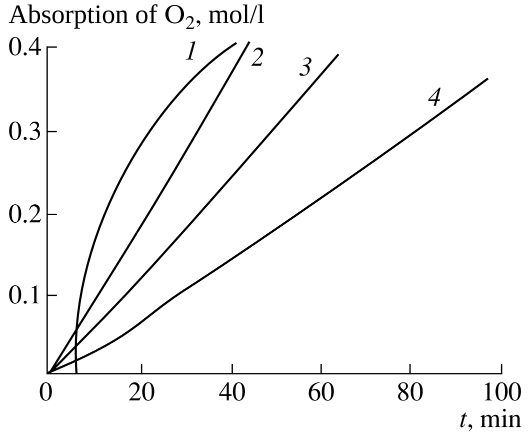


Fig. 7. Oxidation of cyclohexene in the presence of Co-containing catalysts: (*1*) Co(AcAc)$_2$, (*2*) PE-*graft*-PA-Co^{2+}, (*3*) a copolymer of styrene with cobalt acrylate, and (*4*) PE-*graft*-poly(AAm-Co^{2+}). Here, PA is polyacrylate, and AAm is acryalmide.

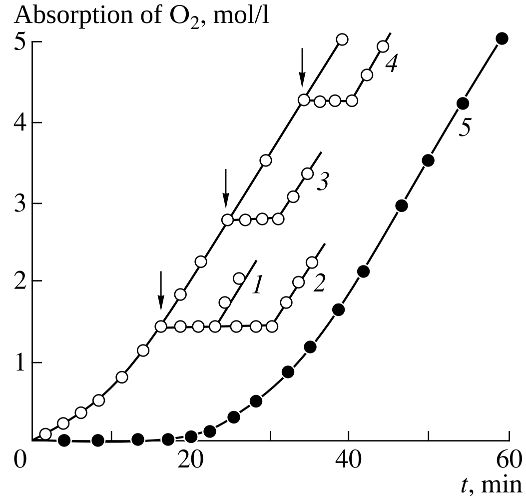
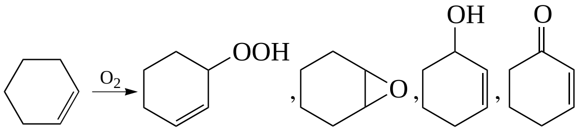


Fig. 8. Inhibition of cyclohexene oxidation by the Φ–Φ dimer. [Cyclohexene] = 5 mol/l; catalyst, PE-*graft*-PA-Co^{2+}; 328 K. [Φ–Φ], mol/l: (*1, 3, 4*) 1.7 × 10^{-4}, (*2*) 3.4 × 10^{-4}, or (*5*) 1.7 × 10^{-5}. Arrows indicate the points in time at which the inhibitor was added.

The oxidation of cyclohexene occurs via two parallel reaction paths with the participation of either >C=C< or ≡C–H bonds:



(IX)

The main products of liquid-phase oxidation are 2,3-epoxycyclohexane, 1-cyclohexen-2-ol, and cyclohexyl hydroperoxide (CHHP).

The mechanism of this reaction was studied in detail using Co^{2+} complexes bound to various types of carboxyl-containing polymers as an example [155, 156]. With the use of Co(AcAc)$_2$ as a catalyst (Fig. 7, curve *1*), the process was characterized by an induction period. Subsequently the rate reached a maximum value and then decreased. In catalysis by macrocomplexes, an induction period was absent, and the rate of oxidation remained constant (Fig. 7, curves *2*–*4*). Catalysts were active up to high degrees of oxidation, and they could be used repeatedly after separation from the reaction mixture. The composition of the resulting products was almost the same; the main products were CHHP, cyclohexenone, cyclohexenol, and cyclohexene oxide.

The oxidation of cyclohexene by these systems is a heterogeneous–homogeneous chain process accompanied by the exit of radicals into the bulk. This was supported using the inhibitor method: the introduction of a free-radical scavenger (the dimer 1,2-bis(4,4'-dimethylaminophenyl)-1,2-diphthaloylethane (Φ–Φ)) into the test system. The addition of the inhibitor resulted in the appearance of inhibition periods, which are independent of the degree of oxidation, in the region of a steady-state development of the reaction (Fig. 8). The rate of initiation at the initial point in time was calculated to be lower than that in the steady-state region by a factor of 30. Consequently, surface processes are responsible for the rate of chain generation; free radicals are not formed in the bulk. At the beginning of the reaction, when ROOH is absent from the system, free radicals are formed in the reaction of polymer-bound cobalt with oxygen

$$\begin{aligned} &]\!-\!\mathrm{Co}^{2+} + \mathrm{O}_2 \rightleftarrows\ ]\!-\![\mathrm{Co}^{3+}\cdots\dot{\mathrm{O}}\!-\!\mathrm{O}^-]^{2+} \\ &\xrightarrow{\mathrm{RH}}\ ]\!-\!\mathrm{Co}^{2+} + \mathrm{R}^{\bullet} + \mathrm{HO}_2^{\bullet}. \end{aligned} \qquad \text{(X)}$$

In the process developed, the main contribution to chain initiation is made by the decomposition of coordinated ROOH

$$\begin{aligned} &]\!-\!\mathrm{Co}^{2+} + n\mathrm{ROOH} \overset{K}{\rightleftarrows}\ ]\!-\!\mathrm{Co}^{2+}\cdots n\mathrm{ROOH}] \\ &\xrightarrow{k_j} \mathrm{RO}^{\bullet} +\ ]\!-\![\mathrm{Co(OH)}]^{2+} + (n-1)\mathrm{ROOH} \end{aligned} \qquad \text{(XI)}$$

(K is the equilibrium constant).

The rate of initiation is determined by the equation

$$w_j = \frac{k_j K[\mathrm{ROOH}]_0^n[\mathrm{Co}^{2+}]_0}{1 + K[\mathrm{ROOH}]_0^n}.$$

Table 10 summarizes the main kinetic parameters of oxidation under the action of macrocomplexes. Because a small increase in the oxidizability parameter ($k_2/k_6^{1/2}$ = 2.3 l$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$ for the uncatalyzed oxidation of cyclohexene with oxygen at 303 K) cannot provide the formation of considerable amounts of oxidation products, it is assumed that they also result from

Table 10. Kinetic parameters of cyclohexene oxidation in the presence of immobilized catalysts (333 K, without solvent)

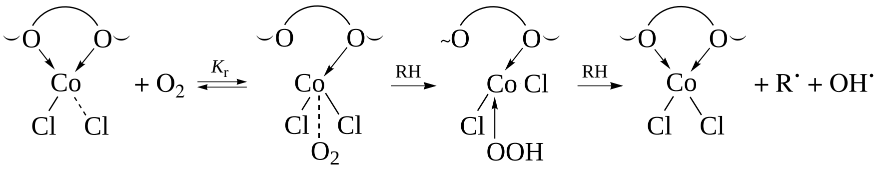
Catalyst	$[Co^{2+}] \times 10^3$, g-atom/l	$w_i \times 10^6$, mol l^{-1} s^{-1}	$w \times 10^4$, mol l^{-1} s^{-1}	$w[Co^{2+}] \times 10^2$, s^{-1}	$k_2k_6^{-1/2}$, $l^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$
PE-*graft*-PA Co^{2+}	0.88	6.5	1.40	160.0	5.4
Copolymer of styrene with cobalt diacrylate	10.00	2.8	0.97	9.7	5.8
Homopolymer of $Co(NO_3)_2$ 4AAm	7.10	1.8	0.22	3.4	4.9

the reaction of linear chain termination with the participation of immobilized Co^{2+} complexes.

The value of K ($>10^2$ l/mol) and the independence of w_i from [ROOH] allowed an important conclusion to be made that a high local hydroperoxide concentration is produced near the surface of a metallopolymeric catalyst (see Section 6). ROOH is transported to active centers by migration over the catalyst surface; after the decomposition of ROOH, the resulting radicals exit into the bulk, where the radical chain oxidation of cyclohexene develops [157].

Under the action of the catalysts under consideration, alkylaromatic hydrocarbons undergo oxidation only due to alkyl substituents. However, examples of benzene oxidation are also known. Among the substrates of this class, the oxidation of toluene, ethylbenzene, and cumene under the action of heterogenized catalysts was best studied [3]. The main regularities are considered below. Compared with aliphatic hydrocarbons, the direct oxidation of aromatic hydrocarbons results in the formation of stronger ternary complexes than those in a homogeneous version; these complexes are difficult to decompose. To prevent this phenomenon, special additives (such as dioxane) are frequently introduced. Kinetic data on the buildup of α-phenylethyl hydroperoxide, methyl phenyl carbinol, and acetophenone indicate that, as a rule, the oxidation of ethylbenzene occurs via consecutive–parallel reaction paths. Under optimum conditions, the process can be performed with up to 96% selectivity for acetophenone. Styrene can be oxidized via two directions: to an olefin oxide, aldehyde, or ketone or to a copolymer of styrene with O_2 (polyperoxide). Dimethyl phenyl carbinol and cumene hydroperoxide are the main products of the liquid-phase oxidation of cumene under the action of transition metal macrocomplexes and ion-exchange resins. The selectivity depends on the nature of the functional groups in the macroligand. For phosphorus-containing macroligands, the yield of the latter increases in the following order of metals: $Co^{2+} < Mn^{2+} < Cu^{2+} < Ni^{2+}$. Iron complexes are almost inactive in this reaction. Note that polymeric Schiff bases containing N and S donor atoms inhibit cumene oxidation because they are peroxide radical scavengers [148].

The oxidation of tetraline (a product of the partial hydrogenation of naphthalene) with molecular oxygen is accompanied by interesting kinetic phenomena (the main products are tetraline hydroperoxide, 1-tetralone, and 2-tetralol). One of them is that the initial rate of oxidation is higher than the rate of uncatalyzed reaction by almost four orders of magnitude. The second is that the traditional reaction scheme of catalytic oxidation, in which the role of an immobilized metal is reduced to the radical decomposition of peroxide, does not describe the reaction kinetics. Finally, a new effect in catalysis by polymer-immobilized metal complexes was found in this reaction [158]. This is a so-called contribution of the energy of nonequilibrium conformations of polymer chains, which appear at the stage of the synthesis of macrocomplexes, to catalysis. The manifestation of this effect (using the complexes of $CoCl_2$ with poly(ethylene glycols) with different chain lengths as an example) can be demonstrated as described below. In the absence of O_2, macrocomplexes in tetraline occur as coils; however, the coordination of oxygen to cobalt can be accompanied by the temporary rupture of a metal–polymer bond (like ligand replacement). This results in a nonequilibrium configuration of the polymer chain, which tends to come unrolled:



(XII)

The equilibrium constant (K_r) is determined by the change in the free energy of macrocomplex formation ($-RT\ln K_r = \Delta G$), which includes a contribution from the rupture of old bonds and the formation of new chemical bonds of the metal ion and the work of chain stretching (ΔG_{ch}) stored in the course of the preparation of the macrocomplex. In this case, K_r for polymer complexes and their low-molecular-weight analogs differ by a value of $\exp(\Delta S_{ch}/R)$, which is a part of the preexponential factor of the general reaction rate equation and depends on the molecular weight of the macroligand. Consequently, the fraction of Co^{2+} complexes with O_2 depends on the chain length of the macroligand, which increases the rate of initiation of the oxidation reaction. Indeed, the rate of tetraline oxidation increased by a factor of 10 as the molecular weight of poly(ethylene glycol) was increased from 4000 to 40000.

The conformational adjustments of both ligand macromolecules to a certain metal ion and the active centers of a metallopolymeric catalyst to the substrate were found with the use of the liquid-phase oxidation of alkylaromatic hydrocarbons and, more recently, hydroxyarenes with molecular oxygen as an example [159–161]. It consists in the formation of soluble complexes in the presence of metal ions or the substrate. Next, the specific adjustment to reactants is fixed by the intermolecular crosslinking of the macroligand, for example, with *N*,*N*'-methylenediacrylamide, followed by the removal of template components from the crosslinked formations. This approach results in a considerable increase in the activity and selectivity of a catalyst, compared to that obtained without the directional formation of its structure.

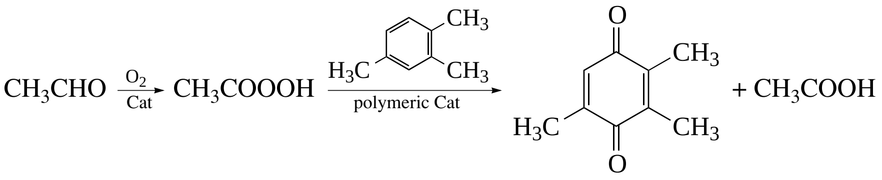
4.3. Peroxidase (Peroxy-Acid) Oxidation of Alkylarenes and Hydroxyarenes

Undoubtedly, in addition to atmospheric oxygen, dilute H_2O_2 solutions are environmentally efficient oxidizing agents for large-scale processes. A comparative study of the model reaction of hydrogen peroxide disproportionation on homogeneous and heterogenized complexes is a traditional approach to the evaluation of their activity. The general equation for the initial rate of hydrogen peroxide disproportionation includes the rates of parallel reactions of uncatalyzed decomposition (at the walls, in the liquid phase, and on the polymer surface) (B) and catalytic decomposition (*k* is its rate constant) on metal ions:

$$w_0 = B + k[M^{n+}][H_2O_2].$$

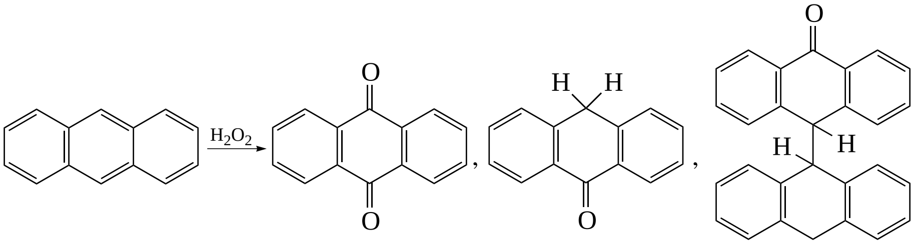
Thus, the fractions of decomposed H_2O_2 (1.1845 M) at 303 K in a homogeneous medium, at the surface of vessel walls, and on a catalyst (0.01 g) containing 0.32 mg-equiv Cu^{2+} g^{-1} were 1.0, 18, and 81%, respectively [148].

The production of 2,3,5-trimethylbenzoquinone, which is a key product for the manufacture of vitamin *E* and vitamin K_3 (2-methyl-1,4-naphthoquinone), in this manner is of practical interest. The peroxy-acid oxidation of arenes is a model of the monoxygenase oxidation of xenobiotics. The following process of the peroxy-acid oxidation of 1,2,4-trimethylbenzene (pseudocumene) to trimethylbenzoquinone with peracetic acid, which is combined with the production of acetic acid in order to reduce the price of the target product, is of interest:



(XIII)

Without going into the oxidation of alkylaromatic compounds with polymer-immobilized catalysts, note that this process can be represented as a set of consecutive–parallel reactions: mononuclear hydroxylation to phenols, oxidation of phenols, oxidative dehydrogenation of hydroquinones, oxidative degradation of quinones, and thermal and catalytic decomposition of per acids. Of the products of the catalytic oxidation of aromatic hydrocarbons, which contain condensed benzene rings, let us consider only anthracene because anthraquinone, which is a product of its conversion, is commercially valuable [148]. In principle, this reaction can be performed noncatalytically. However, it requires severe conditions and is accompanied by a number of by-products, in particular, anthrone and bianthrone:



(XIV)

Table 11. Kinetic parameters of cyclohexene epoxidation on the Mo–furfurylidene resin system (353 K)

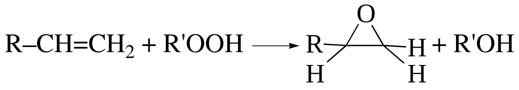
Hydroperoxide	K, l/mol	K_s, l/mol	E_a, kJ/mol
Ethylbenzene	0.25 ± 0.10	6.0 ± 0.6	100 ± 2
Cumene	0.40 ± 0.10	15.0 ± 2.0	85 ± 4
tert-Butyl	0.10 ± 0.05	18.0 ± 2.0	60 ± 2

Note: K is the complex formation constant, and K_s is the sorption constant for products on the catalyst.

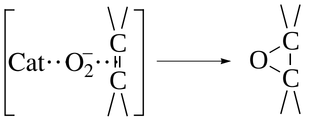
Polymeric acetylacetonates of VO^{2+} are active in the selective (up to 85%) oxidation of anthracene to anthraquinone with hydrogen peroxide in ethyl acetate at 293–345 K. These heterogenized complexes exhibit a comparatively high catalase-like activity in H_2O_2 decomposition (for a recent example, see [162]). Petrov [148] believed that metallopolymers can be good catalysts in the industrial catalytic oxidation of anthracene.

4.4. Catalysis of the Alkyl Hydroperoxyde Epoxidation of Olefins

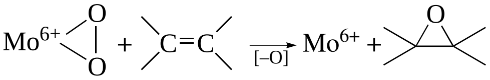
The chemistry of oxiranes is developed toward the commercial production of epoxy compounds (in particular for the production of polymers) by the epoxidation of olefins


R–CH=CH$_2$ + R'OOH ⟶ (XV)

This reaction is of special interest because it has much in common with biological monoxygenation. A necessary condition for this reaction is the heterolysis of the peroxide bond in per acids, which is facilitated by the presence of carbonyl groups in these acids. Because epoxidation occurs by an electrophilic attack, disubstituted and trisubstituted double bonds more easily undergo epoxidation, whereas α-olefins undergo these reactions with more difficulty. In the presence of metal complex catalysts, epoxidation occurs under mild conditions because the heterolysis of the O–O bond in the transition complex is facilitated in this case:


(XVI)

The complexes of high-valence Mo, V, and W exhibit a better ability to catalyze oxygen transfer from a hydroperoxide to an olefin. These complexes bear a high positive charge; they can add an electron pair through vacant orbitals and form complexes (with different stabilities) with olefins and hydroperoxides.[3] These properties are necessary for the formation of mixed-ligand mono- and diperoxo complexes—active agents for direct epoxidation


(XVII)

The first step of homogeneous catalytic hydroperoxide oxidation is the formation of mono- and diolate complexes; the former are more active than the latter by two orders of magnitude.

How does the binding of metal complexes to a polymer affect their catalytic properties in the above reaction? First, their activity increases. This results from the formation of a larger fraction of monoperoxo complexes and from an increase in their stability. For example, molybdenum complexes bound to modified poly(vinyl alcohol) or a furfurylidene resin were active and stable during continuous operation for 500 h [163]. Efficient reusable catalysts for the epoxidation of cyclopentene, cyclohexene, 1-nonene, styrene, etc., with *tert*-butyl hydroperoxide or ethylbenzene hydroperoxide can be developed in this manner. The reaction occurs in either swollen (under the action of the initial hydroperoxide or reaction products) or unswollen catalysts. Kinetic studies demonstrated that epoxidation takes place in the reaction of an olefin with a hydroperoxide adsorbed on a polymer. In this case, comparatively weak complexes of Mo^{6+} with ROOH are formed (Table 11): the formation constant (K) of the complex is much lower than that in a homogeneous mode (3–5 l/mol), whereas the sorption of reaction products is almost not affected by the polymeric nature of the catalyst, and the values of K_s are almost equal.

The reaction selectivity (a ratio of the number of moles of the resulting epoxide to the number of equivalents of oxygen consumed) primarily depends on the adsorption–desorption ability of initial reactants and target products. An increase in the selectivity with temperature is a consequence of a higher E_a of this reaction, as compared with nonselective oxidation. Moreover, the free-radical decomposition of a hydroperoxide, which decreases the selectivity, is due to the presence of low-valence molybdenum species (including Mo^{5+}) in the catalyst, and the fraction of these species in heterogenized complexes is much lower than in homogeneous catalysts. In 1983, Bhaduri and Khwaja [164] noted that molybdenum in the dithiocarbamate complexes of Mo^{5+} undergoes oxidation to Mo^{6+} on binding to chloromethylated PS in the presence of *tert*-butyl hydroperoxide (TBHP), and this Mo^{6+} catalyzes the reaction. The homogeneous system is rapidly decomposed in the presence of TBHP because of the oxidation of ligands, which results in a low (20% in place of 80% in hetero-

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[3] The complexes of Cu, Ni, Co, and Fe exhibit opposite properties; their only function is the homolysis of the peroxide bond by a one-electron mechanism with the formation of free radicals.

genized systems) yield of the target product. Moreover, the resulting olefin oxides are reactive compounds, which can participate in various side reactions under conditions of oxidation. These reactions result in the appearance of glycols, esters, and other oxygen-containing products, which also decrease the reaction selectivity. Under conditions of immobilized catalysts, these processes become slower. Epoxidizing agents, such as sodium hypochlorite (NaOCl) and potassium peroxymonosulfate ($KHSO_5$), as well as $NaBO_3$ and $NaJO_4$ in the presence of polymer-immobilized Mn^{3+}, exhibit an even lower selectivity in the oxidation of alkenes and cycloalkenes [165].

Interesting phenomena were found in a detailed mechanistic study of cyclohexene epoxidation with the use of TBHP (333 K) [166] under the action of Mo^{6+} immobilized on cellulose phosphate. A comparison between the reaction rates and the enthalpies of formation of the intermediate complexes of the catalyst with the reactants resulted in the following important conclusion: the step of decomposition of the ternary complex [TBHP$\cdots$Mo$\cdots$cyclohexene] at the polymer surface is characterized by a much higher activation energy and, simultaneously, by a higher positive entropy of activation ($E_a^{\neq}$ and $\Delta S^{\neq}$ are equal to 136 kJ/mol and 290 J mol^{-1} K^{-1}, respectively) than those in solution (72 kJ/mol and 166 J mol^{-1} K^{-1}, respectively). This difference is due to the heterogeneous nature of the system: a ternary biligand complex is stabilized on a polymer matrix by additional interactions with the surface, and it occurs in an ordered (as if frozen) state. On the one hand, a higher activation energy is required for its decomposition; on the other hand, the release of the reaction product into a solution is accompanied by a more dramatic disordering of the system. Although, in my opinion, this phenomenon is typical of any catalysis by metallopolymers, it was described quantitatively for this reaction.

Of the complexes of other metals bound to polymers, which are active in epoxidation, let us note $VO(AcAc)_2$ on polyvinylbenzoylacetone, microporous PS matrices with the chelate units of iminoacetic acid or with bis(2-hydroxyethyl)amino groups, etc. Oxovanadium(IV) bound to PS modified with chelating ligands exhibits high activity in the epoxidation of chalcone (benzylideneacetophenone) with the formation of *trans*-epoxy-1,3-diphenyl-2-propen-1-one [167]. In the epoxidation of (*E*)-geraniol or its isomer linalool, 100% conversion and 98% selectivity for 2,3-epoxygeranyl acetate were achieved; the 6,7-epoxygeranyl acetate accounted for 2% [168]. That is, the conversion and selectivity were equal to those in the best homogeneous systems. Heterogeneous catalysts can be repeatedly used in the manufacture of fragrance compounds (such as (*E*)-geraniol and linalool derivatives). Moreover, macrocomplexes are preferable because not only an increase in the activity but also the complete removal of catalyst residues from oxidation products is of primary importance in these processes.

Unexpectedly, $Ti(O–iso-Pr)_4$ complexes immobilized on a PS support with chiral groups were found to be active in the asymmetric epoxidation of geraniol with TBHP to form (*S*,*S*)-2,3-epoxygeraniol [169]. The enantiomeric excess was as high as 66%, although the repeated use of the catalyst resulted in a small decrease in the asymmetric induction. Scanty information [3] on the use of immobilized cyclopentadienyl derivatives of Ti, Zr, and Hf in the epoxidation of cyclohexene and cyclooctene is available.

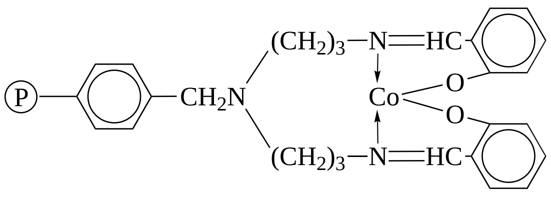
4.5. Catalytic Oxidation of Oxygen-Containing Substrates by Macrocomplexes and Prospects for Oxidative Catalysis

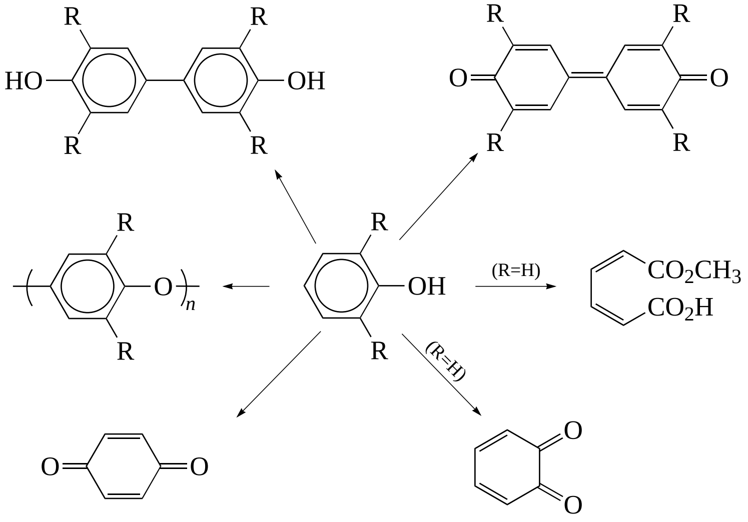
A further oxidation of oxygen-containing products of the partial oxidation of hydrocarbons is a promising method for the preparation of synthetic fats, ionogenic surfactants, herbicides, pharmaceuticals, monomers, auxiliary materials for polymer production, etc. In this case, selectivity is also the most important problem. The point is that the rates of oxidation of alcohols, ketones, and olefin oxides are nearly always higher than the rates of oxidation of the starting hydrocarbons. Therefore, the oxidation process is difficult to terminate until the formation of thermodynamically stable products, ultimately, CO_2 and H_2O. The immobilization of metal complexes is an approach to the solution of this problem.

Chromium complexes immobilized on polymers (better, on PVP or quaternized ammonium resins) are most frequently used for the oxidation of alcohols to the corresponding aldehydes or of carbonyl compounds to acetals and ketals. These catalysts are easy to regenerate by washing with 2N NaOH and HCl solutions without activity losses in subsequent cycles.

As distinct from oxygenation, the peroxidase oxidation of hindered phenols in the presence of immobilized Cu^{2+} complexes occurs only via a radical mechanism. Binuclear Cu^{2+} complexes bound to polymer Schiff bases selectively oxidize 2,4- or 2,6-di-*tert*-butylphenol to the corresponding quinones (the yield of the target product was as high as 42%) [170, 171].

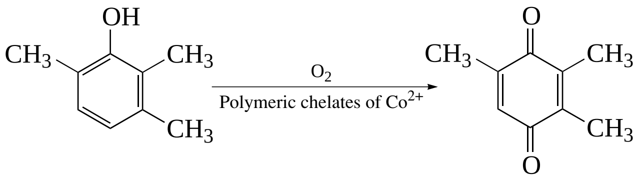
Good results were obtained with the use of Co^{2+} complexes with tetradentate Schiff bases synthesized from salicylaldehyde and diamines (salcomine, H_2Salen) as catalysts for the oxygenation of hindered phenols. However, CoSalen forms monomeric and associated compounds in solutions on oxygenation, whereas the oxidation of hindered phenols occurs only with the participation of monomeric oxygenated complexes. The formation of the dimeric oxygenated complex –Co–O–O–Co– can be prevented by binding salcomine to a polymer support:





Scheme 8.

In this manner, trimethylquinone was prepared [148] by the oxidation of 2,3,6-trimethylphenol with a comparatively high efficiency:



(XVIII)

The oxygenation of sterically hindered phenols results in the formation of various products. Thus, the oxidative coupling of 2,6-xylenol results in poly(phenylene oxide) (C–O coupling) or diphenoquinone (C–C coupling). The reason consists in the formation of phenoxy radicals at the first step; the subsequent reactions of these radicals result in dimeric and polymeric C–C- and C–O-coupled products (Scheme 8).

Selvaraj and Mahadevan [172] studied in detail the kinetics of this reaction catalyzed by copolymers containing tertiary nitrogen groups bound to Cu^+ or Cu^{2+} [173]. The oxidation of a methacrolein dimer or unsaturated 1,3-dioxane derivatives (polymer-bound Co^{2+} and Mn^{2+} complexes) [174] also results in the sets of products.

Note that a so-called ping-pong mechanism was found using the oxidative dimerization of dialkylphenols under the action of Cu^{2+} macrocomplexes (which occurs via the steps of the formation of the intermediate complex phenolate–Cu^{2+} and its one-electron oxidation to the phenoxy radical, which undergoes oxidation to diphenoquinone via a dihydroxybiphenyl intermediate with the simultaneous formation of univalent copper and its oxidation to bivalent copper) as an example. These cycles (the reduction of a metal ion in an act of reaction with a substrate and its reoxidation with molecular oxygen) are observed comparatively often. The immobilized complexes of platinum are also efficient for the oxidation of oxygen-containing substrates.

Asymmetric induction with the participation of immobilized metal complexes shows promise for both hydrogenation (Section 2.9) and oxidation processes. Among three radically different techniques of racemate separation to optically active isomers—spontaneous, biochemical, and chemical—the last named technique is most commonly used. As mentioned above, immobilized metal complexes are best suited for modeling the asymmetric effect of enzymes, which generate large amounts of an enantiomeric product from catalytic amounts of a chiral material.[4] For this purpose, the following two main approaches are used in oxidation processes: the use of metal complexes immobilized on macroligands with optically active groups and the use of metal complexes containing optically active ligands bound to optically inactive polymers. The former approach is more widely used in the asymmetric oxidation of organic substrates. Note that considerable advances have been made in the oxidation of ascorbic acid or 2,5-dihydroxyphenylacetic acid on Cu^{2+} with poly(*L*-histidine) and in the oxidation of 3,4-dihydroxyphenylalanine with Cu^{2+} macrocomplexes with poly(*L*-lysine). Along with poly(amino acids), other macromolecules are used in asymmetric oxidation (polyvinylpyridine is most frequently used); cobalt and iron complexes are also used in addition to copper complexes. It is most likely that the effect of a macrochain conformation on stereoselection is due to both the formation of an appropriate macrochain structure and a

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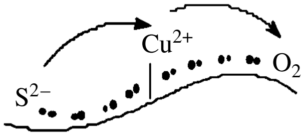
[4] For example, the copper-containing enzyme ascorbate oxidase, which catalyzes the aerobic oxidation of vitamin C, is a polypeptide chain containing 8–10 Cu^{2+} atoms with a molecular weight of about 140000.

difference in the affinity (stability of intermediate complexes) of one of the substrate enantiomers and the catalyst. These and other similar problems (in particular, the oxidation of monosaccharides, especially glucose and aldoses, as well as *L*-thiols, by molecular O_2) received the bulk of attention along with the oxidation of nonbiodegradable molecules such as polychlorinated phenols, catechols, and polycondensed aromatic compounds [174–177]. Macrocomplexes play a very promising role in these processes [178–181]. The polymer-bound chiral complex CoSalen is used for the kinetically allowed epoxidation of terminal groups [182].

The processes of catalytic CO oxidation are intensively studied primarily in the context of environmental problems related to the removal of CO from flue and exhaust gases. Although the results of these studies are mainly concentrated in patents, data on the use of polymeric copper and platinum chelates and platinum-group metals on the completely fluorinated polymer Nafion for this purpose are available. However, the promise of this approach remains unclear.

Of substrates containing heteroatoms other than oxygen, the oxidation of organic and inorganic sulfur-containing thiols, sulfides, and thio salts under the action of immobilized complexes was studied in sufficient detail. These processes are of prime importance for the demercaptization of large-scale petroleum products, natural gas, and gas condensate; the neutralization of thio salts and wastewater; and the solution of other nature-conservation and environmental problems. The liquid-phase (most frequently, in water) autoxidation of thiols with molecular oxygen was studied in detail. The role of metallopolymeric catalysts is almost the same as in the above processes. Moreover, extended electron-transfer chains are formed in a metallopolymer, which play the role of electron carriers from the sulfide anion to oxygen:



5. HYDROFORMYLATION UNDER THE ACTION OF IMMOBILIZED METAL COMPLEXES

The introduction of an oxygen function into an olefin molecule can be accomplished not only with the use of molecular oxygen or peroxides but also through hydroformylation: the addition of CO and H_2 to the multiple bonds of hydrocarbons. This process is performed with the use of synthesis gas as a reagent in the presence of catalysts based on Co and Rh compounds or, more rarely, Ru, Mn, and Fe compounds. Industrial oxo synthesis is performed with the use of cobalt carbonyls (390–410 K; 20 MPa) for the production of the most practically important aldehydes: propionaldehyde and butyraldehyde.

5.1. Hydroformylation of Olefins

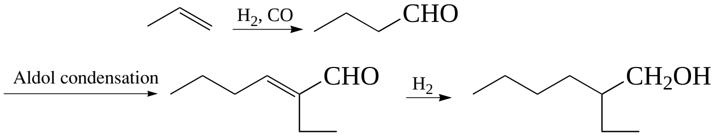
The most important index of selectivity (S) of this reaction is the ratio between normal (n-) and isomeric forms of the resulting aldehydes (S is 4 : 1–8 : 1 in industrial processes with a Rh-catalyst fixed bed). It depends on the relative rates of carbon monoxide insertion into metal–n-alkyl or metal–isoalkyl intermediates (k_n and k_i are the corresponding rate constants):

$$S = k_n/k_i = \exp[(E_a^n - E_a^i)/RT].$$

In the course of the reaction, double bond migration can occur in 2-butene, 2-pentene, 2-hexene, 3-hexene, etc. Although many examples of the use of immobilized metal complexes for the hydroformylation of ethylene, propylene, and butene (including gas-phase reactions at atmospheric pressure) are known, these catalysts are more widely used in the oxo synthesis of C_5–C_7 olefins. Thus, in the hydroformylation of 1-pentene in the presence of Rh complexes on a phosphorylated SDVB copolymer, linear aldehydes were formed with a higher selectivity (S = 12 : 1, whereas S = 3.3 : 1 in catalysis with a homogeneous system). However, this is not always the case: the binding of these complexes with the ion-exchange resin Shirotherm does not result in an increase in their selectivity. This is because the major portion of rhodium passes into solution, where catalysis takes place at a high temperature and complexes are repeatedly bound to the polymer as the temperature is decreased [182]. These systems are referred to as thermoreversible systems [183]. A catalyst based on polyquinones, which are thermally and chemically stable, modified with phosphine groups and immobilized rhodium carbonyl was developed; this catalyst was active at 373–383 K, and its selectivity for aldehydes was 91% [184].

Of many metallopolymeric catalysts for hydroformylation [3], note $Rh_2Cl_2(CO)_4$ on mixed-type supports—stable and highly efficient (the turnover number (TON) per metal atom is as high as 80000) reusable catalysts. High-temperature (to 468 K) polymer-immobilized catalysts based on polyphosphazene with immobilized trinuclear iron and osmium clusters, as well as bimetallic clusters like $RuOs_3$ and $Co_2Rh_2(CO)_{12}$, were described. The hydroformylation of hexene and C_8–C_{16} higher α-olefins with a mixture of CO/H_2O, in which water is a solvent and a source of protons, is accomplished in the presence of hybrid Rh(I) catalysts prepared by the sol–gel method [185].

In Section 3.1, attention was focused on the importance of the displacement of reaction centers to the surface or a near-surface layer of a polymer in heterophase catalytic systems. This approach was also found to be effective in hydroformylation processes, in particular, in the hydroformylation of 1-hexene [186]. Thus, a catalyst active under mild conditions (338 K; 1.6 MPa) was prepared by the immobilization of $Rh(AcAc)(CO)_2$ on the surface of polypropylene-*graft*-poly(styryldiphenylphosphine); the ratio between n-aldehydes and



Scheme 9.

isoaldehydes was higher than that in a homogeneous system by a factor of at least 3.5.

The most important reactions in which the use of metallopolymers is promising are the oxo synthesis of aldehydes (particularly, from higher olefins) with the subsequent conversion of the aldehydes into alcohols and acids, in particular, in coupled reactions.

5.2. On the Problem of Polyfunctional Catalysis in Hydroformylation

Systems of several catalysts, including those bound through a unifying macroligand, can be used in various combinations; they act as follows:

- simultaneously in independent cycles not related to each other;
- independently in consecutive steps or reactions;
- jointly (concertedly) in one reaction.

Polyfunctional catalysts, which activate consecutive steps of a multistep reaction, are used in the syntheses of CH_3CHO from ethylene (Pd–Cu catalysts) and 2-ethylcyclohexanol from propylene and CO + H_2 (Co–Rh catalysts) and in the preparation of 1,4-butanediol by the hydroformylation of allyl alcohol on Rh-containing catalysts with the subsequent hydrogenation of the resulting 4-hydroxybutyraldehyde on Raney nickel (alcohols, including commercially important higher alcohols, are prepared by combining hydroformylation with hydrogenation). The role of an additional metal consists not only in participation in the catalytic reaction but also in M_1–M_2 interactions. On the one hand, one of the metal ions can be a trap, which binds the other more strongly to the support and prevents the processes of its migration and aggregation. On the other hand, useful effects can be achieved when an additional metal ion (in particular, a nontransition metal ion) is embedded between polymer-bound complexes (M_1) to facilitate their matrix isolation $–M_1–M_2–M_1–$.

Moreover, chemical interactions (the formation of weak M_1–M_2 bonds, cocrystallization, and the formation of intermetallic compounds and alloys) can stabilize the catalyst and improve its productivity.

The substrate molecule can react with the active center formed by both metals (concerted reactions) to result in a considerable decrease in diffusion limitations. Thus, the three-stage synthesis of 2-ethylhexanol from propylene and synthesis gas includes [3] the formation of butyraldehyde (step 1), its aldol condensation (step 2), and hydrogenation (step 3) (Scheme 9).

This synthesis can be performed with the use of either two monodentate catalysts (for hydroformylation and hydrogenation) or one bifunctional catalyst (chloromethylated SDVB copolymer modified with secondary amino groups with immobilized $RhCl(PPh_3)_2(CO)$) (Fig. 9). The rates of the first, second, and third steps on the bifunctional catalyst are higher than those on two monofunctional catalysts by factors of 5, 15, and 30, respectively.

In this context, it is reasonable to note the dimerization of butadiene with the hydroformylation of the resulting vinylcyclohexene (Ni–Rh complexes immobilized on a phosphorylated SDVB copolymer), the

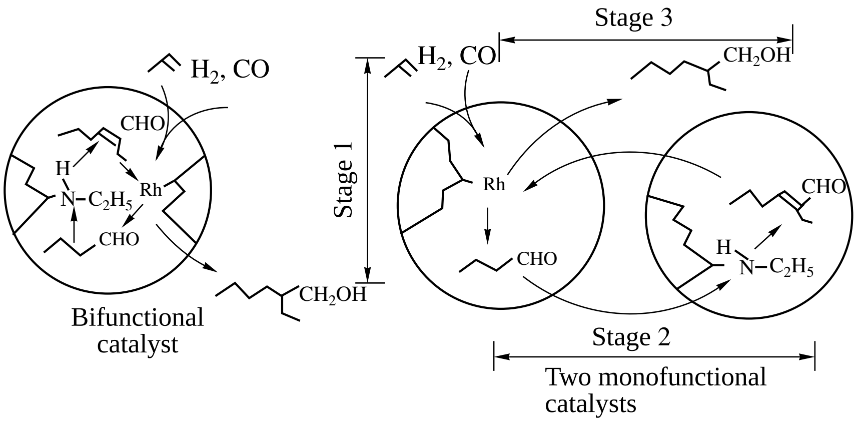
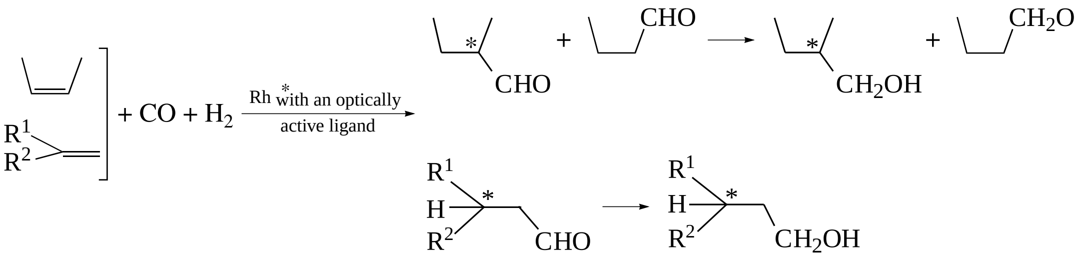


Fig. 9. Comparison of diffusion inhibition in reactions catalyzed by one bifunctional catalyst and two monofunctional catalysts in a three-stage synthesis of 2-ethylhexanol.



Scheme 10.

preparation of 4-methyl-2-pentanone under the action of immobilized bimetallic complexes, etc.

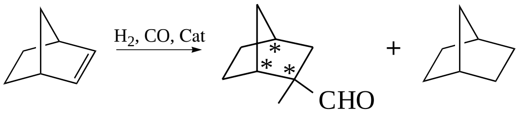
In the use of heterogenized two-center catalysts, the most complicated problem consists in the regulation of the concerted catalytic functions of each active center. In particular, this can be achieved by the controlled spatial arrangement of M_1 and M_2 with respect to each other at the stage of designing macrocomplexes. This arrangement is responsible for the length of reactant transfer paths between M_1 and M_2, diffusion limitations, and the effect of bifunctional catalysis (see also Section 3.7).

5.3. Enantioselective Hydroformylation Reactions

This reaction is most promising for the catalytic synthesis of optically active products with the participation of immobilized chiral complexes. This process most likely appears to have promise for the commercial use of metallopolymeric catalysis. The reaction occurs in accordance with Scheme 10.

The range of macroligands for binding MX_n is practically restricted by the same compounds as in asymmetric hydrogenation (Section 2.9); the rhodium complexes $[Rh(CO)_2Cl]_2$, $HRh(CO)(PPh_3)_3$ are mainly used. In this case, in addition to the saving of expensive rhodium, expensive chiral ligands are also saved.

Of a few examples, let us cite [187, 188] the hydroformylation of *cis*-2-butene under mild conditions with the formation of 2-methyl-1-butanol with the same optical yield (28%) as in the case of analogous homogeneous systems. However, this reaction with styrene (298–353 K) occurred with an increase in selectivity up to 20 : 1 (in place of 2 : 1 for a homogeneous catalyst). Moreover, it was accompanied by a high yield of optically pure (–)(R)-aldehyde. Nevertheless, $PtCl_2/SnCl_2$ complexes immobilized on chelating macroligands with functional groups like **I** and **III** are the best catalysts for asymmetric synthesis. Under optimum conditions, they accomplished the asymmetric hydroformylation of styrene practically to a single enantiomer (*ee* 98%), which also underwent hydrolysis without racemization. Good results were also obtained in the hydroformylation of vinyl acetate, *N*-vinylphthalimide, and norbornadiene. However, although the hydroformylation of norbornadiene occurs with very high rates, the yield of asymmetric 2-formylnorbornane is low (19–26%):



(XIX)

The main parameters of these reactions on immobilized catalysts are no worse than on homogeneous catalysts, and they practically did not decrease on the repeated use of the catalysts.

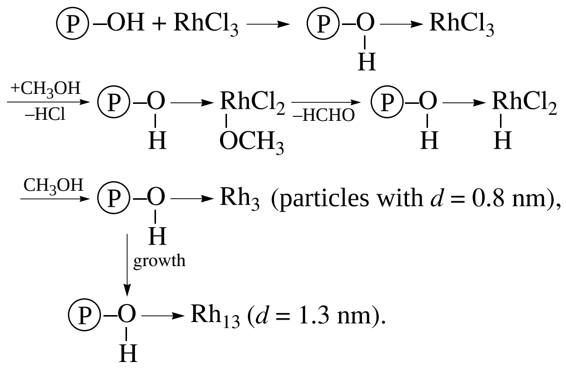
5.4. Other Promising Oxo Processes

Although I disagree with the optimistic predictions [2] concerning the Fischer–Tropsch synthesis

$$nCO + (2n+1)H_2 \longrightarrow C_nH_{2n} + nH_2O, \qquad \text{(XX)}$$

as one of the first future large-scale processes with the use of immobilized metal complexes, nevertheless, considerable progress in this direction has been achieved. The catalytic hydrogenation of CO [189, 190] was adequately studied, in particular, under the action of the complexes of metals from the first transition series on crosslinked polymers. It is most likely that metal nanocrystallites or heterogeneous clusters are responsible for the activity in such systems; homogeneous systems are inactive in this reaction.

The carbonylation of methanol to acetic acid or its esterification product (methyl acetate) is one of a few processes catalyzed by homogeneous systems (cobalt or rhodium catalysts promoted with CH_3J), which has been implemented on an industrial scale. Although a great body of data on the use of macrocomplexes in the catalysis of these reactions is available, all these data are reduced to typical improvements: an increase in activity at practically unchanged selectivity. The catalyst can sometimes be regenerated, and the consecutive steps of reduction of polyethyleneimine-bound rhodium ($Rh^{3+} \longrightarrow Rh^{2+} \longrightarrow Rh^{+}$) can be inhibited. This is also true of the water-gas shift reaction, which is performed in order to increase the yield of hydrogen in the synthesis gas ($CO + H_2O \rightleftharpoons CO_2 + H_2$). In a heterogeneous mode, immobilized clusters ($Os_3(CO)_{12}$ and $Rh_6(CO)_{16}$ on P4VP, functionalized PS, etc.) are mainly used for this purpose. Considerable progress would be



Scheme 11.

expected in the use of macrocomplexes in catalytic hydrolysis, dehydration, and transesterification. These reactions can be formally considered as the activation of the >C=O group and the stable H_2O molecule. An important reaction of this class is the hydrolysis of 2,4-dinitrophenyl acetate to 2,4-dinitrophenol (Cu^{2+} complexes with poly(vinyl alcohol)). This is a real model of enzyme catalysis along with the asymmetric hydrolysis of *D*,*L*-amino acid esters; moreover, this is an accessible procedure for enantioselective enrichment (path to the isolation of a more valuable *L*-amino acid).

In principle, heterogenized metal complexes would be applicable in fine organic syntheses with the use of oxidation, epoxidation, carbonylation, and hydroformylation reactions based on more complex stereochemical molecules (such as geranic acid esters, intermediate products for the manufacture of citronellal, vitamin A, etc.). However, homogeneous catalysis is predominant in this area.[5] The current situation in alkane activation under the action of metal complexes, which has been an area under active development in recent years, is the same.

6. STUDY OF INTERMEDIATE AND ACTIVE CATALYST SPECIES AND THEIR EVOLUTIONARY TRANSFORMATIONS

As mentioned at the beginning of this review, a considerable advantage of heterogenized metal complexes consists in the possibility of the nondestructive examination of the nature of intermediates and, in especially favorable cases, catalytically active species. With the use of hydrogenation reactions, which are likely the simplest reactions of those surveyed in this review, as an example (Section 2), it was demonstrated that an intermediate could almost always be isolated (of course, under inert conditions); sometimes, this could be performed in the course of a catalytic reaction. The state of a transition metal could be studied; the catalytic properties of the metal could be related to its valence state, the dispersity of M^0, its fraction on the surface, etc. Let us cite only a few typical examples. Early IR-spectroscopic and XPS studies of immobilized vinylpyridine complexes of Pd^{2+} demonstrated [193] that the partial reduction $Pd^{2+} \longrightarrow Pd^0$ occurred even at the stage of binding the complex to a polymer. The treatment of the macrocomplex with hydrogen resulted in the almost complete reduction of palladium accompanied by the stabilization of finely dispersed metal cluster particles by the polymer support.

Generally speaking, the mechanism of reduction of metal ions that are chemically bound to a polymer is complicated. It was revealed in detail only for the reaction of $RhCl_3$ with poly(vinyl alcohol) in proton-donor solvents (methanol–water mixtures) as an example; these studies were surveyed elsewhere [194]. At the first step, $RhCl_3$ was coordinated to the hydroxyl groups of the polymer; next, an oxonium product was formed, which was converted into a polymer-bound hydride complex through an alkoxide (Scheme 11).

These reactions provide the formation of a homogeneous colloid, which appears because of the disproportionation of rhodium hydrides with the subsequent particle growth. The structure of the resulting 13-nuclear clusters is a face-centered cubic lattice with the coordination number of the rhodium atom equal to 12. The size of the resulting nanoparticles (0.9–4.0 nm) and consequently, their catalytic properties, can be controlled by varying the reaction conditions and the nature of the medium, introducing additional ligands, and using different macroligands.

A serious effort was made to outline the simplest transformations of MX_n in the course of catalytic reactions [15]. This can be demonstrated using several examples of the metal complex catalysis of polymerization processes.

One of the best studied reactions is the dimerization of ethylene to isomeric butylenes, which occurs under the action of nickel-containing catalytic systems like NiX_2–AlR_xCl_{3-x}. It is characterized by a high efficiency (the total yield of final products is as high as 3–5 kg (g Ni)$^{-1}$); however, the homogeneous catalyst was almost completely deactivated in 1–2 h. Shmidt [195] found that the reason consists in the formation of comparatively coarse Ni^0 (colloid) particles, which are inactive in the reaction:

$$Ni^{2+} \xrightarrow{AlR_xCl_{3-x}} Ni^{+}(+Ni^{0}) \longrightarrow Ni^{0}(\text{colloid}). \quad \text{(XXI)}$$

In heterogenized nickel-containing catalysts, on the one hand, the stabilization of the resulting Ni^0 occurs, which prevents its aggregation, and, on the other hand, Ni^0 is involved in the redox cycle shown in Scheme 12.

Indeed, an examination of intermediates isolated in an inert atmosphere demonstrated [196] that their magnetic susceptibility depends on magnetic field strength.

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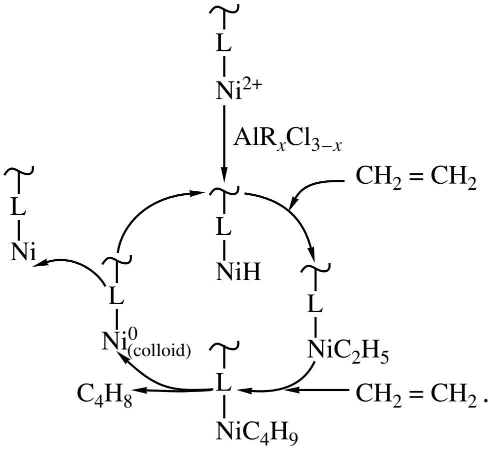
[5] Nevertheless, the reactions of Et_2Zn 1,3-cycloaddition to PhCHO are intensively studied, for example, with the use of enantioselective Lewis acid catalysts like $Ti(OPr)_4$ incorporated in polystyrene matrices [191, 192].

This fact can be interpreted as the presence of ferromagnetic nickel metal along with paramagnetic ions in the products. The fraction of nickel metal significantly increased as the measurement temperature was decreased; on this basis, a conclusion was drawn that, along with coarse (colloid) ferromagnetic particles (>100 Å), smaller finely dispersed superparamagnetic particles (10–100 Å) occurred in the reaction products. Analysis shows (Table 12) that, in homogeneous systems (B), ~30% Ni^{2+} was converted into finely dispersed nickel metal, which cannot be reactivated with an organoaluminum compound, even 30 min after the onset of ethylene dimerization. Under the same conditions, the nickel metal content of a heterogenized system was as low as fractions of a percent. This was due to the fact that polymer-bound Ni^{2+} complexes, which are a magnetically diluted system, cannot freely migrate to form coarse colloid Ni^0 particles because of chemical interactions with the polymer.

Consequently, active centers can be formed as a result of a comparatively simple procedure of binding nickel ions in a macrocomplex so that isolated Ni^0 complexes are primarily formed after reduction, and these complexes are readily involved in a redox cycle (Scheme 12).



Scheme 12.

Moreover, the nature of the so-called bell-shaped dependence of the rate of reaction on the surface density of nickel ions on a macroligand (like the functions described in Section 2.6) was revealed with the use of magnetic techniques [196]. The magnetic susceptibility of intermediates was studied in strong fields (up to 70 kOe) at 4.2–300 K. The distribution of various states of nickel in the course of the reaction of Ni^{2+} with AlR_xCl_{3-x} was derived from the values of magnetic moments as a function of the surface density of metal complexes (for samples containing 0.76 and 1.50% Ni^{2+}). The calculation of the intensity of magnetization using the Brillouin function demonstrated that Ni^0 aggregates with different size distributions were present in both of these catalysts. However, the number of Ni atoms in nanoparticles in the sample with a lower surface density was smaller than that in the sample with a higher surface density by a factor of ~2. Of course, small clusters are more effectively involved in a redox cycle than coarser clusters.

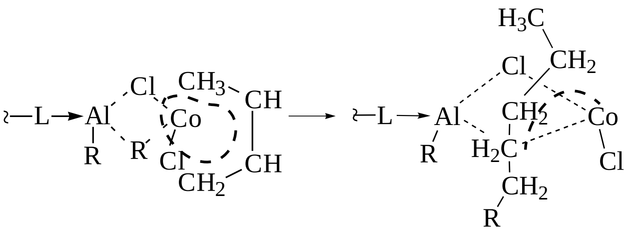
It is of importance that the above transformations are independent of the presence of a dimerized monomer (ethylene) in the system. At the same time, in the polymerization of dienes with cobalt-containing systems, the presence of a monomer plays an important role in the formation of active centers [197]. The concentrations of cobalt in different magnetic states (ferromagnetic (Co^0), diamagnetic (Co^+), and paramagnetic (Co^{2+})) were quantitatively analyzed. It was found (Table 13) that, in the interaction of a $CoCl_2$ macrocomplex with $Al(C_2H_5)_2Cl$ in the absence of a monomer (system aging), ferromagnetic cobalt accounted for about half of the amount added, more than 90% of which was concentrated in relatively coarse (>100 Å) nanoparticles; the remaining cobalt was diamagnetic (Co^+). In contrast to this, in the presence of isoprene, only 6–8% ferromagnetic cobalt was formed; the rest of the cobalt was diamagnetic. This was due to the stabilization of polymer-bound Co^+ at the instant of formation because of inclusion into a π complex, which is active

Table 12. Ferromagnetic nickel content (%) of the products of reactions of PE-*graft*-PA–$Ni(CH_3COO)_2$ (A*) or $Ni(napht)_2$(B**) with $AlEt_xCl_{3-x}$ and C_2H_4

System	*T*, K		
	293	80	4.2
A + $AlEt_2Cl$	0.55	1.20	6.30
A + $AlEt_2Cl$ + C_2H_4	0.17	0.37	
B + $AlEt_2Cl$	27.00	34.00	37.50
B + $AlEt_2Cl$ + C_2H_4	34.00	53.00	
A + $AlEtCl_2$	0.34	0.31	2.30
A + $AlEtCl_2$ + C_2H_4	0.35	0.41	3.80
B + $AlEtCl_2$	31.20	31.60	51.40
B + $AlEtCl_2$ + C_2H_4	14.50	17.60	43.80

*Heterogenized system.
**Homogeneous system.

in polymerization and prevents the further reduction of cobalt:



(XXII)

It is well known that cobalt-containing catalytic systems exhibit maximum activity in polymerization only in the presence of ~20 mol % H_2O with respect to AlR_2Cl. Water additives are of importance only in the reduction of Co^{2+} in the absence of a monomer (in this case, the amount of ferromagnetic cobalt was half as large, Table 13); however, they have almost no effect on the formation of a π complex from diamagnetic Co^+. This refutes published considerations for the role of water as an agent that decreases the reducing capacity of alkylaluminums because of the formation of alumoxanes. By the way, this was also supported by direct experiments on the effect of alumoxanes on the electronic state of cobalt (Table 13). The role of water is likely more significant; it may consist in the action of water as a source of protons on the active center to result in the activation of a metal–carbon bond. Water may also participate in a rearrangement of the geometric structure of the active center and thus produce favorable conditions for the coordination of a monomer to be polymerized.

It was found experimentally that, in polymer-immobilized systems, stable and high activity in polymerization processes is related to a sharp inhibition of concerted reactions in the coordination sphere of a transition metal, which result in the deactivation of active centers [198].

Many of the above examples with the use of various physicochemical techniques demonstrate that substrate enrichment, which was observed in many reactions catalyzed by heterogenized metal complexes, is due to substrate adsorption on the catalyst surface. A superequilibrium concentration of the substrate in domains localized in the immediate vicinity of the active centers is achieved because of electrostatic, donor–acceptor, and π interactions. Thus, it was found using IR spectroscopy [155, 156] that a high local hydroperoxide concentration is produced by ROOH adsorption near active centers at vacant carboxyl groups of the polymer due to hydrogen bonds. Consequently, the process can be controlled by regulating the ratio between vacant functional groups in a macroligand and functional groups bound in a complex (degree of loading). In other words, an additional tool, which is absent from either homogeneous or heterogeneous catalysts, appears in metallopolymeric systems for this purpose. The range of such examples can be considerably extended.

CONCLUSIONS

In a comparison between homogeneous and polymer-immobilized systems, it is common practice to find partial correlations, which describe individual processes at different stages in the development of model systems, in the hope that these partial correlations will be subsequently combined to form a general pattern of the evolution of macrocomplex catalysis. Presently, the accumulation of factual data is still in progress. However, as distinct from the initial stage, which was most frequently performed on a phenomenological level, it is of a quantitative character. Because each section of this review contains its own conclusions and predictions, only the most pronounced trends will be considered below.

Hybrid polymer–inorganic catalysts, including those prepared by the incorporation of components at the stage of a sol–gel synthesis, have come under intense development in the last few years [194, 199]. Various approaches to the heterogenization of molecular homogeneous catalysts are summarized in a recent review [200]. Considerable attention has been given to the laboratory modeling and scaling of catalytic processes with the use of immobilized catalysts and to a change from batch processes to continuous processes (including continuous suspension reactors and plug-flow reactors, in which exothermic process control can be performed more easily, the degree of safety is higher, etc.) [201]. The methodology of laboratory syntheses is developed with the application of combinatorial chemistry to immobilized catalysts, including multicomponent catalysts [202]. There is a trend toward the use of macrocomplex supports as nanoparticles (for example, see [47, 194, 203]), which can also be prepared with the participation of a catalyst or cocatalyst. Thus, metallocene catalysts for olefin polymerization are prepared with the use of chemically functionalized nanoparticles (such as alumoxane *para*-hydroxybenzoate) as strictly homogeneous macroligands [204]. In combination with zirconocene, such a catalyst exhibits a high initial activity (~3000 kg PE (mmol Zr)$^{-1}$ h^{-1}). With consideration for a possibility to control important process characteristics such as the particle size and granulometry of resulting polymers [205, 206], it becomes evident that this line of investigation is promising. Immobilized metal chelates find use in a new area—atom transfer radical polymerization (ATRP) [207, 208]. The possibility to perform coordination polymerization in water is yet under examination [209, 210]. It is likely that hydrophobic macroligands can be the main building element.

The development of reusable metallopolymeric catalysts for the following processes is also of interest: the metathesis of olefins (ruthenium macrocomplexes [211]), the oxidation of thiophene (Pt^{2+} complexes with

Table 13. Magnetic states of cobalt in the reaction products of catalyst components

System	Color	State* of Co, %		
		ferromagnetic	paramagnetic	diamagnetic
PE-*graft*-PVP · $CoCl_2$ + $Al(C_2H_5)_2Cl$	gray	50	–	50
The same + H_2O	–	25	–	75
The same in air after three weeks	blue	–	100**	–
PE-*graft*-P4VP–$CoCl_2$ + alumoxane + monomer	–	–	100	–
PE-*graft*-PBP–$CoCl_2$ + monomer + $Al(C_2H_5)_2Cl$	gray	8	–	92
The same in air after three weeks	blue	–	100**	–

* The fraction of paramagnetic Co was calculated based on μ_{eff} = 4.8 V, and the fraction of diamagnetic Co was obtained by subtracting the amounts of paramagnetic and ferromagnetic components from the total content.

** μ_{eff} = 5.18 V.

oligomer ligands [212]), the selective oxidation of disubstituted phenols and benzoquinone (Cu^{2+} macrocomplexes [213]), the reductive carbonylation of nitroaromatic compounds with carbon monoxide (high-performance metallopolymeric catalysts based on Rh^+ [214]), the asymmetric epoxidation of olefins (polymer-immobilized salen complexes of manganese or chromium [215]), etc. One of the recent advances along these lines is self-organized neutral nickel-containing catalysts for olefin polymerization [216], which are highly active (10^5 g PE (mol Ni)$^{-1}$ h^{-1}) even without a co-catalyst. These are allyl-functionalized $Ni(Ph)(PPh_3)$ complexes with phenyliminophenolate ligands. Their principle of self-immobilization is similar to that shown in Scheme 6. Such catalyst are probably the first members of new-generation heterogenized catalysts.

Many catalytic reactions in which heterogenized catalysts are widely used (for example, the photochemical decomposition of water, the electrochemical stimulation of catalytic processes, the fixation of molecular nitrogen, the cross-coupling reactions of aryl halides with alkenes (the Heck reaction), etc.) are beyond the scope of this review. Probably, these problems will be analyzed in the future. Note that heterogenized metal complexes are highly organized systems [217]; they are the subject matter of supramolecular chemistry. The use of the methodology and organization principles of supramolecular chemistry can provide additional information for understanding the operation mechanisms of these systems.

In conclusion, note that a recent special issue of *Chemical Reviews* [218], which contains 21 review articles, is devoted to an interdisciplinary problem of recoverable catalysts and reagents. Each of the reviews is deals practically with particular aspects of the design of polymer-immobilized catalysts or with special features of catalysis with their participation. This indicates that heterogeneous catalysis by metal-containing polymers is currently under intensive development.

ACKNOWLEDGMENTS

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