Translated from *Uspekhi Khimii* **61** 257–292 (1992) U.D.C. 541.64:66.097+661.8

Specific characteristics of catalysis by polymer-immobilised complexes†

A D Pomogailo
Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka

ABSTRACT. **The most important factors which affect to different extents the activity and selectivity of immobilised complexes in numerous processes have been examined. Attention has focussed particularly on a discussion of the factors responsible for the increase in cooperative stabilisation of active centres in such systems in comparison with homogeneous systems. The basic facts about polyfunctional catalysis based on immobilised complexes are presented. Certain questions and the potential for further advancement in this direction are discussed.**

Bibliography, 107 references.

Contents

I.	Introduction	133
II.	Ligand exchange in metallo-polymeric systems	134
III.	Characteristics of electron transfer reactions in metallo-polymeric systems	135
IV.	Protective functions of the macroligand	136
V.	Local concentration effects in metallo-polymeric catalysis	137
VI.	Problems of homogeneity and evolution of active centres in the immobilised systems	138
VII.	The effect of the surface density of immobilised metallo-complexes on their catalytic activity	140
VIII.	Characteristics of the effect of temperature on the catalytic properties of immobilised complexes	141
IX.	The contribution of energy of non-equilibrium configurations of the chain to catalysis	144
X.	Cooperative stabilisation of active centres in the immobilised systems	145
XI.	The selectivity of immobilised catalysts	148
XII.	The problem of polyfunctional catalysis	148
XIII.	Conclusion	150

I. Introduction

A simple and promising idea, based on the knowledge of the chemical or physical forces which bind metallo-complexes (MX_n) with an organic or inorganic microligand, has promoted the development of many catalytic processes and has become the main factor for subsequent convergence of homogeneous and heterogeneous catalysis. The relevance of the concept itself and the intensity of the investigations have led to the creation of an essentially new avenue of catalysis with its own constructive principles and techniques.

There are two main objectives in the immobilisation of metallo-complexes. The first is the creation of stable catalysts with high activity, selectivity and reproducibility (as in homogeneous systems) and moreover readily separable from the reaction products and recoverable (as in heterogeneous contacts). Thus it was suggested initially that from the practical standpoint such systems should combine the advantages and eliminate the disadvantages of traditional catalysts.

In scientific terms the second objective is no less important, i.e. to construct catalysts possessing a high concentration of active centres with known structures which are also suitable for the analysis of their evolutionary transformations during the catalysed reaction. By resolving this question it would be possible to move towards a scientifically founded selection of catalysts and to predict their catalytic action.

It is necessary immediately to make the proviso that, despite significant advances in this field, it has been found much more difficult than anticipated to resolve the tasks set. Firstly, it was found that it is not easy to obtain isostructural metallo-complexes which can be firmly retained on the surface under the conditions of a catalysis. Secondly, along this route a multitude of specific difficulties arise which are associated with the behaviour of immobilised complexes in heterostructural catalytic reactions. The causes of the increase in rate of certain processes concomitantly may be the causes of the decrease in rate of other processes. Thirdly the nature of such systems which is determined by many factors hinders the prediction of the behaviour of system MX_n, the polymeric support during the catalytic reaction, and the preliminary assessment of the effect of the conditions under which this reaction takes place on all possible transformations of the components. Macromolecular effects including the effect of the microenvironment (local polarity, the neighbour effect, the effect of the size of the polymeric globule, the degree of substitution of the functional groups L, etc.) the electrostatic properties of the ionic groups bound with the polymeric chain (polyelectrolyte catalysis), isolation of active centres (dilution effect), local concentration effects (functional groups during the spherical binding of the chains on one side and the substrate close to the polymeric globule on the other), and the effect of polydentaticity, etc. play a particularly important role. When insoluble polymers are used as supports, it is necessary to take into account the biographic heterogeneity of the surface, and the swelling and migration of the attached complexes in the course of the reaction, etc. The situation becomes much more complicated if the attached complex undergoes partial dissociation during the reaction and if catalysis is achieved simultaneously with mobile and immobile particles.

The author considers that the present review summarises the most important features of catalysis by immobilised complexes, the synthesis and structures of the latter having been the subject of a large number of reviews and monographs.[1–5]

† The first five articles are a continuation of No. 12 in 1990 concerning problems of catalysis.

II. Ligand exchange in metallo-polymeric systems

Almost all studies have shown that immobilised systems have higher stability than normal catalysts even under conditions which are comparatively severe for metallo-complex catalysts (increase in temperature and pressure, highly polar solvents, active substrates). Since the metallo-polymers are formed in an enclosed microvolume in which quite a large number of macromolecules, functional groups, and different types of particles (MX_n, electrons, protons, radicals, oligomers, etc.) is involved, on the whole the state of the metallo-polymeric system is characterised by a combination of concentrations of free functional groups, and also complexes, which may contain different numbers of ligands of each type which may occupy various positions in the macromolecule.

The two main reasons leading to a decrease in the cooperative stabilisation and even to the disruption of the immobilised complexes during catalysis are their instability:

$$\widetilde{L}\text{—}MX_n \overset{K'}{\rightleftharpoons} \widetilde{L} + MX_n, \quad \widetilde{L}\text{—}MX_n + S \overset{K''}{\rightleftharpoons} \widetilde{L} + MX_nS$$

(S is the solvent, substrate, co-catalyst, or specially introduced additive). The overall contribution of these processes is reflected in the decrease in content of the metal on the support or in the concentration of the metal passing into solution. The specific contribution of the chemical instability of macrocomplexes is usually higher than thermodynamic instability. In systems which are used to polymerise olefines,

$$MX_n \cdot D \overset{K'}{\rightleftharpoons} MX_n + D$$

$$MX_n \cdot D + AlR_xCl_{3-x} \overset{K}{\rightleftharpoons} MX_n + D \cdot AlR_xCl_{3-x}$$

when $MX_n = VCl_4$, D = MMA or $AlR_xCl_{3-x} = AlEt_3$ in benzene at 293 K, $K' = 1.8 \times 10^{-3}$ mol l^{-1}, while $K = 8.7 \times 10^2$.[6] Replacement of the ligand environment by the polymeric environment leads to an increase in both the thermodynamic and chemical stability of the complexes. Thus by using the stopped-flow technique the kinetics of the pseudo-first order exchange reaction (pH 9.3–11.0; 298 K; excess of EDTA) was studied,[7]

$$Cu(2+)\text{-PVC} + EDTA \rightarrow Cu(2+)\text{-EDTA} + PVC$$

the kinetic equation of which has the following form:

$$-\frac{d[Cu(2+) - PVC]}{dt} = k_1 \frac{[Cu(2+) - PVC]}{[PVC]} = k_2 \frac{[Cu(2+) - H - PVC]}{[PVC]},$$

and $k_1 = 3.62 \times 10^{-3}$ mol sec^{-1}, $k_2 = 3.68 \times 10^4$ mol sec^{-1}. The ligand exchange occurs by two mechanisms, either by H^+ attack (from EDTA) with the formation of the intermediate complex Cu(2+)-H-PVC and its subsequent dissociation, or by solvolysis involving water.

One of the characteristic examples of exchange reactions involving low- and macromolecular ligands is the exchange of the axial ligand in benzylcobaloxime and in cobaloxime $Co(DH)_2$ covalently linked with chloromethylated polystyrene (PS):[8]

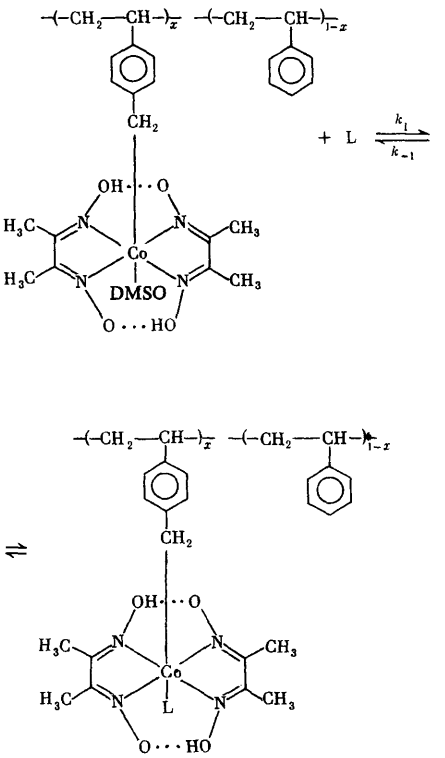


Table 1. Rate constants of ligand exchange in $RCo(DH)_2DMSO$.[8]

R	L	k_1, $l\,mol^{-1}\,sec^{-1}$	k_{-1}, $l\,mol^{-1}\,sec^{-1}$	$K \cdot 10^{-2}$
Polymer	SCN^-	$1 \cdot 10^3$	4.8	2.1
Benzyl	SCN^-	$1.2 \cdot 10^3$	15	0.8
Polymer	Py	23.6	$2 \cdot 10^{-3}$	118
Benzyl	Py	16.5	$1.7 \cdot 10^{-2}$	9.8

Although the Co(3+) complexes are comparatively resistant to substitution, the presence of the macromolecular ligand promotes a more rapid substitution of the axial ligand in the *trans*-position (solvent was DMSO or DMSO + benzene). It is apparent from Table 1 that the rate constants of the forward reaction in the systems compared are similar, although the constants of the reverse reaction for the dissociation of the complex which contains the low molecular weight *trans*-ligand is approximately 3 ($L = SCN^-$) and 9 (L = Py) times higher.

Thus the higher values of the equilibrium constants of ligand exchange in the metallo-polymer systems in comparison with the low molecular weight benzyl complexes may be attributed to the smaller

values of the rate constants for the reverse reactions. This may be associated both with the higher local concentration of cobaloxime in the polymer matrix in comparison with its concentration in the volume of the DMSO solvent and also with steric hindrances which create a macrochain, hampering ligand transport from the polymeric "cells" and promoting its recombination. In the DMSO-benzene mixed solvent with increase in the latter the polymeric globule expands, as a result of which the effect of these factors decreases. Increase in this characteristic viscosity is accompanied by a decrease in the rate constant of the forward reaction and an increase in the rate constant of the reverse reaction (Fig. 1). The higher rate constant of the ligand exchange (L = Py) in polymer-bound cobaloxime (in DMSO) was due to great changes in entropy.

R	ΔF, k J mol^{-1}	ΔH, k J mol^{-1}	ΔS, a.u.
Polymer	−17.6	−38.6	−16
Benzyl	−16.4	−67.2	−40

Similar results have been obtained in studies of other systems. One should note that the calculation of the standard potentials and observed rate constants of outer-sphere exchange involving Co(2+) and Fe(3+) ions taking into account the change in structural parameters of the macrocomplexes indicates that the systems examined are in many ways similar to metallo-protein complex systems.[9]

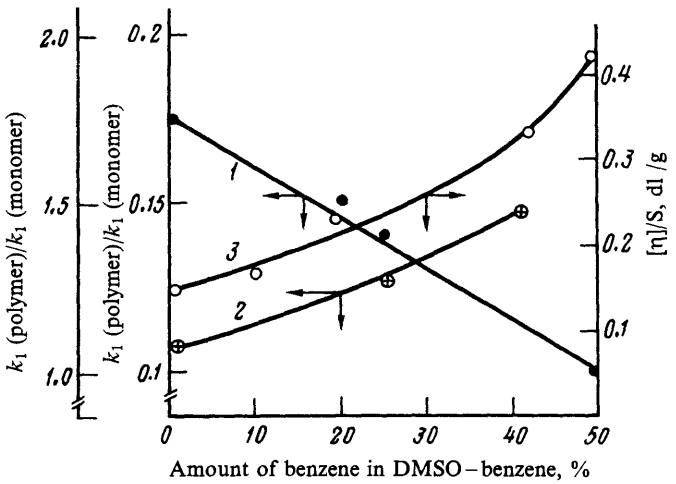


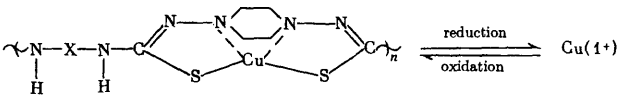
Figure 1. Variation in the relative rate constants of the coordination of pyridine with cobaloxime k_1 (*1*) and k_{-1} (*2*) and the characteristic viscosity of the macrocomplex (3) as a function of the composition of the DMSO-benzene mixture.[8]

Hence the replacement of a low molecular weight ligand environment by a polymeric environment hinders the entry of the reagents into the coordination sphere of the transition metal and causes its additional polarisation in the heterogeneous electrostatic field of the ligands, which also confers increased stability upon the macrocomplex. The ability of the coordinatively saturated metal atom in the macrocomplex to form coordination vacancies should have significant value for ligand exchange. They may arise at the immobilisation stage owing to the prevention of dimerisation of the metallo-complexes or on account of the easy disruption of M–M bonds, as a result of the reduction of the transition metal, the effective adsorption of excess of ligand by the matrix, etc.

III. Characteristics of electron transfer reactions in metallo-polymeric systems

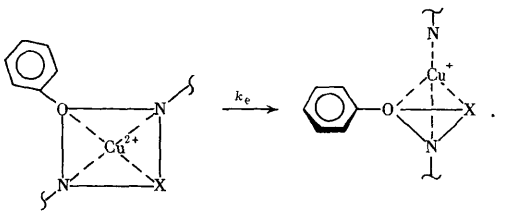
Electron transport in metallo-polymeric systems determines the rate of many processes, and is almost always the slowest stage of the catalytic act. Such an intramolecular process is very sensitive to the active centre environment, i.e. the nature of the ligand, the solvent, the ionic strength, pH, etc. It is accompanied by a rearrangement of the complex and by conformational changes in the polymer.

The primary structure of the support, the distribution of the redox-centres, the charge density, and the polarity of the polymer domains have a strong effect on electron transport in macromolecular formations. The most frequent redox transformations occur in the immobilised systems Fe(2+) ⇄ Fe(3+), Cu(1+) ⇄ Cu(2+), Co(2+) ⇄ Co(3+), and Mo(5+) ⇄ Mo(6+) and certain others. The redox processes sometimes occur even at the metallo-complex immobilisation stage,[5] and they most often occur in oxidation reactions. Thus the chelate complexes of Cu(2+) catalyse the oxidation of aldehydes to acids or cyclohexanol to cyclohexanone. In this case Cu(2+) is reduced to Cu(1+).[10]



In turn the Cu(1+) ion in the polymeric complex is oxidised to Cu(2+) in the reduction reactions of nitrobenzene to azoxybenzene, nitrocyclohexane to cyclohexanoxime, 1,4-benzoquinone to hydroquinone, and $KMnO_4$ and MnO_2. Such a conjugated process is named the "ping-pong" mechanism.

To determine the specific characteristics of the polymeric environment, the oxidation of Cu(1+) complexes with polyvinylimidazoles (PVI) by molecular oxygen was compared with their imidazole analogue.[11] The study was conducted using the stopped-flow technique in buffer systems (Table 2). A higher enthalpy and a lower entropic factor is typical of the oxidation of polymer complexes. The differences in the kinetic and activation parameters are associated with conformational transformations of the macroligand in the course of the redox reaction which lead to a change in bond lengths and the angles between them in the Cu(1+) and Cu(2+) complexes:



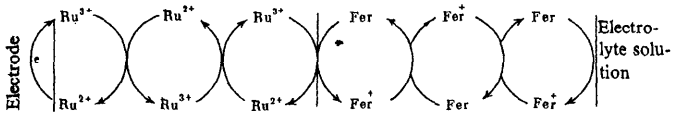
The occurrence of conformational transformations during the oxidation were demonstrated by viscosimetric measurements.

Similar patterns are also found in the redox cycles $Co(3+) \rightleftarrows Co(2+)$. For example the outer-sphere reactions of Co(3+) macrocomplexes with poly-4-vinylpyridine (P4VP), polyethylenimine (PEI), polyvinylimidazole (PVI) and Fe(2+) complexes with electron transport occur at lower rates than the reactions of Co(3+) complexes with low molecular weight ligand-analogues.[12,13] The opposite situation is found, when hydrophobic interactions occur between the polymer ligand and Fe(2+). This is associated with an increase in the local concentration of the reducing agent in the macrocomplex (see Chapter V). Thus addition of styrene sulphonate increases the rate of reduction of Co(3+) in the P4VP-complex 10–30-fold in comparison with the pyridine complex.

Table 2. Kinetic and activation parameters of the oxidation of Cu(1+) complexes at 298 K.[11]

Ligand	pH	$k_{eff} \times 10^2$, l mol^{-1} sec^{-1}	$\Delta F^{\neq}$, kJ mol^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1}, deg^{-1}
Poly-1-vinylimidazole	4.7	2.7	61.3	48.3	−44.1
	4.3	14.0	57.1	29.4	−92.4
Poly-4(5)-vinylimidazole	6.0	0.10	66.0	61.8	−14.4
	4.7	0.26	64.7	57.5	−24.0
Imidazole	8.0	4.9	60.5	13.4	−154.6

Metallo-complexes bonded to the polymers are quite extensively used in electrocatalytic redox processes. With this objective, by immobilising metallo-polymers on electrodes, chemically modified electrodes and also bilayer polymeric electrodes incorporating two types of electroactive films are obtained. In such composites the outer layer is subjected to the action of the substrate, while the inner layer is in direct contact with the surface of the electrode. The scheme for such a bilayer electrode is shown below:[14]



At a particular electrode potential the outer film of poly-[$Ru(Dipy)_3^{2+}$-vinylpyridine] participates in the redox reaction with polyvinylferrocene (PVFer):

$$Poly[Ru(Dipy)_3]^{2+} + PVFer \rightarrow poly[Ru(Dipy)_3]^{+} + PVFer^{+}.$$

At high potentials the reduction of the outer and oxidation of the inner films occur.

It will be shown below (see Section VI) that the extent of chain loading (the extent of coordination of functional groups f) is found to have a significant effect on the specific catalytic activity (SCA) of the macrocomplexes. The extent of chain loading also affects the activation parameters of the electron transfer reaction (Table 3). With increase in f the values of $\Delta F^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ decrease, which may be associated with the state of the polymer chain, and particularly with its elongation (as indicated by the increase in the characteristic viscosity) and hence with a change in the charge density on the polymer chain.[13] The reverse oxidation reaction $Co(2+) \rightarrow Co(3+)$ may be both more rapid and also slower than with the low molecular weight reagents.

Table 3. Activation parameters of the electron transfer reaction and the change in viscosity in the Co(3+).PVI–Fe(EDTA)$^{2-}$ system at pH 5 and 303 K.[13]

f	$[\eta]$, dl mmol^{-1}	$\Delta F^{\neq}$, kJ mol^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, e. e.
0.10	2.26	51.7	144.5	72.8
0.12	2.33	50.4	136.1	67.4
0.15	2.86	49.1	106.3	45.0
0.25	3.25	46.6	97.4	39.3
0.32	3.34	45.3	94.5	30.3
N-vinyl-2-methylimidazole	–	52.0	31.9	15.6

Of the other comparatively numerous examples confirming the concepts being developed, redox-reactions involving molybdenum macrocomplexes should be mentioned, i.e. cyclic redox-processes of peptide Mo(5+) complexes immobilised as a chloromethylated copolymer of styrene with divinylbenzene (CSDVB) (a reductase or oxidase analogue),[15] and also redox reactions of cystein thiolato dioxomolybdenum(6+) centres attached to polyethyleneglycol (molybdo-oxidase model).[16]

It is important that repetition of electron transport acts does not cause changes in the multinuclear state of Cu, Co, and Mo complexes, etc., whereas the macroligand reorganisation relates to certain of the most important factors influencing the reaction with electron transfer in the polymer matrices.[17]

IV. Protective functions of the macroligand

One of the protective functions of the macroligand is the creation of diffusion barriers, which impede the deactivation of the active centres or interaction of the substrates with reactive reagents or microadditives in the reaction medium (for example H_2O, O_2, etc.). Thus to protect high-spin Fe(2+)-porphyrin complexes, which are oxidised in solution to low-spin Fe(3+)-complexes and which thereby bind O_2, their combinations with polymeric ligands in aqueous solution are used (polymers and copolymers based on 1-vinylimidazole, 1-vinyl-2-methylimidazole, 1-vinylpyrrolidone, water-soluble copolymers based on quaternised 4-vinylpyridine, etc.).[18] Such an approach is more effective than the creation of steric hindrances around the active centres, and the use of low temperature, etc.

There have been successful attempts to construct on this basis synthetic O_2 carriers for reverse oxidation in water and other proton media. With this objective the metalloporphyrins are bonded to the hydrophobic regions of water-soluble polymers (oxygen protection).

The spatial stabilisation of active centres also plays an important role. The presence of a hydrophobic environment around them reduces or even excludes the possibility that oxodimers are formed in the presence of O_2 and in the subsequent irreversible oxidation of M^{n+}.[19]

The protective function of the macroligand which is realised for example in the oxidation of phenols by molecular O_2 ensures the protection of the catalytically active binuclear Cu(2+) complex.[20,21] A similar stabilising effect is directed against the so-called substrate inhibition. The mechanism of the reaction incorporating the transfer of two electrons from the substrate to oxygen in the molecular orbital system of the metal is more easily achieved in immobilised binuclear Cu(2+) complexes.

We shall examine certain other variants in which the protective function of the macroligand is exerted. A major defect of traditional heterogeneous catalysts for the isotopic exchange of hydrogen in the liquid phase is their extreme instability caused by the capillary condensation of water and by blocking of the catalyst. To prevent such phenomena different variants of its hydrophobisation have been elaborated, including the use of polymers. Such an approach may be regarded as the microencapsulation of the catalyst in the polymer. Thus, the T−H-exchange catalyst was obtained by immobilising MX_n on CSDVB, and polytetrafluoroethylene (PTFE) is most often used for this purpose.[22] Regeneration involves heating the catalyst to remove water droplets from the pores. The polymer matrix plays such a role by ensuring the protection of diazo-complexes from the action of moisture thereby increasing their life-time even at room temperature.[23]

An unusual hydrophobic protection was used in relation to unstable Mo(5+) complexes. Being immobilised on chloromethylated CSDVB modified with peptide groups, they become stable within several days in the presence of H_2O and O_2.

Another mechanism of the protective action of water and even of the increase in rate of catalytic processes for the water is realised when the water is bound by hydrophilic polymers.[24] For example, on account of the solvate effect observed in the presence of polymers (polyethyleneimine propionate, poly-4-vinyl-N-ethylpyridinium bromide, etc.) there is a 10^5-fold increase in the rate of polyelectrolytic catalytic hydration of *tris*-(oxalato)cobalt in binary mixtures of water with DMSO or DMF. This is associated with the selective adsorption of H_2O from a mixture of solvents. The preferred hydration of the complex close to the polymer on the one hand leads to the localisation of anionic reagents around this polymer, and on the other hand leads to repulsion of H_3O^+.

Hydrophobic protection plays a major role in reactions catalysed by metallo-organic compounds (or by organometal intermediates formed). Polar media are also used for these purposes. This is possible because in many reactions the globules of the functionalised macromolecules with attached catalytic centres surrounded by solvents fulfil the function of isolated microreactors.[25,26]

V. Local concentration effects in metallo-polymeric catalysis

The increased activity of immobilised catalysts may be caused both by an increase in the local concentration of substrate and active forms in such microreactors, despite possible steric hindrances as the reagent approaches the catalyst and during the transport of the reaction products. The super-equilibrium substrate concentration in domains situated adjacent to the active centres is achieved by electrostatic, donor-acceptor, and π-interactions involving active regions and functional groups (L) of the polymers. There are numerous examples of such effects. Thus on hydrogenation of styrene in the presence of Pd(0) bonded to functionalised CSDVB (4−6% DVB) the rate of the reaction increases, if the L group promoted the formation of π-complexes with the substrate.[27] The activity of allylacrylate correlated with the π-acceptor and polar properties of L. The $-NO_2$ and $-OMe$ groups promote the formation of molecular associates with the substrates, while $-OH$, $-NH_2$, $-NR_3$, and $-CH_2OCH_2$ groups react with the substrate owing to polar effects. Polymers with a hydrophobic surface retard the rate of hydrogenation of nonpolar substrates. The introduction of 2,4-dinitrophenyl groups even at a level of 7% causes a marked reduction in the rate of hydrogenation of 4-vinylcyclohexane. The high activity of Rh(1+) on phosphinated CSDVB in hydrogenation reactions of polynuclear heteroatomic compounds is associated with an increased substrate concentration close to the metallo-centre.[28]

Differences in the polarity of the polymer and solvent lead to an increase in substrate concentration in the polymer in comparison with the reaction volume. When a more polar solvent is used, the nonpolar substrate is able to penetrate more readily into the polymer phase owing to the polarity gradient. Transport of the polar substrate into the nonpolar sphere is made difficult, which is reflected in the decrease in rate of the reaction. The form of the catalyst particles (granules, powder, film, fibre) also has an influence.

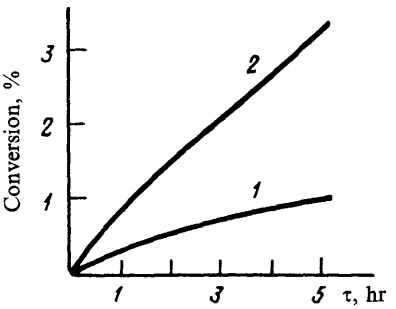


Figure 2. Kinetic curves of the oxidation of ethylbenzene in the presence of macrocomplexes not built (*1*) and built (*2*) on ethylbenzene.[30]

The functional groups may be involved not only in the binding of MX_n but also in the catalytic process itself by protecting the active centre from microadditives and catalyst poisons or by promoting secondary reactions. In principle the interaction of L with the substrate may be accompanied by more profound transformations such as protonation, ionisation, and alkylation, and sometimes also by quaternisation and oxidation in reduction reactions. Such processes apparently play a particularly significant role with metallo-complexes immobilised on strongly cross-linked polymers in which the proportion of the vacant L is comparatively high. However they may occur also in reactions in which grafted macroligands are involved. Thus from a kinetic study of the oxidation of cyclohexene by molecular O_2 in the presence of Co(2+), bonded to PE-grafted-poly(acrylic acid) (PE-pr-PAA) it was concluded that a high

concentration of the peroxide being formed is created close to the surface of the heterogeneous catalyst, and that peroxide decomposition provides the major contribution to the initiation of chains in the developing process. Close to the catalytic centres, the cobalt ions on the polymer, there are vacant carboxylic groups which, owing to the formation of hydrogen bonds, are able to adsorb ROOH molecules, thereby creating their high local concentration. Apparently by regulating the concentration of the vacant L, it is possible to control the course of the reaction, i.e. in the immobilised systems one more control level appears which has no analogues in homogeneous or heterogeneous catalysis.

A new phenomenon of structural adjustment of the active centres on the substrate has been observed in the liquid-phase oxidation of ethylbenzene and xylols by molecular oxygen.[30,31] This process involves the formation of soluble Co(2+) complexes, for example with the copolymer of the diethyl ester of vinylphosphonic acid and AK in the presence of the substrate (ethylbenzene) or α-phenylethylhydroperoxide. The specific structural adjustment for the reacting substances is then fixed by intermolecular cross-linking of the polymer support by *N,N'*-methylene bis-acrylamide with subsequent removal of the template substrates from the cross-linked formations. Such an adjustment markedly increases the activity and selectivity of the catalyst (Fig. 2).

Cases are known in which a "hyperequilibrium" concentration of the product forming in metallo-polymeric particles is attained. Thus on polymerisation of ethylene by gel-immobilised systems,[32] after contact with monomer the catalyst particles swollen in the solvent undergo further swelling and PE accumulates within each particle. The "hyperequilibrium" swelling of cross-linked catalyst particles is caused by the accumulation of polymer within the previously created three-dimensional network of the polymeric support. The energy of extending such particles by the value ΔV (additional increase in volume owing to the "hyperequilibrium" swelling of the three-dimensional structure of the original gel) is equal to

$$A = \int_{V_p}^{V_{ст}} P(V)\mathrm{d}V,$$

where P is the swelling pressure, V_{st} is the particle volume in the stationary working state, V_p is the volume of the particle stably swollen in the pure solvent, and $\Delta V = V_{st} - V_p$. This work is accomplished owing to the free energy of ethylene polymerisation and causes additional stress to the elastic network of the support. Apparently in such systems a specific mechanism also operates to limit material chains. The swelling pressure acting on the growing macromolecules strives to "force" it out on the catalyst granule† (mechanical activation of the elementary act).

Thus the nature of the macrocomplexes is such that they behave as a special phase in which the concentration of reagents is higher than in the volume of the solution (or in the gas phase in the case of gas phase processes).

† It is assumed that a certain prolonged stress arises also at the "growing point" of the macromolcule, i.e. at the metal–carbon bond. It may be the source of the increase in probability of chain restriction.

VI. Problems of homogeneity and evolution of active centres in immobilised systems

The frequently higher specific catalytic activity of the immobilised complexes may be attributed to structural defects in the coordination centres and to unsaturation, which promotes coordination of the substrate, and also to cooperative effects. Many of these factors may be taken into account during the construction of the immobilised catalysts. For example the composition of bonded complexes may be controlled to a certain extent by selecting the L:M ratio. In most reactions between the macroligand and MX_n the equilibrium is established almost immediately after the components are mixed, but sometimes a prolonged period is required for this to be attained, particularly if the macroligand is polyfunctional. In certain cases the total rearrangement of the complex occurs more slowly than the catalysed reaction. Since the structural homogeneity of the complex is important for ensuring high and stable activity, it becomes essential to take into account the rate of such a rearrangement.

The formation of the required structure determined by the electronic configuration of the transition metal ion is also dependent on the conformational exchange in the macroligand which leads to the creation of the appropriate orientation. Such an exchange is associated with energy losses which are greater the more the chain conformation differs from the required conformation. In this sense the "pliability" of the macromolecule is important, and therefore the macroligand cannot be regarded as a certain set of independent functional groups.

Furthermore the polymeric matrix may bind and stabilise coordinatively unsaturated metallo-complexes.[33] The rate of rearrangement (relaxation) of the active centre is low because of the large size of such formations, especially in the case of strongly cross-linked matrices. These processes become complicated in the transition from homogeneous to heterogeneous and especially to enzyme-mediated catalysis.[34] Therefore in a catalysable reaction a nonequilibrium configuration of active centres (and their hyperequilibrium concentration) becomes possible. In heterogeneous catalysis in this case nonequilibrium phases may arise.

During catalysis by immobilised complexes not only the total content (concentration) of the attached MX_n but also its distribution profile in the polymeric matrix (topography) is of great importance. Numerous observations indicate the static distribution of the transition metal on the support. Analysis and calculation of the topography of immobilised complexes opens one of the avenues for increasing the efficiency of the catalysts. Optimisation is achieved by moving the active centres on to the surface (or on to the thin layer adjacent to the surface layer) of the polymeric support.[35] When such catalysts are constructed their main role is attributed to the topography of the functional groups of the macroligand and its accessibility. The latter is determined by the contribution of the polymer chain during a change in the microenvironment of functional groups, viscosity and density of the cross-linkages in gel and microgel particles and by the thermodynamic compatibility of the polymer matrix and reaction medium and by the polymeric support pore structure and their size distribution (including in the swollen state). On account of a certain mobility of the polymeric chains on the surface and at the boundary of the section of the polymer-medium phases, reorientation and rearrangement of the macromolecular fragments occur,[36] as a result of which the polar groups are found to be turned to the side of the polar phases or vice versa. Moreover the nature of the distribution may also affect even

the properties of the functional groups. For example the surface sulpho-groups possess lower acidity than groups situated within the polymer mass.[37] The interaction between adjacent dicarboxylic groups (a copolymer of maleic acid and methylvinyl ether) leads to the emergence of alternating singly and doubly charged dicarboxylic groups, etc.[38]

When coordinatively unsaturated Rh(3+) complexes situated within the polymeric globules are reduced, they form multinuclear associates, which are active centres for photoinduced catalytic evolution of H_2 from H_2O (the rate of the process reaches 640 mol H_2/g-atom PRh. h^{-1}) and there is no reduction in activity after 6000 cycles).[39]

The nature and topography of the functional groups have a significant effect on the migration processes. We shall follow this process using two examples.[40] Active centres of ethylene dimerisation with homogeneous "nickel" systems are formed from Ni(2+) compounds via a series of transformations:

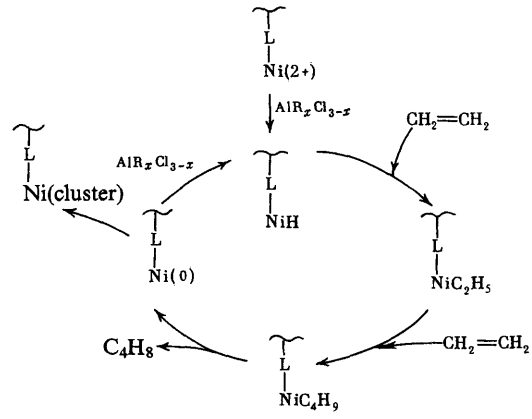
$$\begin{array}{c} Ni(2+)+AlR_xCl_{3-x}\rightarrow Ni(1+)+Ni(0)\rightarrow(\text{colloidal}) \\ \downarrow AlR_xCl_{3-x} \\ Ni(2+)+Ni(0)\ \text{etc.} \end{array} \qquad (1)$$

The average productivity of the active complex ("chain length") is $(2-3)\times 10^3$ moles of monomer per mole of σ-alkyl (or hydride) Ni(2+) complex. It is important that regeneration of the active centres is ensured through the presence of Ni(0) complexes into the redox ring (1). However in homogeneous systems even at 333–343 K the system is essentially totally deactivated within only 1–2 h. The role of the polymeric support in the Ni-immobilised catalysts is reduced to the stabilisation of active centres and to the prevention of the association of Ni(0) in the course of the reaction.[41] In fact the magnetic susceptibility of the isolated products is dependent on the intensity of the magnetic field apparently because of the presence in them of ferromagnetic nickel in addition to the paramagnetic ions.

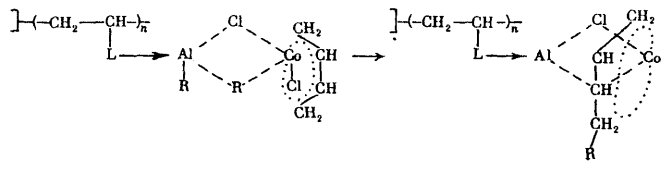
Table 4. Content of ferromagnetic nickel (%) in products of the interaction of $Ni(CH_3COO)_2$ with PE-pr-PAK (A) and Ni(naphthenate)$_2$ (B) with $Al(C_2H_5)_xXCl_{3-x}$.[41]

System	Measurement temperature, K		
	293	80	4.2
(A)+$Al(C_2H_5)_3$	0.34	0.56	2.4
(A)+$Al(C_2H_5)_3$+C_2H_4	0.48	0.50	1.4
(Б)+$Al(C_2H_5)_3$	1.2	2.1	
(A)+$Al(C_2H_5)_2Cl$	0.55	1.2	6.3
(Б)+$Al(C_2H_5)_2Cl$	27	34	37.5
(Б)+$Al(C_2H_5)_2Cl$+C_2H_4	34	53	
(A)+$Al(C_2H_5)Cl_2$	0.34	0.31	
(Б)+$Al(C_2H_5)Cl_2$	31.2	31.6	51.4
(Б)+$Al(C_2H_5)Cl_2$+C_2H_4	14.5	17.6	43.8

The proportion of the latter increases significantly with decrease in the temperature of the measurement, which can be attributed to the presence of finely dispersed superparamagnetic particles of smaller size (10–100 Å)[42] among the products of the reduction in addition to the large ferromagnetic particles (>100 Å). On dimerisation of the ethylene by homogeneous systems (B) within only 0.5 h ca. 30% of the Ni(2+) ions are converted into finely dispersed metallic nickel, which is unable to undergo reoxidation (Table 4).[41] Under these conditions the content of metallic nickel in immobilised system (A) is only a fraction of a percentage. In the attached complexes constituting a magnetically diluted system, aggregations of Ni(0) particles should precede their migration over the surface of the support. The functional surface coat apparently prevents such a migration as a result of which during the formation of active centres isolated Ni(0) complexes are formed which have the ability to become involved once more in the redox-cycle even in the absence of substrate (ethylene):



When this is absent in the PE-pr-P4VP.$CoCl_2$–$Al(C_2H_5)_2Cl$ system, the presence of the substrate (on polymerisation of butadiene or isoprene) significantly affects the formation of ferromagnetic cobalt.[43] A quantitative calculation of the cobalt content in the different magnetic states, ferro-[Co(0)]-, dia[Co(1+)], and the Co(2+)-paramagnetic states showed that the fraction of ferromagnetic cobalt is equal to ca. 50%, the same level as in diamagnetic cobalt.[43] The interaction between components of the "cobalt" systems in the absence of monomer leads to the reduction of a significant part (up to 50%) of Co(2+) to the metallic state. At least 90% of the total ferromagnetic cobalt is concentrated in relatively large (>100 Å) particles. The formation of such associates is the main reason for the fall in activity of "cobalt" systems on ageing in the absence of monomer. When the catalysed reaction takes place, only 6–8% ferromagnetic cobalt is found in the transformation products, and most is present in the diamagnetic state, Co(1+). This is probably attributable to its stabilisation *in statu nascendi* by the monomer as a result of the formation of the π-complex active in the polymerisation:



A similar transformation was observed also in immobilised systems based on Mo(5+),[44] V(4+),[45] etc. complexes.

VII. The effect of surface density of immobilised metallo-complexes on their catalytic activity

The well-known effect of "chain loading" or surface density (ρ_s) on the specific catalytic activity of heterogeneous immobilised systems may be linked with the association of the metal on the support.

Catalysts, the active particles of which are accessible to the substrate, usually possess maximum specific catalytic activity. For example if the Kramer complex $Rh_2Cl_4(C_2H_4)_4$ on phosphinated CSDVB containing different quantities of cross-linking agent (2–60%) are obtained under conditions which essentially exclude polymer matrix swelling (and penetration of the metallo-complex into it), its activity in the hydrogenation of hexene-1 is found to be 1.5–4-fold greater than that in analogues synthesised under conditions in which the polymer becomes greatly swollen (Table 5).[46] Aggregation efficiency is also dependent on the nature of the functional groups. Amino groups usually hinder aggregation more markedly than phosphine groups.[47]

Table 5. Hydrogenation of hexene-1 in the presence of the immobilised Kramer complex.[46]

Divinylbenzene (DVB) content, %	P/Rh in the catalyst		Activity *, sec^{-1}	
	Non-swollen	Swollen	Non-swollen	Swollen
2	25	6.5	2.35	0.49
25	5.6	3	1.02	0.60
60	2	3	0.66	0.40

* Product yield in moles per mole of Rh.

The dependence of the specific catalytic activity on ρ_s is usually a complex relationship. Most often with increase in ρ_s the specific catalytic activity increases, reaches a maximum value, and then decreases. Experiments have shown that such patterns exist for the hydrogenation (Fig. 3),[48,49] oxidation,[50] dimerisation,[51] and polymerisation of ethylene, etc.[52] Maximum specific activity of the PE-pr-P4VP.VCl_4–$AlEt_2Cl$ system during ethylene polymerisation is attained for example at a bonded vanadium content of 0.6 mass% (18 atoms/100 Å^2).

Such patterns are undoubtedly the consequence of the distribution characteristics of the active component. It has been quite reliably established that metal ions are distributed on the support both as isolated complexes and as cluster formations with a high local concentration of attached complexes.[5] With change in ρ_s the ratio between them also changes. There is a general tendency that with decrease in phosphorus content of the phosphinated macroligand and also with decrease in P/Rh the Rh particle size increases and gradually approaches the particle size in the polymer containing no functional groups.[53] An increase in the phosphorus content decreases the rate of decomposition of rhodium complexes to the metal. When P/Rh = 40, crystallites are not found even after heating to 398 K for several days.

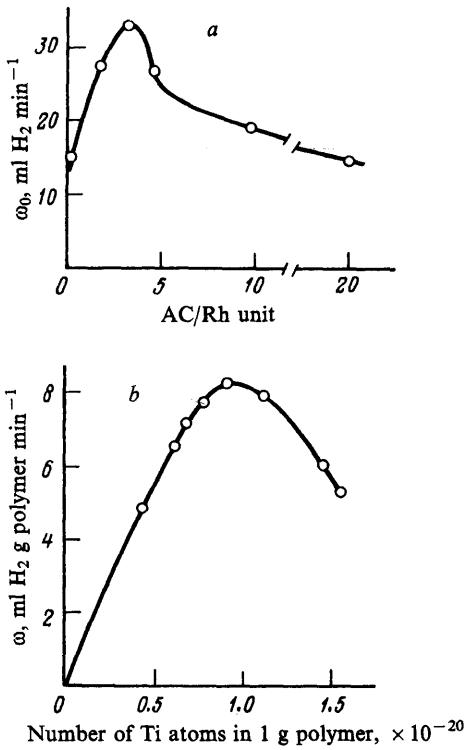


Figure 3. The variation in reaction rate as a function of the quantity of bonded metal in the macrocomplex: *a*, hydrogenation of furfurol in the presence of Rh on PAA;[49] *b*, hydrogenation of hexene-1 in the presence of titanocene bonded to CSDVB modified with cyclopentadienyl groups.[48]

However one cannot associate the observed nature of the dependence of the specific catalytic activity on ρ_s with either the concentration of isolated ions or with the concentration of associates. At the same time it is evident that, on increase in ρ_s, the concentration of associates consisting of a small number of particles, for example dimers or trimers, should pass through a maximum. The suggestion that active particles in the immobilised systems are formed from isolated transition metal ions stabilised by cluster formations is justified. Their content should also be markedly dependent on the surface density. In fact an analysis of the magnetic susceptibility of different spin states of "nickel" systems confirms that with increase in the surface density of Ni(2+) during the formation of active centres the dimensions of the clusters increase and the relative content of the boundary nickel atoms stabilised by the electron system of the entire cluster passes through a maximum.[41] In other words the dome-shaped plot representing the dependence of the specific catalytic activity on ρ_s correlates with the distribution function of the clusters with respect to size. One should note that in certain systems the dependences of the specific catalytic activity on ρ_s are different. For example the rate of H_2O_2 decomposition in the presence of Cu(2+) complexes with a polyampholite (copolymer of 2-methyl-5-vinylpyridine and AK)‡ is

‡ (Owing to the strong dependence on pH this reaction closely resembles enzyme-mediated processes.)

determined by the formation of complexes with different compositions.[54] A correlation is found between the catalytic activity and the content of diamagnetic Cu(2+) complexes, when the latter may include binuclear complexes§ (similar to the active centres of haemocyanin) with a strong antiferromagnetic interaction.

The presence of the ascending branch of the dependence of the specific catalytic activity on ρ_s may be attributed to the collective interaction of immobilised vanadium atoms.[56] A decrease in the activity of the attached $TiCl_4$ complexes during the polymerisation of ethylene continues until each active centre becomes adequately separated from the other.[57]

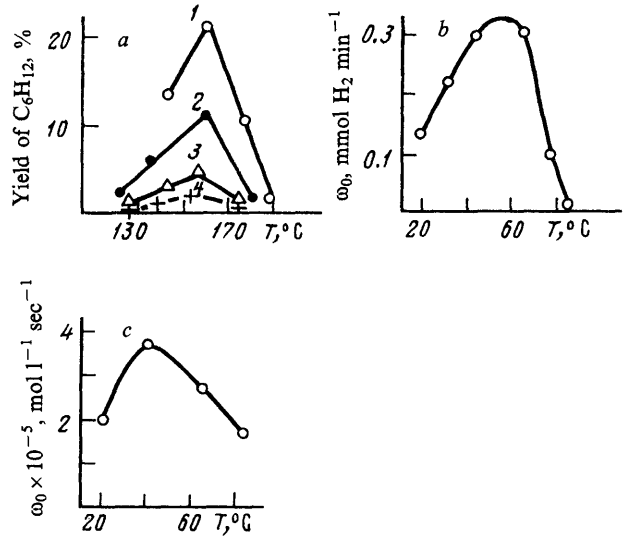


Figure 4. The effect of temperature on the rate of hydrogenation in the presence of the immobilised complexes. *a*, Hydrogenation of benzene with the use of Pt–nylon-66 (*1*), Rh–nylon-66 (*2*), Ir–nylon-66 (*3*) and Pd–nylon-66 (*4*) systems;[59] *b*, hydrogenation amination of 2-methylpropanol in the presence of Pd on polytrimethylolmelamine;[61] *c*, hydrogenation of allylbenzene on the $Ni(acac)_2$–copolymer of butylacrylate, acrylonitrile, acrylic acid and methylolacrylamide–$Al(C_2H_5)_2Cl$.[60]

Thus one of the principal transformations of the immobilised complexes may be associated with the evolutionary transformations accompanied by an increase (more rarely a decrease) in nuclearity. The following sequence of such transformations is observed: immobilised monomer complex → formation of small (bi-, tri- etc.) particles (clusters) → formation of multinuclear associates (diameter 10–20 Å or more) → appearance of metal phase. Small sized particles interact very intensively with the polymer matrices. sized particles interact very intensively with the polymer matrices. Usually as a result of an electronic transition at the metal atoms a positive charge arises promoting coordination of substrate molecules which also affects the activity of the catalyst. The deep interaction of such particles with the support facilitates the conservation in them of a developed π-electron system.[58] The situation becomes complicated because the systems examined are dynamic formations. The concentration and structure of the metallo-complexes may be altered in the course of the catalytic reaction as a consequence of cluster formation, aggregation, crystallisation, and displacement of the metal on to the surface from the body of the matrix, which are especially intensive at the stage of activtion of the attached complex.

VIII. Characteristics of the effects of temperature on the catalytic properties of immobilised complexes

When the catalytic systems under the examination are used one should remember that the temperature usually affects the rate of the reaction in a complicated manner. Since the MX_n-macroligand system itself undergoes certain transformations, the dependence of the reaction rate on temperature often has a bell-shaped relationship. Such dependences are found particularly during the hydrogenation of benzene in the presence of the platinic group of metals on nylon-66 (Fig. 4),[59] hydrogenation of allylbenzene by gel-immobilised nickel complexes,[60] hydrogenised amination of 2-methylpropane by nitrobenzene on Pd-polytrimethylolmelamine,[61] and oxidation of ethylbenzene on Co(2+) macrocomplexes (Fig. 5), etc.[50]

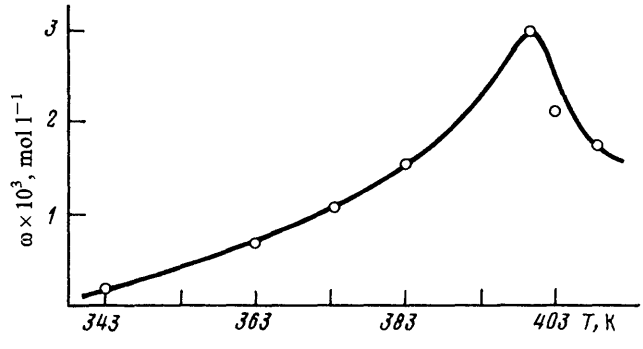


Figure 5. The effect of temperature on the rate of oxidation of ethylbenzene by Co(2+) macrocomplexes.[50]

There may be several reasons for such unusual temperature behaviour. One reason is the occurrence of destructive process initiated in the polymer matrix by the metallo-complexes especially at elevated temperatures. The appearance of descending branches of the curves may also be a consequence of the aggregation of metallo-complexes, occurring vigorously on increase in temperature.

However the most probable reason is the effect of temperature on the phase transformations in the metallo-complex matrices on heating. With increase in temperature the reaction rates at first increase in accordance with the Arrhenius law, and then after the

§ Binuclear complexes cannot be formed, while only one Cu(2+) ion occurs in each polymer globule at high dilution (< 0.05 mass% of the polymer). In this case infinite dilution conditions are modelled.[55]

second-order transition temperature (T_c) is reached or after softening of the polymeric support the rates of the reactions fall. Thus in the temperature range in which the chain segments possess adequate mobility and in which the relaxation processes associated with the reorientation of the entire macromolecular support become controlling, there is a change in the structure of the active centres (a change in the coordination unsaturated state of the transition metal, aggregation of the active centres, reduction of the metal, etc.).

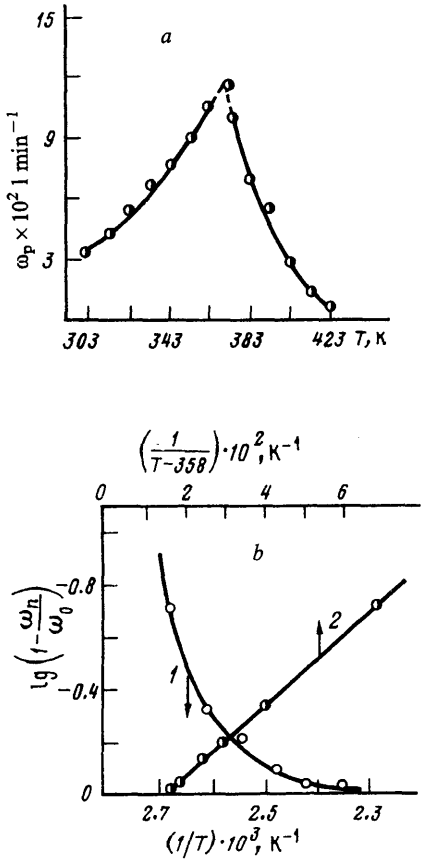


Figure 6. The variation in the rate of ethylene polymerisation in the gas phase as a function of temperature (*a*) (catalytic system, P4VP.VCl_3 – $Al(C_2H_5)_2Cl$; the calculated rate is indicated by the dotted line) and the temperature dependence $\lg(1-\omega_p/\omega_0)$ (*b*) on $1/T$ (*1*) and $1/(T-358)$ (*2*).

In particular the rate of gas phase polymerisation of ethylene (P4VP.VCl_4 – $AlEt_2Cl$ system) is dependent on the mobility restoration temperature (the rate of the relaxation process).[62] In the Arrhenius region the process is reversible (Fig. 6) and E_a has a normal anionic-coordination polymerisation value (16 kJ mol^{-1}). In the T_{mp} range and higher the polymerisation temperature coefficient becomes negative (−130 kJ mol^{-1}). If one assumes that the decrease in polymerisation rate (ω_{II}) on the descending branch of the curve is caused by the exceptionally irreversible deactivation of active centres (n_p) caused by the movement of segments of the polymer chain, then

$$\omega_{II} = kn_p\left(1-\frac{\Delta n}{n_p}\right) = kn_p(1-\omega_D\Delta t),$$

where ω_D is the specific decay rate of the active centres according to any of the possible mechanisms. From here

$$\omega_D\Delta t = 1-\omega_{II}/\omega_0$$

(ω_0 is the polymerisation rate in the absence of deactivation). The form of the curve in Fig. 6*b* resembles the normal observed dependence for the relaxation time of segmental movement. The apparent activation energy increases sharply as the mobility defrosting temperature is approached. As usual in such cases the temperature dependence of the rate of the relaxation process is linearised in the coordinates $\lg\omega_D \sim (\Delta T)^{-1}$, i.e. it has the form

$$\omega_D = A\exp\left(-\frac{B}{T-T_0}\right).$$

The value B is associated with T_c and the free volume fractions (α_c) by the relationship:[62]

$$B = (T_c-T_0)/2.3\alpha_c.$$

In this specific case T_c = 360 K (α_c = 0.025) and this is the temperature at which the mobility of the P4VP segments is restored and at which a marked fall in the rate of polymerisation commences. Hence the increase in the progressive diffusion n_p is one of the important factors for the deactivation of immobilised metallo-complex catalysts for the polymerisation of olefins.

The temperature dependences of the rate of polymerisation by gel-immobilised systems also pass through a maximum (in the T_{mp} range of polyethylene). They are totally temperature-reversible, i.e. the decrease in rate in the elevated temperature range was not due to thermal deactivation n_p. An important feature of gel-immobilised systems is their structural and conformation adaptation,[63] i.e. at elevated temperatures microsyneresis of the polyhydrocarbon gel occurs in the aromatic solvent medium, leading to a decrease in the concentration of the monomer in the vicinity of the active centres present in this type of gel. Therefore in the case of local overheating in a particular region of a granule of the immobilised catalyst, temporary retardation of the exothermic reaction occurs. Other authors have suggested that such an inverse relationship ensures the "self-defence" of the catalyst from irreversible thermal deactivation.[63] This is yet another basic similarity between the immobilised catalysts and biomembranes into which enzymes have been incorporated.

At the same time restoration of the mobility may ensure that different sized aggregates of the particles are formed from the zero-valent metals, and the activity of such aggregates is possibly higher than the activity of isolated atoms. Such a local convergence of the metallo-complexes is found to have a favourable influence on hydrogenation and other processes. This phenomenon was studied in greatest detail in the case of gaseous phase hydrogenation of ethylene by Rh complexes attached to triple copolymers consisting of styrene and diphenyl-*p*-styrylphosphine (DRSP) (5–10%) cross-linked with divinylbenzene (2%).[64,65] The temperature dependence is readily reproducible over a broad range. At T_c a discontinuity in

the Arrhenius curve is found (Fig. 7). The activation barrier of the reactions at $T > T_c$ remains essentially the same, i.e. all changes in the rate constant are associated with the entropic factor. This phenomenon arises as a result of the restoration of the mobility of the polymeric segments and the creation of the most suitable configuration of the active centre for the catalytic act. One also cannot rule out the effect of other factors. When $T > T_c$, relaxation of the micro-Brownian movement promotes diffusion and an increase in the probability that the substrate collides with the active centres. Furthermore movement of the adjacent groups and ligands may increase steric hindrances for the coordination of ethylene and may reduce the stability of the bond of the coordinated substrate.[65] Finally a change in the nature of the movement in the polymer leads also to structural transformations of the active centre, since in this case there are changes in the coordinating capacity of the functional groups, their configuration, and the coordination non-saturation of the transition metal, etc. Furthermore the anomalous nature of the temperature dependence cannot be associated either with an increase in ethylene diffusion into the small pores of the catalyst (which would become limiting close to the T_c) or with the fact that at a certain temperature the overall rate of the process begins to be determined by another stage (since the slope of the Arrhenius plot remains virtually constant).

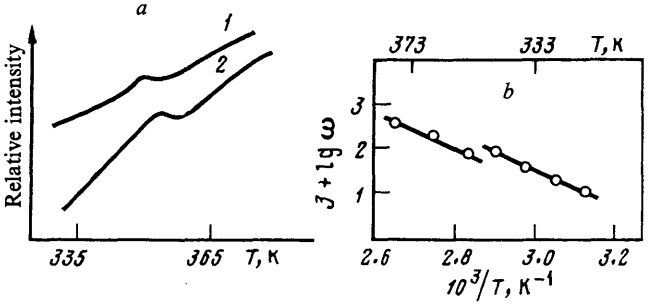


Figure 7. Differential scanning calorimetry curves (*a*) (*1*, T_c = 349; *2*, T_c = 354 K) and the Arrhenius dependence of the rate of ethylene hydrogenation in the gas phase on the rhodium macrocomplex (*b*).

The reversible discontinuity in the Arrhenius dependence may be explained, if one assumes the existence of two different coordination states differing in catalytic activity in the T_c region. The somewhat nonuniform slope of the curve at different sides from the T_c (33 kJ mol^{-1} at higher and 35 kJ mol^{-1} at lower temperatures) may probably be attributed to the fact that the enthalpy or entropy of ethylene coordinated at various Rh-centres differs somewhat on account of the movement of the polymer network.

It is interesting that similar effects are also found in soluble metallo-polymeric catalysts. Thus the effective rate constant (k_{eff}) for the oxidation of cholesterol by molecular O_2 in the presence of soluble porphyrin-containing metallo-polymers temperature-dependent,[66] and there were no analogies in normal homogeneous catalysis. The nonmonotonous nature of the dependence $k_{ef}(T)$ (Fig. 8) indicates that conformational transitions possibly occur in such systems. One such transition may be caused by the disruption of the ordering of polymeric fragments associated with hydrogen bonds, coordinate bonds, and other bonds during their concomitant rupture. In this temperature range the temperature dependence of the characteristic viscosity has the form $\eta = \eta_0 \exp(-E/RT)$, as in any activation process which is also associated with conformational transitions in metalloporphyrin-containing macromolecules. In the transition region a significant fluctuation of the conformations of the chains in the solutions is found, and each conformation corresponds to its reaction rate constant value, because of the difference in the pre-exponential multiple, which reflects steric factors, or because of the mutual effect of the active centres. Since there is a set of different rate constants corresponding to metastable conformational states in the transition region, the dependence $k_{eff}(T)$ also has a non-Arrhenius extremal nature.

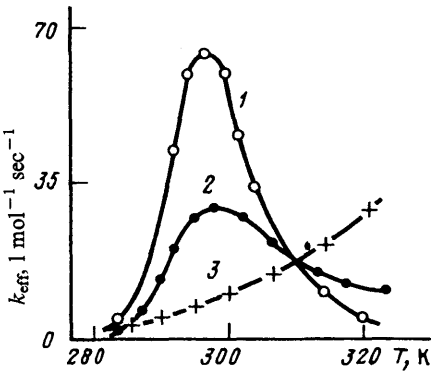


Figure 8. The dependence of the k_{eff} of cholesterol oxidation in the presence of $NaBH_4$ and copolymers of N-Mn-porphyrinate acrylamide with methacrylate (*1*) and butylacrylate (*2*) on the temperature (*3*, the analogous dependence for the low molecular weight analogue, magnesium tetraaminophenylporphyrinate).[66]

In principle such effects may influence not only the activity but also the selectivity of the immobilised catalysts. Only one example will be presented, viz. a reduction in temperature during the synthesis of cyclopropane ethers leads to an increase in the proportion of the *cis*-isomer, probably as a consequence of the limitation in the mobility of the macromolecular chain.[67]

Finally one should also mention such an important phenomenon as the total thermo-reversibility of the binding of MX_n by certain ligands, which form the basis of the construction of "thermo-regulatable" immobilised catalysts. The line diagram of this phenomenon may be represented in the following form:

$$\left|\text{—L—MX}_n\right| \xrightarrow{\text{catalysis}} \left|\text{—L} + \text{MX}_n\right| \xrightarrow[\text{catalyst}]{\text{Isolation of the}} \left|\text{—L—MX}_n\right|$$

Low temperature (Immobilised catalyst)	High temperature (homogenous catalyst)	Low temperature (Immobilised catalyst)

Complexes of $ClRh(PPh_3)_3$ with phosphinated ethylene oligomers are an example of thermo-regulatable catalysts.[68] At 373 K the macrocomplexes dissolved in xylol operate as hydrogenation catalysts, but when the reaction medium is cooled to 298 K, the catalyst is quantitatively (losses of Rh do not exceed 0.1% per cycle) bound to the support. This method is especially effective when the so-called "undeposited" homogeneous catalysts are used.

The question of the thermostability of the immobilised complexes warrants special examination. Binding of MX_n is usually accompanied by a change in the structural organisation of the system and leads to an increase in its thermostability. The best known example is the binding of first transition series metal ions with nucleic acids into a stable complex, which ensures the resistance of the complex to elevated temperatures and its conservation in the denaturation area.

IX. The contribution of energy of non-equilibrium configurations of the chain to catalysis

Not only the nature of the polymeric support and its functional groups but also the distribution profile of L with respect to the copolymer chain (statistical, modular, alternant), and the stereoregular, conformational and configurational structure of the macroligand affect the composition, structure and stability of the macrocomplexes during their formation. There is only a limited amount of information on these questions. Thus, during the oxidative coupling of 2,6-xylenol the activity of the Co(2+) chelates attached to atactic and isotactic polyacrylamidoximes (PAAO) significantly differ.[69] The kinetics of the reactions in both cases obey the Michaelis–Menten equation, although the k_2 value (constant for the second stage determining the rate of the process) is higher for the isotactic ligand (at 303 K, k_2 = 0.304 and 0.284 min^{-1} respectively), whereas the Michaelis constants have similar values (0.274 and 0.282 mmol l^{-1}). These phenomena are caused primarily by an increase in entropy. Since the chain of the isotactic macroligand has a spiral ordered form, it has a lower $\Delta S^{\neq}$ value (Table 6).

Table 6. Thermodynamic and activation parameters of the oxidative combination of 2,6-xylenone at 303 K.[69]

Catalyst PAAO–Co(2+)	ΔG, kJ mol^{-1}	ΔH, kJ mol^{-1}	ΔS, J mol^{-1} deg^{-1}	$\Delta G^{\neq}$, kJ mol^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} deg^{-1}
Isotactic	20.6	58.4	260.4	88.2	35.7	−172.2
Atactic	20.7	45.4	218.4	89.0	40.0	−163.6

The Rh and Ru complexes attached to isotactic or atactic phosphorylated polystyrene exhibit different activities in oxidation, hydrolysis and isomerisation, etc. reactions,[26] although it is difficult to make clear conclusions on the causes of this phenomenon.

The activity is dependent on the form of the macromolecules containing attached MX_n. For example Rh and Ru attached to alternating copolymers of maleic acid and vinyl esters and occurring in the reaction medium in the more compact configuration (in *n*-octane) express lower activity in the hydrogenation reaction.[70] In many cases the nature of the solvent is also important. At 343 K modified polystyrene in *n*-hexadecane is present in the glassy state, but occurs in the gum-like state in aromatic solvents. Furthermore, when the chain is compressed, the principal fragment of the metal is localised within the polymer and is not involved in the catalysis. However on oxidation of the hydroquinone by Cu(2+) with a partially quaternised P4VP, an increase in pH, temperature, and the degree of quaternisation of the macroligand on introduction of the electrolytes leads to a decrease in viscosity of the system, to the compression of the polymer chain, and to the creation of conditions required to form intramolecular chelates, which promotes a charge transfer between the neutral hydroquinone or semihydroquinone anion and the Cu(2+) ion of the polymer complex.[71] This causes an increase in catalytic activity, whereas the reverse factors promoting the extension of the polymer chain and hindering the formation of the chelate reduce the catalytic activity.

The rate of oxidation of di-substituted phenols in the presence of Cu(2+) on the copolymer formed from styrene and 4-VP or dimethylaminostyrene increases with increase in the proportion of aminogroups ([N]) to 0.4.[72] This is associated with a change in the activation parameters caused by an increase in the conformational mobility of the intermediates during the deformation of the intermediate catalyst-substrate complex, the formation of which precedes the electron transfer from the substrate to Cu(2+) (limiting stage of the process). In addition at small [N] values in the copolymer there are steric hindrances, which hamper the formation of the binuclear triple complex. At least six intermediate styrene units are required to form the bridging binuclear complexes.[73]

A feature of the soluble macrocomplexes is that not only the structure and conformation of the chain but also chain length has a significant effect on their activity and selectivity. Thus the rate of oxidation of tetralin increases ten-fold with increase in the length of PEG containing attached MCl_2 (M = Co, Mn, Cu) (Table 7).[74,75]

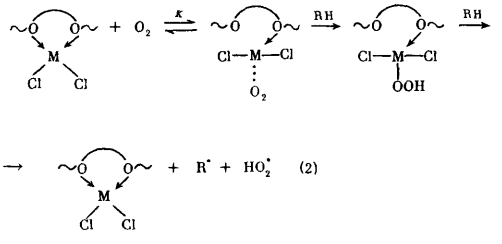
Table 7. Variation in the decomposition of rates (ω_i) of hydroperoxide and the oxidation (ω_0) of tetralin as a function of the relative molecular mass of PEG (355 K, $[ROOH]_0$ = 0.4 mol l^{-1}, O_2).[75]

Relative molecular mass of PEG	ω_0, mol O_2/(g-ion Co min^{-1})	ω_i, mol ROOH/ /(g-ion Co min^{-1})	ω_s/ω_i
4 000	180	35	5
20 000	900	40	22.5
40 000	1800	33	54.5

Macrocomplexes function as initiators and the PEG chain length affects the rate of the initiation stage. In contrast to the oxidation rate the rate of decomposition of ROOH is essentially not dependent on the molecular mass of the polymer. Since E_a is also not

dependent on the molecular mass of PEG, differences in activity are associated with a change in the pre-exponential factor in the reaction rate equation, i.e. with entropy factors. This is an example of a new effect in catalysis, an increase in rate of the process owing to the energies of non-equilibrium configurations of the polymer chains arising in the course of the reaction. The energy increases with increase in chain length, and under certain conditions (for example when the rate of the catalytic act is greater than the rate of relaxation of the polymer nonequilibrium) may be transmitted to the reacting components, thereby increasing the rate at which they undergo transformation.

We shall analyse the mechanism of this phenomenon with a specific example. Macrocomplexes PEG.MCl_2 in tetralin occur as globules, the dimensions of the latter being less than those of the corresponding globules of the original PEG. However activation of O_2 at the metal ion may be accompanied by the temporary rupture of one of the M–O–PEG bonds (according to the type of substitution of ligands in the macrocomplexes described in Section II). This leads to the appearance of the nonequilibrium configuration of the macromolecule striving to unfold. Such an irreversible process is characterised by a constant K, the magnitude of which is determined by a change in the free energy of macrocomplex formation, $RT \ln K = \Delta G$.



(2)

In turn ΔG may be provisionally divided into two components. One component (ΔG_x) is determined by the rupture of old and the formation of new chemical bonds with the metal ion, while the other component (ΔG_{ts}) is determined by the operating of chain stretching which was "stored away" during macrocomplex formation. The entropy component ($T\Delta S_{ts}$ is precisely the function of the molecular mass of PEG and increases with increase in molecular mass) makes the principal contribution to the equation $\Delta G_{ts} = \Delta H_{ts} - T\Delta S_{ts}$. Then $\Delta G = \Delta G_x + \Delta G_{ts}$. From the expression

$$K = \exp(\Delta S/RT) \exp(\Delta S_{ts}/R) \exp(-\Delta H/RT) = K_0 \exp(-\Delta H/RT)$$

it follows that the K values for the polymer complexes and their low molecular weight analogues differ in magnitude ($\Delta S_{ts}/R$) which is part of the pre-exponential factor in the overall reaction rate equation and is dependent on the molecular mass of the macroligand.

Thus one condition for the appearance of the effect examined in the catalysis is an increase in the rate of the catalytic reaction over the rate of relaxation of nonequilibrium conformations of the macroligand.

Apparently this is a common effect and occurs in processes catalysed by soluble immobilised complexes.¶ This effect is similar to the energy recuperation effect in enzymic catalysis in which the protein molecule assumes the role of an energy reservoir. The energy released in the course of the reaction is not dissipated as heat but is utilised to activate the reagents. During the enzymic reaction the protein macromolecule may be transformed from the equilibrium into the nonequilibrium state. The energy of this transition is utilised to overcome the substrate transformation activation barrier, whereas the energy released as a result of the reaction is utilised to return the protein molecule to the original equilibrium state.[77]

Other hypotheses suggest that the small height of the activation barrier of the enzymic reactions may be attributed to the fact that even before the enzyme-substrate complex is formed in the active centre of the enzyme a functional group with high potential energy is present {the hypothesis of the eptatic [entatic? (Ed. of Translation)] state of the active centre of the enzyme}.[78] For example the zinc ion within carboxypeptidase or carbonic anhydrase is much more reactive than zinc occurring in the normal ionic form or in a complex with a low molecular weight ligand. The reason is that in the active centre the zinc atom is only partially associated with protein ligands (as in M in Scheme 2), forming the stressed configuration of the deformed tetrahedron. Such formations are a specific feature of protein macromolcules with secondary and tertiary structures.

X. Cooperative stabilisation of active centres in the immobilised systems

A significant number of segments in the polymer chain is usually involved in the binding of MX_n (and active centres based on these structures). The rupture of one of the bonds between the metal ion and the macroligand unit requires the expenditure of approximtely the same amount of energy as for the rupture of the bond in the complex with the low molecular weight ligand analogue. However these losses in the first case are not compensated by the appearance of new progressive degrees of freedom (i.e. they are not accompanied by an increase in configurational entropy). Thus the probability that the active centre in the immobilised systems is disrupted under stable equal conditions sharply declines, whereas the stability of the intermediate forms may be increased owing to the rapid spontaneous conformational transformations in adjacent units in the chain, fluctuations in its structure, etc. Cooperative interactions of this type increase the stability and activity of immobilised catalysts. Thus in polymers based on Rh(1+)-bis-(4,4'-diisocyanodiphenyl)chloride (the catalyst for the hydrogenation of olefins) [79] in which the Rh is arranged regularly in a tetragonal or

¶ The value of the Michaelis constant (K_m) and the activation parameters for the oxidation of 2-mercaptoethanol by molecular O_2 in the presence of complexes of sodium Co(2+)-phthalocyaninetetrasulphonate with polyvinylamine (PVAm) are dependent on the degree of polymerisation of the latter,[76] which are associated with conformational transformations of the globule. The $\overline{M}_n$ of the 2,4-ionene type of quaternised polyammonium resin is found to have an effect on the charge density of the polymer chains. On increase in $\overline{M}_n$ from 1740 to 6600 the constant K changes from 11.3 to 6.8 mol l^{-1}, whereas the turnover number alters from 3700 to 3300 sec^{-1} (for polyvinylamine with $\overline{M}_n = 3 \times 10^4$ these values are 90 mol l^{-1} and 2800 sec^{-1} respectively).

hexagonal environment where each rhodium atom is associated with 2 or 4 isocyanate ligands, there are three types of active centres (Fig. 9). The first of these (a) incorporates Rh at the end of chain, the second (b) incorporates Rh is the macroligand chain, and the third (c) incorporates Rh on the outer side (001) of the material. The number of centres active in catalysis does not exceed 1% of the number of Rh atoms, but cooperative interactions are observed between the centres (a) arranged at close distances from each other, which increase the activity of the catalyst in the isomerisation of the substrate, whereas the cooperative effect created by the interaction between centres (b) and (c) or adjacent centres (b) is the reason for the increase in activity in the hydrogenation reactions (in this case the Rh–Rh interactions have the characteristics of a metal bond). The relationship between the different centres is dependent on the previous history and the method of preparation of the catalyst, its topography, ρ_s value, temperature, and other factors.

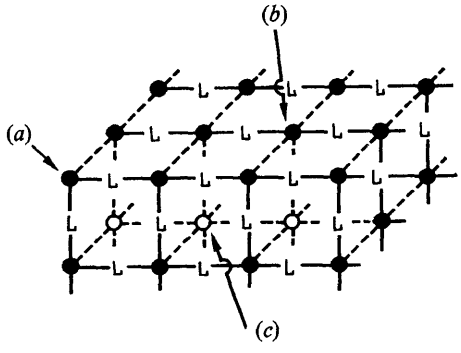
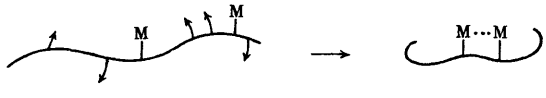


Figure 9. Types of active centres in Rh(1+)-bis-(4,4′-diisocyanodiphenyl)chloride polymers.[79]

In those cases in which matrix isolation of the active centres is an important condition for the completion of the reaction, cooperative interactions of the segments in the chains may lead to their deactivation.



In order to establish the reason for the stability of attached catalysts for ethylene polymerisation, the decomposition of individual organometallic Ti(4+) compounds (which form the basis of active centres of homogeneous catalysts and catalysts heterogenised by polymeric supports of the catalysts)[80] was studied. Decomposition of $RTiCl_3$ type compounds is known to occur mainly as a result of the completion of processes within the coordination sphere of the transition metal, including β-elimination or disproportionation reactions. The activation energies of these stages are lower than metal–carbon bond energy, and therefore to increase the stability of organometallic compounds it is essential to exclude completely the possibility of the occurrence of inner sphere reactions of the alkyl group. For example CH_3TiCl_3 complexes with 4-substituted derivatives of pyridine decompose in the homogeneous system even below room temperature with the splitting of the $Ti-CH_3$ bond and with the formation of methane according to a coordinated mechanism in the coordination sphere of titanium, and in the course of these reactions Ti(4+) is not reduced. The macrocomplex PE-pr-P4VP.CH_3TiCl_3 is more stable. The Ti–C bond is gradually decomposed only at 298 K with the formation of methane, ethane, and C_4 hydrocarbons. Above 353 K there is an increase in the proportion of homolytic decomposition of the Ti–C bond with the formation of CH_3 radicals, and this is accompanied by the reduction of Ti(4+) to Ti(3+) (Table 8).

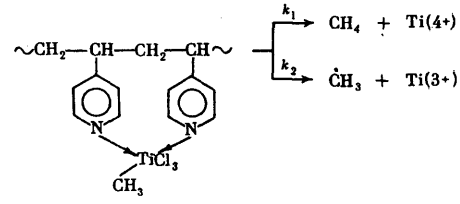


Table 8. Ratio between the rate constants k_1 and k_2 and the quantities of Ti(3+) and Ti(4+) during the decomposition of the complex CH_3TiCl_3.PE-pr-P4VP.[80]

T, K	$k_1 \cdot 10^4$, c^{-1}	$k_2 \cdot 10^4$, c^{-1}	k_2/k_1	Ti(3+)/Ti(4+)
303	0,59	–	–	0
313	0,77	–	–	0
323	1.0	0.7	0,7	0,6
333	1,3	2,1	1,7	1,5
348	1,6	8,0	5,0	2,3

The rate constant value for the coordinated decomposition reaction (k_1) of the macrocomplex examined is two orders of magnitude lower than that for the decomposition of the CH_3TiCl_3 complex with the monomeric ligand. This may be attributed to the extremely low value of the pre-exponential factor ($10^{-2}-10^{-3}$ sec^{-1} against 10^3-10^5 sec^{-1} for the homogeneous system) since the "fine tuning" (deformation) of the polymeric ligand essential for the coordinated reactions to take place, requires significant changes in entropy in the transition state in comparison with the monomeric analogue. It is important that the rate of homolysis of the $Ti-CH_3$ bond occurring with the formation of free radicals (the rate constant of this reaction k_2) in the heterogenised and homogeneous systems are identical.

Thus the thermodynamic stability of the Ti–C bond (and hence the active centres) in the systems compared remains essentially unchanged (similar bond energies). Therefore the stability and high activity of the immobilised systems for example during the polymerisation of ethylene (Fig. 10) are mainly caused by the sharp fall in rate of the coordinated processes in the coordination sphere of the transition metal.

One more important situation should be noted. Apparently reactions leading to the deactivation of active centres require significantly more rearrangement of the ligand environment of titanium than reactions in which the polymerisable ethylene is introduced at the Ti–C bond,[81] which is indicated by the closeness of the rate constants of the chain elongation reactions in the systems compared.[52] An extremely interesting phenomenon is the "fine tuning' of the polymer matrix to create the most favourable configuration of the catalytic centre. Thus on heterogenisation of the bulky $Ti(OC_4H_9)_4$ on the polymer the structure of the active centre is probably such that the energy barrier of the introduction reaction is small, and the effective activation energy for ethylene polymerisation is significantly (up to 11 kJ mol^{-1}) lower than that in the homogeneous system (58 kJ mol^{-1}). However in this case K_p essentially does not change. It therefore follows that there is a sharp decrease in the pre-exponential multiple of the reaction rate constant. The compensation effect indicates that in reactions in which these active centres are involved many closely lying fragments of the polymeric ligands are affected, and hence there is a fall in entropy.

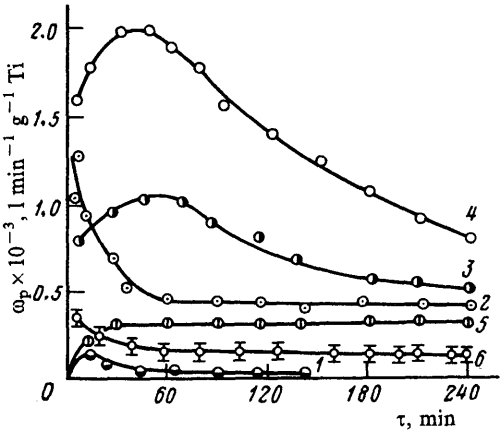


Figure 10. Variation in the rate of ethylene polymerisation by heterogenised systems based on $Ti(OC_4H_9)_4/Al(C_2H_5)_2Cl$ as a function of the reaction time. Polymeric supports: *1*, without support (homogeneous system); *2*, PE-pr-poly(diallylamine); *3*, PE-pr-poly-(allylamine); *4*, PE-pr-poly(allyl alcohol); *5*, PE-pr-PAA; *6*, hydrolysed copolymer of styrene with vinylacetate.

However other patterns are also observed. Thus the rate constants of the homolytic splitting of the Co–R bond in monomeric (R = benzyl) and polymer-associated (R = chloromethylated CSDVB) cobaloximes (L = Py or DMSO)

$$RCo(DH)_2L \overset{h\nu}{\rightleftarrows} R^{\cdot} + Co(2+)(DH)_2L$$

in DMSO have similar values (1×10^{-2} sec^{-1}).[8] In benzene $k_{mono}/k_{poly} = 4.2$. This is associated with the promoting action of the polymer chain on photodecomposition and may be attributed to energy migration along the polymer chain containing aromatic rings, which have the ability to absorb photoenergy. This may be attributed to the fact that the polymer-associated cobaloxime is partially decomposed also on irradiation with light at a wavelength below 350 nm, whereas with benzyl cobaloxime this process occurs only on irradiation with light at a $\lambda_{max} = 450-550$ nm.

Their interaction with the microligand surface caused by the presence of functional groups and surface imperfections and also by physical causes creates yet another possibility for the cooperative stabilisation of the active centres. This has been analysed in greatest detail in the case of the hydroperoxide (tert-butyl hydroperoxide, TBHP) epoxidation of cyclohexane (CH) by Mo(6+) complexes attached to cellulose phosphate (Mo):[82]

$$Mo + TBHP \overset{K_r}{\rightleftharpoons} Mo \cdot TBHP,$$

$$Mo + CH \overset{K_D}{\rightleftharpoons} Mo \cdot CH,$$

$$Mo \cdot TBHP \cdot CH \xrightarrow{k} Mo + CHO + TBA,$$

where CHO is cyclohexane oxide, TBA is tert-butyl alcohol, k is the rate constant of the inherent catalytic act which is achieved in the triple bi-substrate complex, catalyst–hydroperoxide–olefin.

Table 9. Activation parameters of the principal stages in the epoxidation of cyclohexene by heterogenised and homogeneous molybdenum systems.[82]

Rate constant of the reaction	ΔH ($\Delta H^{\neq}$), kJ mol^{-1}	ΔS ($\Delta S^{\neq}$), J mol^{-1} deg^{-1}	E_a, kJ mol^{-1}
K_r	−72	−220	
K_D	−36	−130	
k	133	290	136
K_r'	−24	−92	
k'		166	72

Enthalpy values for the formation of intermediate complexes of the catalyst with reagents (i.e. enthalpies of their chemosorption at the active centres containing Mo) and the activation energies of the decomposition stage of the triple complex into the reaction products are presented in Table 9. For comparison the corresponding parameters of the homogeneous reaction of the direct oxidation of cyclohexene by the molybdenum diperoxocomplex with hexamethylphosphortriamide are presented.[83] The enthalpy and entropy changes during complex formation of diperoxomolybdate with cyclohexene (the rate constant of this reaction, K_r') and also the activation energies and entropies of the transformation of the triple complex (rate constant k') are indicated. The comparative analysis shows that a similar stage of the decomposition of the triple bisubstrate complex Mo.TBHP.CH on the support surface is distinguished by a significantly higher activation energy and by a simultaneously higher positive activation energy. This difference is apparently caused by the heterogeneous nature of the catalyst. The triple complex immobilised on the support matrix is apparently stabilised on account of the addition interaction with the surface and it occurs in a highly ordered, and as a frozen, state. Therefore it

requires a higher activation energy, whereas the release of the products formed into solution is accompanied by a more abrupt disordering of the system. This effect is apparently quite often encountered in catalysis by immobilised complexes.†

A change in the bond energy of the substrate with the support area by 5–10 kJ mol^{-1} may significantly affect the mechanism and selectivity of the reaction. Thus the rate of styrene hydrogenation in the presence of Pd(0) on functionalised CSDVB sharply increases when supports are used containing functional groups which have the ability to form π-complexes with styrene and thereby to increase the lifetime of the adsorbed complexes of the substrate.[27]

XI. The selectivity of immobilised catalysts

Usually immobilised metallo-complexes not only increase the rate of the overall process but also improve its selectivity. Examples are known of the inversion of the selective action of MX_n when they are attached to the support.

In contrast to the homogeneous catalysts the immobilised catalysts are mainly more sensitive to the steric effects of the substituents in the substrate. This is confirmed by the distinct dependence of the reaction rate on geometric sizes of the molecules. Geometrical or matrix selectivity is one of the important features of the processes in immobilised catalysts. For example the rate of hydrogenation decreases on transition from an acrylic to a cyclic olefin. This applies to both individual compounds and components of different fractions or mixtures. The activity of polymer-bound $PdCl_2$ during hydrogenation of substrates forms the following series:[58] dienes > allyl alcohol > alkene-1 > alkene-2 > methyl-alkene-2. The stability of such contacts reaches 1000 or more cycles.

A particularly high order of selectivity is attained on reduction of aromatic and heteroaromatic substrates, including those containing functional groups. Catalysts obtained in this way are suitable for the preparation of cyclohexanol from phenol, and polyols from sugars, and for converting inner alkenes into α-alkenes.[85] The regio-selectivity is especially pronounced in olefin hydroformulation reactions (the ratio of alehydes with the normal structure and the isostructure), and hydrosilylation (α- and β-addition) and oxidation (the predominant formation of a particular product) reactions, and in the formation of an enantiomeric excess (enantioselectivity).

Essentially the same factors which affect the activity of the catalysts also affect selectivity, i.e. the nature and topography of the bonded complex, the nature of the matrix and ligand, the L:M ratio, and also the reaction conditions. For example since the selectivity is associated with the specific adsorption of one of the reagents or the product on the surface, the selectivity of the reaction is dependent on whether the catalyst is swollen or not swollen. The selectivity decreases, also as a consequence of the side reactions including those in which vacant functional groups are involved (hydrolysis, esterification, re-esterification, amination, etc.) and in which the solvent in addition to the substrate is involved. Furthermore, owing to the dissociation of a certain portion of the ligands, the pH of the medium may be altered, which also affects the selectivity. Such effects are extremely varied. For example the ratio between the quantities of ammonia and hydrazine formed in the presence of the titanocene polymers is markedly dependent on the rigidity of the polymeric chain, which regulates the formation of mono- and binuclear diazo complexes of Ti.[86]

During the dimerisation of ethylene by "nickel" immobilised systems the isomeric butenes are primary products, whereas the ratio between *cis*- and *trans*-isomers is regulated at the stage of the transition state in which the ethylene molecules occur at the time of dimerisation.[51] Double bond migration processes and also the geometric isomerisation mainly occur prior to the release of the butylene molecule from the "cell", and the secondary isomerisation reaction arising after its displacement by ethylene is reduced to a minimum. This confers "isomerisation passivity" upon the immobilised complexes in numerous reactions and increases their selectivity. Attention has already focussed on the ratio of isomerisation and hydration active centres (see Fig. 9).[79]

The conformation of the macroligand has a controlling effect on the catalytic properties and selectivity. There are many examples of this effect, which especially concerns polymers possessing the α-helical structure with accurately fixed distances between the ions of the bonded metals. This phenomenon is typical of enantioselective catalysis, where an increase in the stereospecificity is accomplished by limitation of conformational diversity, for example on oxidation of *L*(+)-ascorbic acid catalysed by *trans*-$[Fe(2,2',2'',2'''\text{-}Py_4).(OH)_2]^+$ bonded by Na-poly-(*L*- or *D*-glutamate).[87] When the complex is fixed on a peptide chain it becomes "renaturated" which is associated with the emergence of conformational asymmetry in the metallo-polymeric chains, and asymmetric induction proportional to the content of α-helices in the polymer (stereospecificity factor K_{FeD}/K_{FeL}) is observed. This is associated with a change in the standard free energy of the diastereomer transition states G_{LL} and G_{DL}. The diastereomer *DL* undergoes less steric hindrance than diastereomer *LL*. Consequently electron transport occurs more efficiently because of the more preferable changes in the activation parameters ($G^{\neq}_{LL} - G^{\neq}_{DL}$ = 1.25–3.4 kJ mol^{-1}, Fe_{FeD}/K_{FeL} = 1.5–4.0 on increase in chain load, f = 0.01–0.20) and an increase in relative conformational mobility of intermediate formations of segments in the chain.

Thus the effect of the conformation on asymmetric induction may be associated on the one hand with the formation of a suitable chain structure and on the other hand with a difference in affinity (stability of intermediate complexes) of enantiomers of the substrate and the catalyst. Such a substrate complex should probably contain at least two bonded Cu(2+) ions (on oxidation of 3,4-dihydroxyphenyl-alanine) so that stereoselection is achieved in the catalytic act (Fig. 11).[88] Like enzymic catalysis such a method ensures the generation of large quantities of the enantiomeric product from catalytic quantities of chiral materials.

In principle the selectivity of immobilised complexes may be increased by introduction of a second (supplementary) metal.

XII. The problem of polyfunctional catalysis

Systems consisting of several transition metal compounds (including those bound by a uniting ligand) may be used in different variants in catalysis. They may act either in parallel in one or several unbound rings or independently in sequential stages or in reactions or coordinatively in one reaction.[89] Polyfunctional catalysts, by means of which it is possible to react with successive stages of one multi-stage reaction, are extensively used in the chemical industry.[90] The attachment of two metals within one

† However converse examples are also known. Grafting of peroxides increases the rate of their decomposition, which is associated with their destabilisation as a result of the interaction of the peroxy group with functional groups on the surface.[84]

reaction centre, or statistically in one catalyst grain, often causes a synergistic effect of increasing activity and selectivity.

The role of the additionally introduced metal (M_1) in catalytic hydrogenisation, oxidation, (co)polymerisation and other reactions may be very diverse. On the one hand M_1 (usually nontransitional) may serve as a "trap" for active centres, binding them more firmly with the support and preventing migration and aggregation. On the other hand these effects may be achieved as a result of the insertion of the introduced metal ion between the attached complexes (the $-M-M_1-M-$ type), which promote their matrix isolation. In addition the chemical interactions (formation of weak $M-M_1$ bonds, co-crystallisation, formation of intermetallic compounds, and alloys, etc. on the support) may promote an increase in catalyst yield (as a result of an increase in activity or an increase in concentration of single centres) and its selectivity. For example immobilised bimetallic chloride complexes $AlCl_3-TiCl_4$ on CSDBV,[89] $AlCl_3-SnCl_4$ on polystyrene,[90] and $AlCl_3-FeCl_3$ and especially $AlCl_3-CuCl$ on polystyrene ($CuAlCl_4$/polystyrene)[91] etc. are the strongest solid superacids. Immobilisation of such "dibasic" acids not only increases the acidity but also prevents their irreversible deactivation in a moist atmosphere.

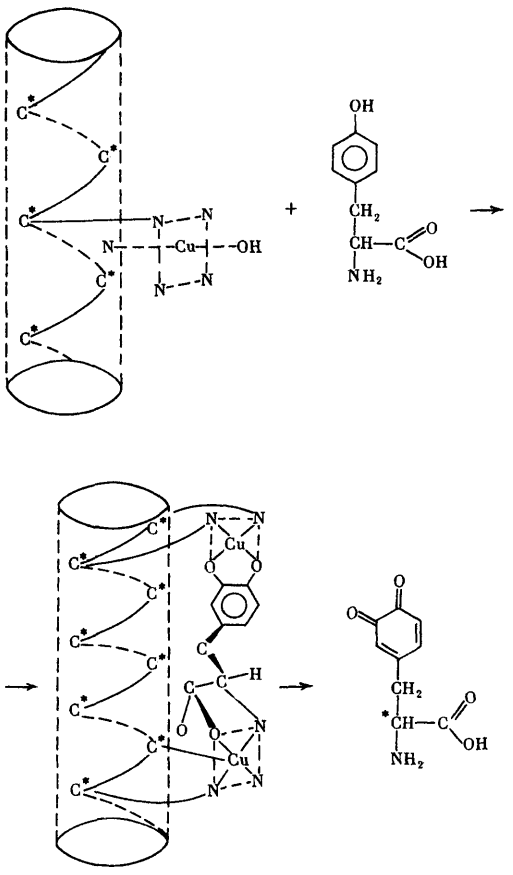
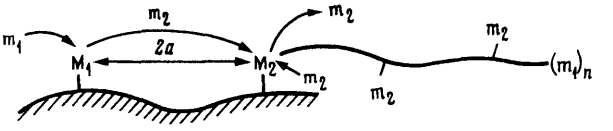


Figure 11. Model of the bifunctional coordination and oxidation of 3,4-dihydroxyphenylalanine on Cu(2+)–poly(L-lysine).[88]

However, those cases in which each of the bonded complexes achieve (according to the coordinated mechanism in the optimal variant) its own stage in the multi-stage process are of more interest. Only one of the most typical examples in the author's opinion will be presented. The case in point is the relay (coordinated) copolymerisation in the presence of immobilised complexes in which two types of active centre (dimerising and copolymerising) are bonded on to one support.[92,93] The line diagram of the process examined may be presented as follows:



The original monomer (in this case ethylene) at the active centre M_1 [for example Ni(2+)] is converted into monomer m_2 as a result of a simple reaction of di-, tri- and oligomerisation, etc. (in particular as a result of the dimerisation of ethylene into butene). In situ copolymerisation of m_1 with m_2 occurs at the active centre M_2 [for example Ti(4+), V(4+), etc.]. The size of the microcell containing different types of active centres is a, which comprises half of the average distance between the centres of pairs of the bifunctional catalyst. The distance between M_1 and M_2 is required during the construction of such catalysts.

The stationary mass-transfer in an individual microcell of this type is determined by the equation:[94]

$$D_i \frac{d^2C_i}{dx^2} = 0 \qquad (i = 1, 2),$$

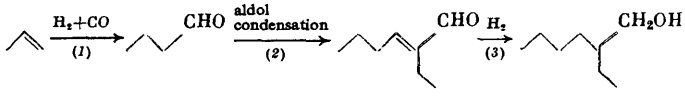
where C_i and D_i is the concentration and effective diffusion coefficient of monomer m_i in microcell respectively. The composition of the copolymer formed (in this case a copolymer of ethylene with butene, so-called branched polyethylene or linear low-density polyethylene) is characterised by the ratio of effective reaction rates of co- and homopolymerisation. In addition to other factors the regulation of the degree of branching is also attained by varying the average distance between different types of centres and has an extremal nature.

The effect of the cell in the immobilised bifunctional centre in principle may lead to an increase in the factor of the first encounters and also to an increase in the contact time of the reacting molecules (to an increase in the number of repeating encounters with the active centre). The metaphor used by the authors is that the operation of the bimetallic centre is "like the action of a conveyer on which each participant operates with great skill and speed".[95] This is promoted by the possibility of more precise control of the synthesis of active centres in the immobilised systems. However, as on a real conveyer, fragments are also found during the operation of such a centre. The complex composition of the gas mixture and the incompletely understood dependence of the behaviour of the centre on the reaction conditions hinder the control of "relay" copolymerisation and even its quantitative description.

The macroligand essentially possesses unlimited combination possibilities within the single matrix of active centres differing widely in nature, so that diffusional limitations should be less than when the corresponding number of monofunctional catalysts are used if a multi-stage reaction is performed on such a catalyst. The magnitude

of the areas of the monofunctional action of the active centres has been estimated to be 12 Å.[96] Both types of active centres should react on the substrate molecule, so that the coordinated mechanism is realised. It has already been mentioned that the most complicated task in the construction of polyfunctional systems is the coordination of the action of the diverse centres and the prevention of their autonomous operation. The main approach to resolve this problem is the control of the spatial arrangement of the active centres, which determines the extension of the transfer pathways of reagents between them, regulates diffusional limitations, and promotes the existence of the bifunctional catalysis itself.[94]

This may be shown in the case of the three-stage synthesis of 2-ethylhexanol from propylene and synthesis gas.[97] The process includes the formation of butyric aldehyde (stage 1), its aldol condensation (stage 2), and hydrogenation (stage 3).



It may be achieved by the use of both two monofunctional catalysts (hydroformylation and hydrogenation) and also one bifunctional catalyst [chloromethylated CSDVB, modified by secondary amino groups with grafted $RhCl(PPh_3)_2(CO)$] (Fig. 12). The rate of the first, second, and third stage on the bifunctional catalyst is 5-, 15- and 30-fold higher respectively than that on two monofunctional immobilised catalysts.

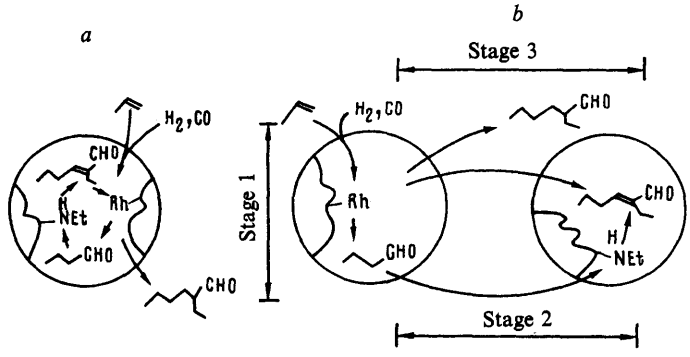


Figure 12. Comparison of diffusional inhibition in reactions catalysed by one bifunctional (*a*) and two monofunctional (*b*) catalysts in the case of the three-stage synthesis of 2-ethylhexanol.[97]

Yet another typical example relates to the reduction of O_2 to H_2O_2. Although the electroreduction of O_2 to H_2O_2 occurs readily on electrodes coated with immobilised metallo complexes, the catalysts used for the reduction of H_2O_2 to H_2O exhibit low efficiency in the O_2 reduction reaction. However it has been found basically possible to bond more than one type of metallo complex on to one graphite electrode.[98] The method involving the modification of the electrode surface by a single bifunctional catalyst for the total 4-electron reduction of O_2 was based on this principle. Ru(3+) and Cu(2+) on a chlorinated copolymer of methacrylic acid and methyl methacrylate are used as such a catalyst.[99]

The range of such examples has been extended significantly in recent years. We shall refer only to the oligomerisation of butadiene with the hydroformylation of vinyl cyclohexene on Ni–Rh-complexes bonded to phosphorylated CSDVB and the preparation of 4-methyl-2-pentanone on composites of polymers consisting of polyamines and polycarboxylic acids impregnated with PVC and incorporating two transitional metals.[100]

All examples mentioned above relate to immobilised heterometallic clusters, which have higher stability than that of the monometallic clusters under the conditions of the catalysed reactions. A search for methods to construct such systems is a promising direction for metallocomplex catalysis.[101]

The action of polyfunctional immobilised complexes is the most adequate model of catalysis by enzymes (an example is the attachment of Mo(6+)–Fe(3+) within a single elementary unit of phosphorus-containing ampholytes, the nitrogenase mode).[102] Such analogies are extremely deep-rooted and they can be extended also to polynuclear metalloenzymes. In the latter the role of multifunctionality consists of the creation of favourable energy and probability factors owing to the optimal use of the respective active centres at each stage of the reaction. In other words in the catalyst-substrate complex there is a restriction of the number of inefficient diffusional movements from the standpoint of the catalytic reaction which do not lead to the formation of products.[103]

An important condition for the realisation of catalytic synchronous processes is the possibility of the dynamic adaptation of the form of the catalytic matrix to the structure of the substrate and the active centres changing in the course of the reaction (fine-tuning). Rapid and reversible conformational transitions both in enzymes and in macroligands and also fluctuations in the matrix structure ensure the necessary structural adaptation. The specific characteristics of the enzyme systems reside in the presence of secondary and tertiary structures, which limit the spatial orientation of metal ions and the possibility of side reactions occurring. By using synthetic metalloproteins it has still not been possible to create a model which under similar conditions (pH, temperature, catalyst, and substrate concentrations) would approach enzyme systems in activity and selectivity. However, the extent to which such a condition can be approached is quite high, for example the efficiency of the binding of O_2 by metallopolymeric complexes is equivalent to the level of efficiency of haemoglobin and myoglobin.[104]

XIII. Conclusion

The author considers that by analysing the fundamental problems considered in this review it is possible to explain the growing scientific interest in catalysis by immobilised complexes and the characteristics of their operation. During the study of immobilised systems new patterns and phenomena have been revealed which are of fundamental importance (it is sufficient to mention those studies in which chelatogenic macroligands,[105] polymerisation and transformation products of metallomonomers,[106] and the use of the lanthanides and transuranium elements etc. have been investigated).

The macroligand stabilises the mononuclear complexes incorporated into unidimensional chains, two-dimensional networks, and three-dimensional frameworks. This increases the thermodynamic and kinetic stability of such systems. The polymeric structure of the ligand environment hampers ligand exchange and

introduces specific properties to the electron transfer reactions and redox processes. Nonvalent interactions affect reactivity, especially the geometry of the transition state. The differences in the kinetic and activation parameters of the reactions of polymeric and monomeric complexes are associated with conformational changes in the macroligands. The systems examined are multi-parameter systems, and it is necessary to take into account the effect of many factors, in order to optimise their activity and selectivity. Total optimisation with respect to all variables would be an incredibly complicated experimental objective. Theoretically founded economically-viable methods for its resolution in immobilised systems are only beginning to be developed.

Catalysis by immobilised complexes is accompanied by a whole series of macromolecular effects, i. e. an increased local concentration of active centres and substrate in the macromolecular globules or in domains close to the active centres, the effect of the spatial structure and polymer chain length, etc. Evolutionary transformations of multinuclear complexes into associates in the immobilised systems occur to a lesser extent than in homogeneous systems.

The realisation of the potentials of these interesting systems (for example in membrane catalysis, when by regulation of the rate at which a substrate passes through a metallopolymeric membrane it is possible to increase the selectivity of the process) will help to explain in detail both homogeneous and heterogeneous catalysis, whereas the information obtained will help to explain the basis of the catalytic action.

Finally the methodological approaches developed during the construction, study and use of immobilised complexes will be extremely useful in a new field of science, chemical biomimetics, in the physicochemical modelling of processes occurring in living nature. Thus the cooperative actions of the macroligand and Zn(2+) or Co(2+) ions as biomimetic catalysts have been found in the study of the hydrolysis of *p*-nitrophenylpicolinate.[107]

References

1. Yu I Ermakov, V A Zakharov, B N Kuznetsov *Zakreplennye Kompleksy na Okisnykh Nositelyakh v Katalize* (Complexes Attached to Oxide Supports in Catalysis), Nauka, Novosibirsk, 1980, 248 pp
2. G V Lisichkin, A Ya Yuffa *Geterogennye Metallokompleksnye Katalizatory* (Heterogeneous Metallo-Complex Catalysts), Khimiya, Moscow, 1981, 160 pp
3. Y Chauvin, D Commereuc, F Dawans *Prog. Polym. Sci.*, 1977, **5** 95
4. F Hartley *Bonded Metal Complexes. A New Generation of Catalysts* (Translated into Russian), Mir, Moscow, 1989, 360 pp
5. A D Pomogailo *Polimernye Immobilizovannye Metallokompleksyne Katalizatory* (Polymeric Immobilised Metallo-Complex Catalysts), Nauka, Moscow, 1988, 303 pp
6. A D Pomogailo, E B Baishiganov, G M Khvostik *Kinet. Katal.*, 1990, **21** 1535
7. T Suzuki, F Shirai, N Hojo *Polym. J.*, 1983, **15** 409
8. H Nishikawa, E-I Terada, E Tsuchida, Y Kurimura *J. Polym. Sci., Polym. Chem. Ed.*, 1978, **16** 2453
9. D B Rorabacher, M J Martin, M Malik, et al. *179th Am. Chem. Soc. Nat. Meet., Houston (Tex.)*, 1980, Abstr. Pap., Washington, 1980, p. 98
10. L G Domaruma, S Kiton, G Walsworth, et al. *Macromolecules*, 1979, **13** 435
11. M Sato, K Kondo, K Takemoto *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17** 2729; 1980, **18** 101
12. E Tsuchida, S Kiyotaka, K Yoshimi *J. Polym. Sci., Polym. Chem. Ed.*, 1974, **12** 2207
13. E Tsuchida, S Kiyotaka, K Yoshimi *J. Polym. Sci., Polym. Chem. Ed.*, 1975, **13** 1457
14. P Denisevich, K W Willman, R W Murray *J. Am. Chem. Soc.*, 1981, **103** 4727
15. J Topich *Inorg. Chim. Acta*, 1980, **46** L97
16. N Ueyama, E Kamada, A Nakamura *Polym. J.*, 1983, **15** 519
17. A V Vannikov, A D Grishina *Usp. Khim.*, 1989, **58**(12) 2056 [English translation in *Russ. Chem. Rev.*, 1989(12)]
18. M Ohyanagi, H Nishide, K Suenaga, E Tsuchida *Macromolecules*, 1988, **21** 1590
19. A B Solov'eva, E I Karakozova, L V Karmilova, S F Timashev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2445
20. G Challa, H C Meinders *Relations Between Homogeneous and Heterogeneous Catalysis*, Lion, 1977, p. 309
21. H Nishide, E Tsuchida *Makromol. Chem.*, 1982, **183** 1883
22. S Mao, Z Z Miao, W Gao, et al. *J. Nucl. Radiochem.*, 1987, **9** 34
23. H Nishide, H Kawakami, Y Kurimura *J. Macromol. Sci. A*, 1988, **25** 1339
24. M Sugimura, T Okubo, M Ise *Intern. Symp. Macromol. Pisa*, 1980, Vol. 4, p. 174; *Macromolecules*, 1981, **14** 124
25. G Challa *Intern. Symp. Macromol. Pisa*, 1980, Vol. 1, p. 101
26. C Carlini, G Sbrana *J. Macromol. Sci. A*, 1981, **16** 323
27. G Bar-Sela, A Warchawsky *React. Polym.*, 1983, **1** 149
28. R H Fisch, A D Thormodsen, H Heinemann *J. Mol. Catal.*, 1985, **31** 191
29. A W Nikitin, A D Pomogailo, W L Rubailo *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, p. 36
30. A A Efendiev, G L Shik, L F Vekilova, T N Shakhtakhtinskii *Katalizatory Soderzhashchie Nanesennye Kompleksy* (Catalysts Containing Applied Complexes), Papers Presented at the Symposium, Institute of Catalysis, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk, 1980, Part 2, p. 179
31. A A Efendiev, D D Orudzhiev, T N Shakhtakhtinskii, V A Kabanov *Kinet. Katal.*, 1986, **27** 520
32. V G Popov, N M Fomina *Kompleksnye Metalloorganicheskie Katalizatory Polimerizatsii Olefinov* (Complex Organometallic Catalysts for the Polymerisation of Olefins), Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka, 1991, Collection 11, p. 59
33. G Braca, C Carlini *Inf. Chim.*, 1987, (175) 149
34. O V Krylov *Mekhanizymy Kataliza* (Mechanism of Catalysis), Institute of Catalysis, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk, 1984, Part 1, p. 51
35. A D Pomogailo *Kataliz Immobilizovannymi Kompleksami* (Catalysis by Immobilised Complexes), Nauka, Moscow, 1991
36. J D Andrade, W-Y Chem *Surf. Interface Anal.*, 1986, **8** 253
37. H Widdecke *Prague Meet. Macromol. 30th Microsymp. Polym. Supported Org. Reagents and Catal.*, Prague, 1987, Programme P. L14
38. A W Schultz, P Strauss *J. Phys. Chem.*, 1972, **76** 1767
39. V N Parmon, Dissertation for Doctor of Chemical Sciences, Institute of Catalysis, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk, 1985, 707 pp

40. F K Shmidt *Kataliz Kompleksami Metallov Pervogo Perekhodnogo Ryada Reaktsii Gidrirovaniya i Dimerizatsii* (Catalysis of Hydration and Dimerisation Reactions by First Transition Series Metal Complexes), Irkutsk State University, Irkutsk, 1986, p. 158
41. S B Echmaev, I N Ivleva, A D Pomogailo, et al. *Kinet. Katal.*, 1986, **27** 394
42. S V Vonsovskii *Magnetizm* (Magnetism), Nauka, Moscow, 1971, p. 65
43. I N Ivleva, A D Pomogailo, S B Echmaev, et al. *Kinet. Katal.*, 1979, **20** 1282; 1983, **24** 663
44. S B Echmaev, I N Ivleva, A D Pomogailo, et al. *Kinet. Katal.*, 1983, **24** 1428
45. A D Pomogailo, A T Nikitaev, F S D'yachkovskii *Kinet. Katal.*, 1984, **25** 166
46. A Guyot, C Graillat, M Bartholin *J. Mol. Catal.*, 1977/1978, **3** 39
47. E W Thornton, H Knozinger, B Tesche, et al. *J. Catal.*, 1980, **62** 117
48. H Grubbs, C P Lau, R Currier, C H Brubaker, Jr. *J. Am. Chem. Soc.*, 1977, **99** 4517
49. E A Karakhanov, E B Neimerovets, V S Pshezhetskii, A G Dedov *Khim. Geterotsikl. Soedin.*, 1986, 303
50. L F Velikova, E A Blyumberg, A A Efendiev, et al. *Azerb. Khim. Zh.*, 1987, (3) 79
51. A D Pomogailo, F A Khrisostomov, F S D'yachkovskii *Kinet. Katal.*, 1985, **26** 1104
52. A D Pomogailo, F S Dyachkovskii *Acta Polym.*, 1984, **35** 41
53. M S Jarell, B C Gates, E D Nicholson *J. Am. Chem. Soc.*, 1978, **100** 5727
54. E A Bekturov, S E Kudaibergenov, V A Sigitov *Polymer*, 1986, **27** 1269
55. J H Schutten, P Piet, A L German *Makromol. Chem.*, 1979, **180** 2341; *Angew. Chem.*, 1980, **89** 201
56. T M Ushakova, I L Dubnikova, I N Meshkova, et al. *Vysokomol. Soedin., Ser. A*, 1979, **21** 2713
57. J C W Chien, J T T Hsieh *Coordination Polymerization* (Edited by J C W Chien), Acad. Press, New York, 1975, p. 305
58. A A Belii, L G Chigladze, M E Vol'pin, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2678; 1989, 1961
59. E N Rasadkina, T V Kuznetsova, A T Teleshov, et al. *Kinet. Katal.*, 1974, **15** 969
60. G P Potapov *React. Kinet. Catal. Lett.*, 1983, **23** 281
61. M V Klyuev *Zh. Org. Khim.*, 1984, **20** 1908; 1987, **23** 581
62. G V Vinogradov, A Ya Malkin *Reologiya Polimerov* (The Rheology of Polymers), Khimiya, Moscow, 1977, 438
63. V V Volodin, A N Shupik, A M Shapiro, et al. *Vysokomol. Soedinen., Ser. B, Krat. Soobshch.*, 1987, **29** 496
64. T Uematsu, F Saito, M Miura, H Hashimoto *Chem. Lett.*, 1977, (2) 113
65. T Uematsu, Y Nakazawa, F Akutsu, et al. *Makromol. Chem.*, 1987, **188** 1085
66. A B Solov'eva, Dissertation for Doctorate of Chemical Sciences), Lomonosov Institute of Fine Chemical Technology, Moscow, 1989, 253 pp
67. P Viout, I Artaud *J. Chem. Soc., Perkin Trans. 1*, 1984, (6) 1351
68. D E Bergbreiter, R Chandrar *J. Am. Chem. Soc.*, 1987, **109** 174
69. Wei Chen, Guangfu Ma, Zhaoying Lo, Mangjun Gao *J. Macromol. Sci. A*, 1987, **24** 243
70. G Valentini, G Braca, G Sbrana, et al. *Inter. Symp. Macromol. Pisa*, 1980, **4** 143
71. Y Lin, B Zou *J. Catal.*, 1985, **6** 273
72. C E Koning, F J Vierson, G Challa, J Reedijk *J. Mol. Catal.*, 1988, **44** 245
73. W Breemhaar, H C Meinders, G Challa *J. Mol. Catal.*, 1981, **10** 33
74. A V Artemov, V A Seleznev, E F Vainshtein *Izv. Vuzov. Khim. Khim. Tekhnol.*, 1983, **26** 1298; 1984, **27** 64
75. V A Seleznev, Yu P Tyulenin, E F Vainshtein, A V Artemov *Kinet. Katal.*, 1983, **4** 1085; *Neftekhimiya*, 1981, **21** 114
76. K H Streun, P Piet, A L German *Eur. Polym. J.*, 1987, **23** 941
77. A P Purmal, L A Nikolaev *Usp. Khim.*, 1985, **54**(5) 786 [English translation in *Russ. Chem. Rev.*, 1985(5)]
78. R J Williams, P A Serman, I Feinstein-Jaffe *J. Mol. Catal.*, 1989, **51** 117 [this reference appears to be incorrect (Ed. of Translation)]
79. S A Lawrence, P A Serman, I Feinstein-Jaffe *J. Mol. Catal.*, 1989, **51** 117
80. I V Serebryanaya, N E Khrushch, A D Pomogailo, et al. *Kinet. Katal.*, 1986, **27** 389; 1990, **31** 540
81. F S Dyachkovskii, A D Pomogailo *Homogeneous and Heterogeneous Catalysis* (Edited by Yu Yermakov, V Likholobov, VNU Science Press, Utrecht, 1986, p. 447
82. A P Filippov, O A Polishchuk *Kinet. Katal.*, 1984, **25** 1341, 1348
83. H Akarawa, Y Morooka, A Ozaki *Bull. Chem. Soc. Jpn.*, 1974, **47** 2958
84. N Yablokova, A V Ganyushkin, G B Sadikov, Yu A Aleksandrov *Vysokomol. Soedin., Ser. B, Krat. Soobshch.*, 1985, **27** 553
85. E Bayer, W Schumann *J. Chem. Soc., Chem. Commun.*, 1986, (12) 949
86. M Koide, E Tsuchida, Y Kurimura *Makromol. Chem.*, 1981, **182** 749; *Makromol. Chem., Rapid. Commun.*, 1981, **2** 627
87. M Barteri, B Pispisa *Intern. Symp. Macromol. Pisa*, 1980, **4** 155; B Pispisa, M Barteri, M Farinella *Inorg. Chem.*, 1983, **22** 3166
88. M Hatano, T Nozawa, S Ikeda, T Yamamoto *Makromol. Chem.*, 1971, **11** 11, 31
89. R Ran, W Pei, Kh Jia, et al. *Gaofen'tsy Tunsyun* (Polym. Commun.), 1986, (6) 453
90. R Ran, Kh Jia, X Wu, et al. *Chem. J. Chin. Univ.*, 1986, **7** 645; 1987, **8** 1141
91. N Toshima, K Kanaka, M Komijma, H Hirai *J. Macromol. Sci. A*, 1988, **25** 1349
92. N S Enikolopyan, L N Raspopov, A D Pomogailo, et al. *Dokl. Akad. Nauk SSSR*, 1984, **278** 1392; *Vysokomol. Soedin., Ser. A*, 1989, **31** 2624
93. V A Kabanov, V I Smetanyuk, V G Popov, et al. *Vysokomol. Soedinen., Ser. A*, 1980, **22** 335
94. N F Surkov, S P Davtyan, A D Pomogailo, F S D'yachkovskii *Kinet. Katal.*, 1986, **27** 714
95. V A Likholobov, A S Lisitsyn *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1989, **34** 340
96. K G Ione *Polifunktsional'nyi Kataliz Na Tseolitakh* (Polyfunctional Catalysis on Zeolites), Novosibirsk, 1982, 272 pp
97. R F Batchelder, B C Gates, F J P Kuijpers *6th Intern. Congress on Catalysis*, London, 1976, Preprint A40
98. N Oyama, F C Anson *J. Am. Chem. Soc.*, 1979, **101** 3450

99. K Shigehara, F C Anson *J. Electroanal. Chem.*, 1982, **132** 107
100. C U Pittmann, Jr., Y Kawabata, Y F Liang *179th Am. Chem. Soc., Nat. Meet. Houston (Tex.)*, 1980, Abstr. Pap., Washington, 1980
101. I I Moiseev *Itogi Nauki i Tekhniki. Kinetika i Kataliz* (Advances in Science and Technology. Kinetics and Catalysis), All-Union Institute of Scientific and Technical Information, Moscow, 1984, Vol. 13, p. 147
102. V D Kopylova *Teoriya i Praktika Sorbtsionnykh Protsessov* (Theory and Practice of Sorption Processes), Voronezh State University Press, Voronezh, 1986, No. 18, p. 3
103. G I Likhtenshtein *Mnogoyadernye Okislitel'no-Vosstanovitel'nye Metallofermenty* (Multinuclear Redox Metalloenzymes), Nauka, Moscow, 1979, 323 pp
104. E Antonini, M Brunori *Haemoglobin and Myoglobin in Their Reaction with Ligands*, North-Holland Publ. Co., Amsterdam, 1971, 349 pp
105. A D Pomogailo, I E Uflyand *Makromolekulyarnye Metallokhelaty* (Macromolecular Metallo-Chelates), Khimiya, Moscow, 1991, 304 pp
106. A D Pomogailo, V S Savost'yanov *Metallosoderzhashchie Monomery i Polimery Na Ikh Osnove* (Metal-Containing Monomers and Polymers Based on Them), Khimiya, Moscow, 1988, 384 pp
107. R S Brown, M Zamkaneli, J L Cocho *J. Am. Chem. Soc.*, 1982, **106** 5222