

Chapter 1

Introduction

1.1 Types of Homogeneous Catalysis with Metal Complexes, Their Advantages and Drawbacks

The analysis of one of the most important materials—from both the experimental and theoretical point of view—in the history of chemistry since Boyle's times has allowed us to systematize and reduce it to four conceptual systems: composition doctrine (approximately since 1660), structural chemistry (approximately since 1800), chemical process doctrine (after 1880) and evolutionary chemistry (approximately since 1960). Once we start to consider the nature of the substance, the following hierarchy of its material carriers can be observed: (1) atoms of chemical elements; (2) molecules of chemical compounds; (3) systems of reacting substances, including using of catalysts and (4) highly-organized catalytic systems (enzymes) as a result of evolutionary development of living substances [1].

Therefore higher and higher consecutive levels of chemical knowledge can be distinguished, each subsequent level incorporating the material of lower levels (conceptual systems) in the transformed form. Such an approach serves as the original guide in the strategic development of scientific and technical progress in chemical production.

Nowadays, the fundamental science is not only the basis of current chemical production—it also promotes other fundamental levels (on the new conceptual basis), the creation of quite new production, characterized by sharp increases in labour productivity and the enhanced quality of products obtained. In this regard, the third and fourth conceptual systems—the doctrine of chemical processes and evolutionary chemistry—have been developing very rapidly in last few decades, promising really fantastic results in the fields of both fundamental and applied research.

In these two conceptual systems the problems of redox homogeneous catalysis with transition metals coordination compounds (metal complexes) occupy a very important place.

Unlike other forms, homogeneous catalysis with metal complexes has some peculiarities [2]:

1. The possibility of revealing the mechanism of catalyst action, its composition and the identification of its intermediate forms on the qualitative, semi-quantitative and sometimes quantitative levels.
2. The ability to obtain practically unlimited amounts of catalytically active and specifically acting systems.
3. Improvement of catalyst specificity and directed change of its activity at the expense of medium parameter variations (nature and number of metal ions, ligands, character of solvent, etc.).
4. Use of the greater part or even of all the molecules of catalyst in catalytic activity, which is impossible in the case of classical heterogeneous catalyst.
5. Decrease in rigidity of process conditions.
6. Comparative ease of the creation of continuous processes.

A characteristic feature of homogeneous catalysis with metal complexes is its clearly expressed practical orientation. As early as the 1940s and 1950s, a series of organic synthesis directions appeared (syntheses with metals carbonyls, catalytic polymerization on Ziegler-Natta systems, cyclohexane oxidation into cyclohexanone, butane into acetic acid, etc.). The number of works on fermentology increased at the same time and research on immobilized enzymes was started. The rapid growth in the amount of work on the thermodynamics of complex formation in solutions at that time promoted studies devoted to the role of coordination in catalysis (approximately since the 1960s).

Homogeneous catalysis today is at the stage of rough development. Although the leading position in the practical use of catalytic phenomena historically belongs to heterogeneous catalysis, and its application is quite considerable from the practical aspect, there are still considerable problem with understanding catalytic processes mechanisms. The existing theories of heterogeneous catalysis mainly have a qualitative character and can only explain some catalytic processes.

The situation with homogeneous catalysis is somewhat different. Its practical applications are still considerably behind those of the heterogeneous version. This is illustrated by the fact that systematic study of homogeneous catalysis at the mechanism level has only been active since the 1960s. Therefore it is not surprising that heterogeneous catalysis has occupied the cardinal position in the chemical industry and that the applications of homogeneous catalysis (in spite of rapid progress) have not yet reached the appropriate level. Though heterogeneous catalysis in its practical applications has built up a good start, theoretical understanding of this phenomenon did not progress as quickly. Some homogeneous-catalysed reaction mechanisms have become clear after 5–10 years study, whereas for some heterogeneous reactions this has taken up to 50 years research.

This can apparently be explained by the fact that, up to the early 1960s, the greatest successes have come in equilibria studies of homogeneous systems (specifically regarding complex compounds of transition metal solutions). By then it became possible to apply various modern physical methods (especially

spectroscopy) to detect the intermediate compounds. The simplicity (absence of a border surface) and reproducibility of homogeneous systems was also an important factor.

On the other hand, fast successes in the study of homogeneous reactions mechanisms will help to resolve certain problems in heterogeneous catalysis (for instance, mechanisms of hydrogenization in solution and on the catalyst surface are often similar, although there are also differences). In fact, within approximately the two last decades, great theoretical successes have been achieved in this area, and because of these the mechanisms of some reactions can be described semi-quantitatively and even quantitatively (although quite rarely).

In the field of homogeneous catalysis with metal complexes, certain successes were achieved in the explanation of catalytic activity during the transition from activated metal ion to metal coordination compounds with various ligands. Thus, it became possible to show that the essential importance involves a change in the redox potential during the transition from activated metal ion to metal complexes. Thus, the addition of EDTA to the system $\text{Fe}^{3+}_{\text{aq}}/\text{Fe}^{2+}_{\text{aq}}$ EDTA changes the potential from 0.771 V to 0.143 V, thus greatly reducing the initiation rate of H_2O_2 decomposition. Proceeding from the different lability of the coordination sphere of a metal ion, one can explain the different process mechanisms (for example, H_2O_2 decomposition in the presence of Fe^{3+} complex and Mn^{2+} ions, isoelectronic with it, although quantum-chemical explanations of this difference have appeared lately).

Nowadays the prospects of homogeneous catalysis with metal complexes are fascinating. Its significant advantage is that it frequently provides a way for a reaction which is either extremely difficult without the catalyst or cannot be realized by other means. As such reactions proceed frequently under mild conditions, they result in high selectivity products. Homogeneous catalysts are also potentially more effective than heterogeneous, as in the former the reacting substrate interacts with each molecule of catalyst but in the latter only with superficial atoms or ligands of catalyst.

Varying the ratio between the concentration of ligand and metal it is possible to create homogeneous catalytic systems in which all metal atoms are active and act as catalysts. In its turn this leads to the possibility to use them in much lower concentrations than in the case of heterogeneous catalysts, thus economizing on compounds of rare and precious metals.

Comparative peculiarities of homogeneous and heterogeneous catalysis are given in Table 1.1, and their types are described in details in certain papers [2–4].

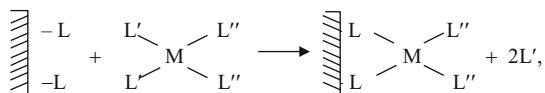
The application of homogeneous catalysis in industry, despite its obvious profitability, is complicated by various practical difficulties. For example, it is often rather difficult to regenerate and to extract the catalyst from the reactionary medium, and to separate it from the reaction products.

To solve this problem, another method of catalyst preparation can be used which in essence is binding the transitionmetal complex in a properly prepared solid

Table 1.1 Comparison of homogeneous and heterogeneous catalysis

Parameters	Catalysis	
	Homogeneous	Heterogeneous
Active centers	All the metal atoms	Surface atoms only
Concentration	Low	High
Structure	Definite	Indefinite
Stoichiometry	Definite	Indefinite
Reaction conditions	Mild	Strict (high T° and pressure)
Activity	High	Low
Determination of catalyst composition	Rather complicated	Easy
Stability	Low	High
Catalyst regeneration	Complicated	Easy

matrix. The matrix should have functional groups (ligands) which are bound with the dissolved metal complex:



where L, L', L'' are various ligands.

In this way, the advantages of homogeneous and heterogeneous catalysts are combined, whereas the differences between them reduce considerably. Therefore, it becomes clear that there is no principal difference between the mechanisms of homogeneous and heterogeneous catalysis in many reactions. For example, in the case of olefin and diene catalytic polymerization, irrespective of whether the reaction proceeds in the solution or on the surface, the mechanism is the same—incorporation of monomer occurs along the bond “transition metal–carbon.” The difference is in the method of active center formation but not in the mechanism of their action.

There is no generally accepted name for such catalysts. The most widely used are “heterogenized,” “hybridized,” “immobilized homogeneous,” and “exact” catalysts. The last name indicates that all the metal ions can be included in the composition of active centers, and thus the equality between metal ion and active center concentrations is observed. Unlike traditional heterogeneous catalysts, the role of carrier is not reduced only to active component deduction on the surface. While the catalyst is binding with the surface, the significant change in its chemical nature occurs. In addition it becomes possible to preserve the catalyst in the dispersed form and thus to prevent its aggregation.

The opportunity to create heterogenized catalysts by fixation of metal complexes on a substrate (polymeric carrier) is very important [5, 6].

Enzymatic catalysis and the possibility of its modeling is no less interesting. Currently, it has found broad industrial applications [7]. The main difference between enzymatic catalysis and the other catalysis types is singularity of the enzyme active centre structure (caused in particular by its albumen part) not

present in other cases, for example in homogeneous solutions of low molecular substances—complex compounds of transition metals, though the latter can also be components or analogues of active centres. This is because in enzymes globula the activation of molecular groups occurs (for example, metal coordination compounds), which in the usual state are not very active catalysts.

The structure of active centres and influence of surrounding albumen determine the unique properties of enzymes: (1) their high catalytic efficiency (sometimes exceeding non-biological catalysts 10^{10} – 10^{13} times), (2) their exceptional selectivity and (3) their ability to respond on the regulating interaction of small changes in properties and medium structure [8].

Immobilized enzymes are used today when working at higher temperatures (higher than 333 K) and for the convenience of their introduction and extraction from the reaction medium. Immobilized enzymes are those connected with some carrier. Immobilization consists of: (1) covalent joining of enzyme to polymer carrier (cellulose, glass, polystyrol, polyaminoacids, etc.); (2) covalent joining of enzyme molecules to each other with the help of added polyfunctional reagent; (3) enzyme incorporating into three-dimensional network of gel of polymer; (4) enzyme adsorption on water insoluble carriers (for example ionites); and (5) enzyme incorporation into semipermeable microcapsulas or polymeric fibers. In these ways a considerable increase in enzyme stability can be reached. Besides, it can be easily separated from the products of catalysed reaction and thus catalytic processes can be stopped at the required stage, and the catalyst can be used in a flow regime or repeatedly. Immobilized enzymes have rather large advantages in their use in medical applications since it is possible to avoid the allergic reaction of organisms.

As a rule, immobilization increases the effective lifetime and temperature stability of enzymes, although there can be exceptions.

1.2 Perspectives of the Industrial Use of Homogeneous Catalysis with Metal Complexes

High activity, specificity and possibility to modify metal complex catalysts—these are the features that would determine their wide industrial applications.

High activity can be achieved due to the change in ligand nature, fastening of an active centre on the appropriate carrier, creation of the multi-centered catalysis structure, selection of solvent and certain process conditions, etc.

Because of the high efficiency of homogeneous catalysts, it became possible to develop a highly effective technological process of olefin production by ethylene polymerization. Synthesis of acetic acid is possible by methanol carbonylation (mild conditions, rhodium complexes as catalysts, many times exceeding the activity of cobalt or acid catalysts, which makes them competitive in spite of the high cost of rhodium). The hydrogenase analogues were created via complex homogeneous and heterogeneous catalytic systems of aromatic nitrocompound hydration (high rate, mild conditions). Thus it became possible to realize the continuous hydration of

aromatic nitrocompounds to corresponding amines such as aniline, toluidine and chloraniline. Earlier, such processes were carried out under the hard conditions of high temperature and hydrogen pressure, which often resulted in low yields of main product, required complicated equipment and made the process expensive.

Until now, various complex catalysts and catalytic system types have been developed that make it possible to hydrate the benzene into cyclohexane under mild conditions and at a high rate (sometimes exceeding the corresponding values for heterogeneous catalysts).

Another factor of homogeneous catalysis with metal complexes is its specificity. It can be achieved by variation of nature and number of coordinated ligands, carriers and solvent. So the process of tetralene production by naphthalene hydration was developed using the highly-selective homogeneous complex catalyst, its selectivity being tens of times higher than that of skeleton nickel one, usually applied in these instances.

The use of enzymes and especially immobilized ones is varied. Thus, catalase is used in cheese production as H_2O_2 arrests decomposition after the cold sterilization, in the production of foamy rubber and foamy cement, and also to accelerate fur and feather bleaching.

In the early 1970s it became possible to carry out the covalent binding of amyloglucosidase (a fermentation that ensures starch transformation into glucose–starch sugaring) with porous glass. A multitonnage process using immobilized enzymes is the transformation (conversion) of D,L-glucose (obtained from corn starch) into D,L-fructose, in which the sugar contents is approximately 1.5 times higher. For these purposes the immobilized enzyme glucoisomerase is used. Suitable equipment with the capacity of 250,000 tonnes and more per year was developed in the USA.

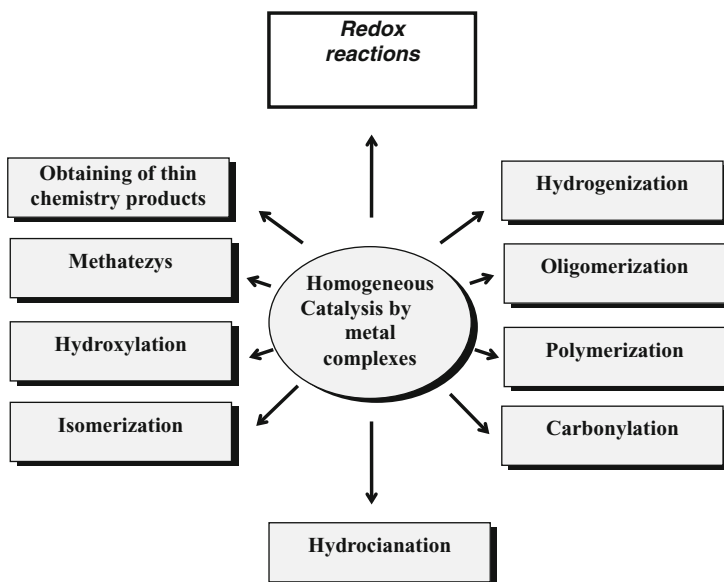
Using of immobilized enzymes makes it possible to transform cane sugar into a glucose–fructose mixture. The economic benefit of such a transformation is quite considerable.

The opportunity to develop the synthesis of heterogenized low-temperature and efficient catalysts of ammonium and nitrogen-containing compounds from the molecular nitrogen under ordinary pressure, using the principles of immobilized enzymes and heterogenized metal complexes, is attractive.

Existing and possible basic areas for the use of homogeneous catalysis with metal ions and complexes in various reactions are extensive, as can clearly be seen from Scheme 1.1.

The field of homogeneous catalytic processes with metal complex participation is comprehensive and universal. Therefore, it is necessary to put certain limitations on subsequent consideration of the experimental and theoretical data discussed in this book.

We should consider only the redox catalytic processes in the liquid phase (mainly in polar solvents—basically in water—and in nonpolar solvents). This is because of the exceptional importance of redox processes in relatively simple chemical systems, in the reactions proceeding in living organisms, in environmental processes (in atmosphere, water and soil), and in industrial technologies (especially in the food-processing industries).



Scheme 1.1 Applications of homogeneous catalysis with the transition metal complexes

Only the ions or complex compounds of iron, manganese, cobalt, copper (and in part those of zinc and molybdenum) at different oxidation degrees will be considered, these metal compounds being necessary for living organisms catalysing redox transformations.

Many are involved as catalysts in the environmental redox processes. For example, iron or manganese compounds are catalysts of the redox reactions proceeding in the atmosphere with the formation of so-called “acid rain.” They—and also copper compounds—are responsible for catalytic processes occurring worldwide in oceans, seas, rivers and water basins. These elements’ compounds are used as catalysts in various chemical technologies, and also in spontaneous processes, associated with raw (food) or prepared materials.

Many substances can act as oxidizers in these processes. Only those catalytic processes will be considered in which dioxygen or products of its reduction are used as oxidants, in particular hydrogen peroxide, H_2O_2 , as these oxidizers are unique with regard to their biological activity, environmentally friendly behaviour and adaptability to production. To a smaller degree, catalytic systems will also be considered where hydroperoxides ROOH related to hydrogen peroxide, iodozyl benzene and some other oxidants are used.

The solvent in such systems is usually water, but also possibly certain organic substances. The temperature conditions of these processes are close to standard ones ($t = 25^\circ\text{C}$, $p = 1\text{ atm}$), although there can be small deviations from these conditions.

Despite these consciously chosen limitations, the circle of possible interesting catalytic redox systems still remains huge. We will not be considering all these systems here. For example, information on catalytic redox systems at the phenomenological description level is omitted. Only the most important systems examined at the process mechanisms level are considered (quantitatively, semi-quantitatively and—in rare cases—qualitatively).

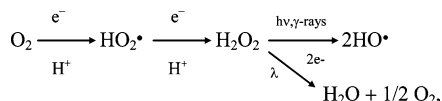
As a high number of special books, reviews and original works are devoted to composition, electronic structure and functional properties of enzymes, here they will be discussed very briefly, and only the most important of them which realize the transformation of certain substrates under the action of O_2 or H_2O ($ROOH$, C_6H_5IO). Most attention is paid to the creation of these enzyme models and the description of their catalytic properties. In addition, a certain amount of attention is given to the behaviour of oxygen and products of its reduction (H_2O_2 , free radicals $OH\cdot$, HO^{2-}), superoxidized intermediates (of ferryl and manganyl particles) in living organisms and the toxicity influence of all these substances on certain biological processes (for example lipids reoxidation) and the occurrence of certain diseases.

This book contains the brief theoretical description of the basic laws and mechanisms of the redox reactions with O_2 and H_2O_2 in association with water compartments, catalysed by transition metal coordination compounds. There is also a detailed discussion of these processes and their applications in various fields of industrial chemistry, the food-processing industry, biochemistry, medicine, analytical chemistry, ecological chemistry and other areas.

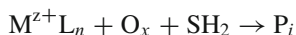
Nowadays it is mainly the compounds of twelve elements (Ti, V, Mn, Fe, Co, Zn, Mo, Rh, Pd, W, Cu and Ni) that are used as catalysts in industry. Among them, the extremely interesting and well studied catalysts are the coordination compounds of manganese, iron and copper. Not only was the composition of these complexes defined in the solutions, but also their stability constants and the formal kinetics of various substrates redox transformations were studied. The mechanisms of these processes were revealed on a good qualitative (and sometimes on semi-qualitative and even quantitative) level, and quantum-chemical calculations were made, confirming the probability of the occurrence of certain reactive intermediates. All this creates the basis for further optimisation of important reactions.

Consideration of other metal complexes, other than those of manganese, iron, copper and cobalt, as redox transformations catalysts is not expedient here for the following reasons: (1) some of them are considered in detail in certain papers; (2) experimental material and redox transformations mechanisms are often given in literature only on the descriptive level.

Besides, as there is a great variety of catalytic redox reactions, some model of these processes should be chosen, selecting those that will reveal the general regularities and mechanisms of such processes. As oxidizers in such models the particles were chosen which are the products of four-electron reduction of the oxygen molecule:



i.e., O_2 , H_2O_2 , HO_2^\bullet , OH^\bullet and also ferryl ($\text{Fe}^{\text{IV}} = \text{O}^{2+}$) and manganyl ($\text{Mn}^{\text{IV}} = \text{O}^{2+}$) ions or their complexes with ligands. The oxidizer in most cases was hydrogen peroxide. The substrates were carbonic acids, alcohols, aldehydes, dyes, etc. The ligands of metal coordination compounds were carbonic acids, alcohols, aldehydes, dyes, etc. Thus, the summary scheme of processes to be considered further can be presented as



where M^{z+}L_n represents copper, iron, manganese, cobalt and sometimes other elements coordination compounds, O_x the oxidizer H_2O_2 , ROOH , O_2 , HO_2^\bullet , OH^\bullet , etc., SH_2 substrates (more often organic compounds), and P_i the reaction products.

Even such self-restriction of the reactions considered results in the necessity to describe only the main material from the huge experimental and theoretical information available from the scientific literature and from data obtained by the authors. Therefore plenty of interesting experimental data are deliberately not given in this book. After a brief theoretical statement of basic laws and mechanisms of the redox catalytic processes, the main regularities and mechanisms and their role, and the possibility of their use are shown in biochemistry, medicine, environmental chemistry, analytical chemistry (catalymetry) and, for practical purposes, in various areas of industrial and food chemistry.

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Duca, G.

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