

1

Introduction

1.1

The Phenomenon Catalysis

Catalysis is the key to chemical transformations. Most industrial syntheses and nearly all biological reactions require catalysts. Furthermore, catalysis is the most important technology in environmental protection, that is, the prevention of emissions. A well-known example is the catalytic converter for automobiles.

Catalytic reactions were already used in antiquity, although the underlying principle of catalysis was not recognized at the time. For example, the fermentation of sugar to ethanol and the conversion of ethanol to acetic acid are catalyzed by enzymes (biocatalysts). However, the systematic scientific development of catalysis only began about 200 years ago, and its importance has grown up to the present day [1].

The term “catalysis” was introduced as early as 1836 by Berzelius in order to explain various decomposition and transformation reactions. He assumed that catalysts possess special powers that can influence the affinity of chemical substances.

A definition that is still valid today is due to Ostwald (1895): “a catalyst accelerates a chemical reaction without affecting the position of the equilibrium.” Ostwald recognized catalysis as a ubiquitous phenomenon that was to be explained in terms of the laws of physical chemistry.

While it was formerly assumed that the catalyst remained unchanged in the course of the reaction, it is now known that the catalyst is involved in chemical bonding with the reactants during the catalytic process. Thus, catalysis is a cyclic process: the reactants are bound to one form of the catalyst, and the products are released from another, regenerating the initial state.

In simple terms, the catalytic cycle can be described as shown in Figure 1.1. The intermediate catalyst complexes are in most cases highly reactive and difficult to detect.

In theory, an ideal catalyst would not be consumed, but this is not the case in practice. Owing to competing reactions, the catalyst undergoes chemical changes, and its activity becomes lower (catalyst deactivation). Thus, catalysts must be regenerated or eventually replaced.

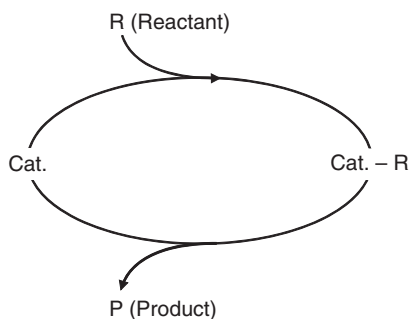


Figure 1.1 Catalytic cycle.

Apart from accelerating reactions, catalysts have another important property: they can influence the selectivity of chemical reactions. This means that completely different products can be obtained from a given starting material by using different catalyst systems. Industrially, this targeted reaction control is often even more important than the catalytic activity.

Catalysts can be gases, liquids, or solids. Most industrial catalysts are liquids or solids, whereby the latter react only via their surface. The importance of catalysis in the chemical industry is shown by the fact that 75% of all chemicals are produced with the aid of catalysts; in newly developed processes, the figure is over 90%. Numerous organic intermediate products required for the production of plastics, synthetic fibers, pharmaceuticals, dyes, crop protection agents, resins, and pigments can only be produced by catalytic processes [2].

Most of the processes involved in crude oil processing and petrochemistry, such as purification stages, refining, and chemical transformations, require catalysts. Environmental protection measures such as automobile exhaust control and purification of off-gases from power stations and industrial plant would be inconceivable without catalysts.

Catalysts have been successfully used in the chemical industry for more than 100 years, examples being the synthesis of sulfuric acid, the conversion of ammonia to nitric acid, and catalytic hydrogenation. Later developments include new highly selective multicomponent oxide and metallic catalysts, zeolites, and the introduction of homogeneous transition metal complexes in the chemical industry. This was supplemented by new high-performance techniques for probing catalysts and elucidating the mechanisms of heterogeneous and homogeneous catalysis.

The brief historical survey given in Table 1.1 shows just how closely the development of catalysis is linked to the history of industrial chemistry [4].

1.2

Mode of Action of Catalysts

The suitability of a catalyst for an industrial process depends mainly on the following three properties:

Table 1.1 History of the catalysis of industrial processes [3, 4].

Catalytic reaction	Catalyst	Discoverer or company/year
Sulfuric acid (lead chamber process)	NO_x	Désormes, Clement, 1806
Chlorine production by HCl oxidation	CuSO_4	Deacon, 1867
Sulfuric acid (contact process)	$\text{Pt}, \text{V}_2\text{O}_5$	Winkler, 1875; Knietsch, 1888 (BASF)
Nitric acid by NH_3 oxidation	Pt/Rh nets	Ostwald, 1906
Fat hardening	Ni	Normann, 1907
Ammonia synthesis from N_2, H_2	Fe	Mittasch, Haber, Bosch, 1908; Production, 1913 (BASF)
Hydrogenation of coal to hydrocarbons	Fe, Mo, Sn	Bergius, 1913; Pier, 1927
Oxidation of benzene, naphthalene to maleic anhydride or phthalic anhydride	V_2O_5	Weiss, Downs, 1920
Methanol synthesis from CO/H_2	$\text{ZnO/Cr}_2\text{O}_3$	Mittasch, 1923
Hydrocarbons from CO/H_2 (motor fuels)	Fe, Co, Ni	Fischer, Tropsch, 1925
Oxidation of ethylene to ethylene oxide	Ag	Lefort, 1930
Alkylation of olefins with isobutane to gasoline	AlCl_3	Ipatieff, Pines, 1932
Cracking of hydrocarbons	$\text{Al}_2\text{O}_3/\text{SiO}_2$	Houdry, 1937
Hydroformylation of ethylene to propanal	Co	Roelen, 1938 (Ruhrchemie)
Cracking in a fluidized bed	Aluminosilicates	Lewis, Gilliland, 1939 (Standard Oil)
Ethylene polymerization, low pressure	Ti compounds	Ziegler, Natta, 1954
Oxidation of ethylene to acetaldehyde	Pd/Cu chlorides	Hafner, Smidt (Wacker)
Ammonoxidation of propene to acrylonitrile	Bi/Mo	Idol, 1959 (SOHIO process)
Olefin metathesis	Re, W, Mo	Banks, Bailey, 1964
Hydrogenation, isomerization, hydroformylation	Rh and Ru complexes	Wilkinson, 1964
Asymmetric hydrogenation	Rh/chiral phosphine	Knowles, 1974; L-Dopa (Monsanto)
Three-way catalyst	Pt, Rh/monolith	General Motors, Ford, 1974
Methanol conversion to hydrocarbons	Zeolites	Mobil Chemical Co., 1975

(continued overleaf)

Table 1.1 (Continued.)

Catalytic reaction	Catalyst	Discoverer or company/year
α -Olefins from ethylene	Ni/chelate phosphine	Shell (SHOP process) 1977
Sharpless oxidation, epoxidation	Ti/ROOH/tartrate	May & Baker, Upjohn, ARCO, 1981
Selective oxidations with H_2O_2	Titanium zeolite (TS-1)	Enichem, 1983
Hydroformylation	Rh/phosphine/aqueous	Rhône-Poulenc/Ruhrchemie, 1984
Polymerization of olefins	zirconocene/MAO	Sinn, Kaminsky, 1985
Selective catalytic reduction SCR (power plants)	V, W, Ti oxides/monolith	~1986
Acetic acid	Ir/I ⁻ /Ru	“Cativa”-process, BP Chemicals, 1996
W.S. Knowles, R. Noyori, K.B. Sharpless	Ti compounds, diphosphine ligands	Nobel Prize for asymmetric catalysis, 2001
Y. Chauvin, R.S. Grubbs, R.R. Schrock, G. Ertl	Mo, Ru	Nobel Prize for studies of catalysis in metathesis, 2005
	–	Nobel Prize for chemical processes on solid surfaces, 2007
Propylene oxide from propylene and hydrogen peroxide	Ti-zeolite	BASF, Evonik/Uhde, 2008
R.F. Heck, A. Suzuki, E. Negishi	–	Nobel Prize for cross-couplings in organic synthesis, 2010

TS-1 = titanium (iv) silicalite zeolite catalyst, MAO = methylaluminoxane, and HPPO = hydrogen peroxide to propylene oxide.

- activity
- selectivity
- stability (deactivation behavior).

The question which of these functions is the most important is generally difficult to answer because the demands made on the catalyst are different for each process. First, let us define the above terms [5, 6, 7, 8].

1.2.1

Activity

Activity is a measure of how fast one or more reactions proceed in the presence of the catalyst. Activity can be defined in terms of kinetics or from a more practically oriented viewpoint. In a formal kinetic treatment, it is appropriate to measure reaction rates in the temperature and concentration ranges that will be present in the reactor.

The reaction rate r is calculated as the rate of change of the amount of substance n_A of reactant A with time relative to the reaction volume or the mass of catalyst:

$$r = \frac{\text{converted amount of substance of a reactant}}{\text{volume or catalyst mass} \cdot \text{time}} (\text{mol l}^{-1}\text{h}^{-1} \text{ or } \text{mol kg}^{-1} \text{ h}^{-1}) \quad (1.1)$$

Kinetic activities are derived from the fundamental rate laws, for example, that for a simple irreversible reaction $A \rightarrow P$:

$$\frac{dn_A}{dt} = kVf(c_A) \quad (1.2)$$

k is the rate constant and $f(c_A)$ is a concentration term that can exhibit a first-order or higher order dependence on adsorption equilibria (see Section 5.2).

The temperature dependence of rate constants is given by the Arrhenius equation:

$$k = k_0 e^{-\left(\frac{E_a}{RT}\right)} \quad (1.3)$$

where E_a is the activation energy of the reaction; k_0 is the pre-exponential factor; and R is the gas constant.

Equations (1.2) and (1.3) show that there are three possibilities for expressing catalyst activity, which are as follows:

- reaction rate
- rate constant k
- activation energy E_a .

Empirical rate equations are obtained by measuring reaction rates at various concentrations and temperatures. If, however, different catalysts are to be compared for a given reaction, the use of constant concentration and temperature conditions is often difficult because each catalyst requires its own optimal conditions. In this case, it is appropriate to use the initial reaction rates r_0 obtained by extrapolation to the start of the reaction.

Another measure of catalyst activity is the turnover number (TON), which originates from the field of enzymatic catalysis.

In the case of homogeneous catalysis, in which well-defined catalyst molecules are generally present in solution, the TON can be directly determined. For heterogeneous catalysts, this is generally difficult, because the activity depends on the size of the catalyst surface, which, however, does not have a uniform structure. For example, the activity of a supported metal catalyst is due to active metal atoms dispersed over the surface.

The number of active centers per unit mass or volume of catalyst can be determined indirectly by means of chemisorption experiments, but such measurements require great care, and the results are often not applicable to process conditions. Although the TON appears attractive due to its molecular simplicity, it should be used prudently in special cases.

In practice, readily determined measures of activity are often sufficient. For comparative measurements, such as catalyst screening, determination of process parameters, optimization of catalyst production conditions, and deactivation studies, the following activity measures can be used:

- conversion under constant reaction conditions;
- space velocity for a given, constant conversion;
- space–time yield;
- temperature required for a given conversion.

Catalysts are often investigated in continuously operated test reactors, in which the conversions attained at constant space velocity are compared [5].

The *space velocity* is the volume flow rate \dot{V}_0 , relative to the catalyst mass m_{cat} :

$$\text{Space velocity} = \frac{\dot{V}_0}{m_{\text{cat}}} \quad (\text{m}^3 \text{ kg}^{-1} \text{ s}^{-1}) \quad (1.4)$$

The *conversion* X_A is the ratio of the amount of reactant A that has reacted to the amount that was introduced into the reactor. For a batch reactor,

$$X_A = \frac{n_{A,0} - n_A}{n_{A,0}} \quad (\text{mol mol}^{-1} \text{ or } \%) \quad (1.5)$$

If we replace the catalyst mass in Eq. (1.4) with the catalyst volume, then we see that the space velocity is proportional to the reciprocal of the residence time.

Often the performance of a reactor is given relative to the catalyst mass or volume, so that reactors of different size or construction can be compared with one another. This quantity is known as the *space–time yield (STY)*:

$$\text{STY} = \frac{\text{Desired product quantity}}{\text{Catalyst volume} \cdot \text{time}} \quad (\text{mol l}^{-1} \text{ h}^{-1}) \quad (1.6)$$

Determination of the temperature required for a given conversion is another method of comparing catalysts. The best catalyst is the one that gives the desired conversion at a lower temperature. This method cannot, however, be recommended since the kinetics are often different at higher temperature, making misinterpretations likely. This method is better suited to carrying out deactivation measurements on catalysts in pilot plants.

1.2.1.1 Turnover Frequency TOF

The turnover frequency (TOF) (the term was borrowed from enzyme catalysis) quantifies the specific activity of a catalytic center for a special reaction under defined reaction conditions by the number of molecular reactions or catalytic cycles occurring at the center per unit time. For heterogeneous catalysts, the number of active centers is derived usually from sorption methods (Eq. (1.7)).

$$\text{TOF} = \frac{\text{volumetric rate of reaction}}{\text{number of centers/volume}} = \frac{\text{moles}}{\text{volume} \cdot \text{time}} \frac{\text{volume}}{\text{moles}} = \text{time}^{-1} \quad (1.7)$$

For most relevant industrial applications, the TOF is in the range $10^{-2} - 10^2 \text{ s}^{-1}$ (enzymes $10^3 - 10^7 \text{ s}^{-1}$).

Examples:

TOF values for the hydrogenation of cyclohexene at 25 °C and 1 bar (supported catalysts, structure-insensitive reaction) are provided in Table 1.2).

Table 1.2 TOF values for the hydrogenation of cyclohexene [9].

Metal	TOF (s ⁻¹)	
	Gas phase	Liquid phase
Ni	2.0	0.45
Rh	6.1	1.3
Pd	3.2	1.5
Pt	2.8	0.6

1.2.1.2 Turnover Number TON

The TON specifies the maximum use that can be made of a catalyst for a special reaction under defined conditions by a number of molecular reactions or reaction cycles occurring at the reactive center up to the decay of activity. The relationship between TOF and TON is (Eq. (1.8))

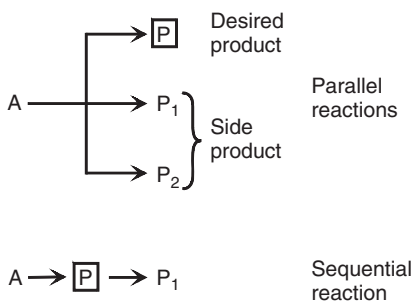
$$\text{TON} = \text{TOF} [\text{time}^{-1}] \cdot \text{lifetime of the catalyst} [\text{time}] [-] \quad (1.8)$$

For industrial applications the TON is in the range $10^6 - 10^7$.

1.2.2

Selectivity

The selectivity S_p of a reaction is the fraction of the starting material that is converted to the desired product P. It is expressed by the ratio of the amount of desired product to the reacted quantity of a reaction partner A and therefore gives information about the course of the reaction. In addition to the desired reaction, parallel and sequential reactions can also occur (Scheme 1.1).



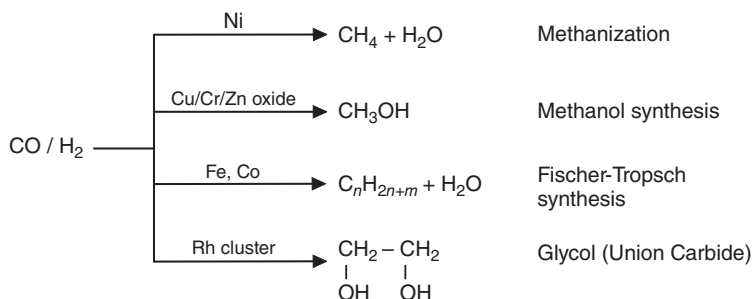
Scheme 1.1 Parallel and sequential reactions.

Since this quantity compares starting materials and products, the stoichiometric coefficients ν_i of the reactants must be taken into account, which gives rise to the following equation [5]:

$$S_p = \frac{n_p/\nu_p}{(n_{A,0} - n_A)/|\nu_A|} = \frac{n_p/\nu_A}{(n_{A,0} - n_A)/\nu_p} \quad (\text{mol mol}^{-1} \text{ or } \%) \quad (1.9)$$

In comparative selectivity studies, the reaction conditions of temperature and conversion or space velocity must, of course, be kept constant.

If the reaction is independent of the stoichiometry, then the selectivity $S_p = 1$. The selectivity is of great importance in industrial catalysis, as demonstrated by the example of synthesis gas chemistry, in which, depending on the catalyst used, completely different reaction products are obtained (Scheme 1.2) [9].



Scheme 1.2 Reactions of synthesis gas.

Selectivity problems are of particular relevance to oxidation reactions.

1.2.3

Stability

The chemical, thermal, and mechanical stability of a catalyst determines its lifetime in industrial reactors. Catalyst stability is influenced by numerous factors, including decomposition, coking, and poisoning. Catalyst deactivation can be followed by measuring activity or selectivity as a function of time.

Catalysts that lose activity during a process can often be regenerated before they ultimately have to be replaced. The total catalyst lifetime is of crucial importance for the economics of a process.

Today the efficient use of raw materials and energy is of major importance, and it is preferable to optimize existing processes than to develop new ones. For various reasons, the target quantities should be given the following order of priority:

Selectivity > Stability > Activity

1.2.4

Mole Balance and Conversion

To calculate the conversion of a reaction and the composition of the reaction mixture we shall perform a mole balance on a particular chemical species of interest,

Table 1.3 Mole balance for methanol synthesis.

Species	Remaining n_i (mol)
CO	$1 - X$
H ₂	$2(1 - X)$
CH ₃ OH	X
N ₂	3
Sum	$6 - 2X$

for example, the reactant A [5]. We have to develop the stoichiometric relationship for all reaction species that give the change in the number of moles for each species. Species A is our basis of calculation and $n_{A,0}$ is the number of moles of A initially present in the reactor. Of these, $n_{A,0} X$ moles of A are consumed in the system as a result of the chemical reaction, leaving $(n_{A,0} - n_{A,0} X)$ moles of A in the system. That is, the number of moles of A remaining in the reactor after conversion X has been achieved is

$$n_A = n_{A,0} - n_{A,0} X = n_{A,0}(1 - X)$$

Equation (1.10) shows a mole balance for methanol synthesis, CO/N₂ = 1 : 3 molar ratio:

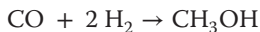


After writing similar relationships for the other reactants, the number of moles remaining in the system at time t can be expressed as a function of the conversion X (Table 1.3).

From this table, we can calculate the composition of the reaction mixture at the end of the conversion.

Example

The methanol synthesis in a laboratory reactor is carried out at 80 bar and 250 °C with the addition of inert gas nitrogen. Under these conditions, the conversion of CO is 30%.



The feed of the reactor consists of 1 mol/h CO, 2 mol h⁻¹ H₂, and 3 mol h⁻¹ N₂. In the condenser, it results in 9.2 g h⁻¹ liquid methanol.

- Calculate the composition of the gas phase at the reactor outlet (mol%).
- Calculate the volume flow rates at the reactor outlet.
- Which amount of liquid methanol/h should be obtained theoretically?

Solution

- At the end of the conversion, there should be obtained

Species	n_i	n_i (mol) gas	%	(b) flow rate (l h ⁻¹)
CO	$1 - X$	0.7	13.7	15.7
H ₂	$2(1 - X)$	1.4	27.5	31.4
CH ₃ OH	X	—	—	—
N ₂	3	3	58.8	67.2

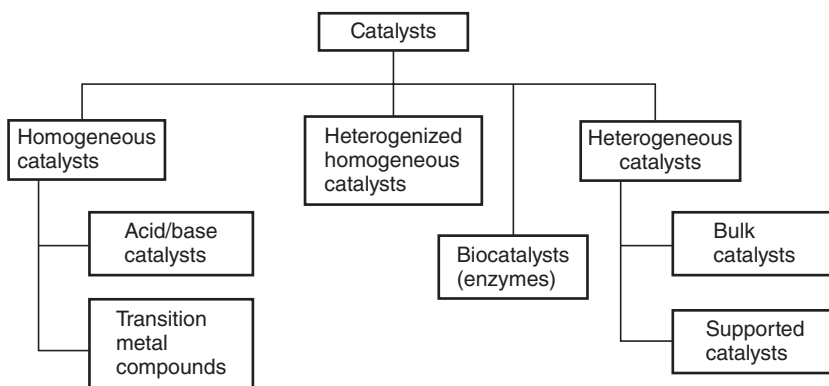
(c) 0.3 mol methanol = 9.6 g CH₃OH/h.

1.3

Classification of Catalysts

The numerous catalysts known today can be classified according to various criteria: structure, composition, area of application, or state of aggregation.

Here, we shall classify the catalysts according to the state of aggregation in which they act. There are two large groups: heterogeneous catalysts (solid-state catalysts) and homogeneous catalysts (Scheme 1.3). There are also intermediate forms such as homogeneous catalysts attached to solids (supported catalysts), also known as immobilized catalysts [4].



Scheme 1.3 Classification of catalysts.

In supported catalysts, the catalytically active substance is applied to a support material that has a large surface area and is usually porous. By far, the most important catalysts are the heterogeneous catalysts. The market share of homogeneous catalysts is estimated to be only about 10–15%. In the following, we shall briefly discuss the individual groups of catalysts.

Catalytic processes that take place in a uniform gas or liquid phase are classified as homogeneous catalysis. Homogeneous catalysts are generally well-defined chemical compounds or coordination complexes, which, together with the reactants, are molecularly dispersed in the reaction medium. Examples of homogeneous catalysts include mineral acids and transition metal compounds (e.g., rhodium carbonyl complexes in oxo synthesis) [10].

Heterogeneous catalysis takes place between several phases. Generally, the catalyst is a solid, and the reactants are gases or liquids. Examples of heterogeneous catalysts are Pt/Rh nets for the oxidation of ammonia to nitrous gases (Ostwald process), supported catalysts such as nickel on kieselguhr for fat hardening, and amorphous or crystalline aluminosilicates for cracking petroleum fractions.

Of increasing importance are the so-called biocatalysts (enzymes). Enzymes are protein molecules of colloidal size (e.g., poly(amino acids)). Some of them act in dissolved form in cells, while others are chemically bound to cell membranes or on surfaces. Enzymes can be classified somewhere between molecular homogeneous catalysts and macroscopic heterogeneous catalysts.

Enzymes are the driving force for biological reactions [4]. They exhibit remarkable activities and selectivities. For example, the enzyme catalase decomposes hydrogen peroxide 10^9 times faster than inorganic catalysts. The enzymes are organic molecules that almost always have a metal as the active center. Often the only difference to the industrial homogeneous catalysts is that the metal center is ligated by one or more proteins, resulting in a relatively high molecular mass.

Apart from high selectivity, the major advantage of enzymes is that they function under mild conditions, generally at room temperature in aqueous solution at pH values near 7. Their disadvantage is that they are sensitive, unstable molecules that are destroyed by extreme reaction conditions. They generally function well only at physiological pH values in very dilute solutions of the substrate.

Enzymes are expensive and difficult to obtain in pure form. Only recently, enzymes have been increasingly used, often in immobilized form, for reactions of non-biological substances. With the increasing importance of biotechnological processes, enzymes will also grow in importance.

It would seem reasonable to treat homogeneous catalysis, heterogeneous catalysis, and enzymatic catalysis as separate disciplines.

1.4

Comparison of Homogeneous and Heterogeneous Catalysis

In heterogeneous catalysts, phase boundaries are always present between the catalyst and the reactants, whereas in homogeneous catalysis, catalyst, starting materials, and products are present in the same phase. Homogeneous catalysts have a higher degree of dispersion than heterogeneous catalysts because in theory each individual atom can be catalytically active. In heterogeneous catalysts only the surface atoms are active [11].

Due to their high degree of dispersion, homogeneous catalysts exhibit a higher activity per unit mass of metal than heterogeneous catalysts. The high mobility of the molecules in the reaction mixture results in more collisions with substrate molecules. The reactants can approach the catalytically active center from any direction, and a reaction at an active center does not block the neighboring centers. This allows the use of lower catalyst concentrations and milder reaction conditions.

Table 1.4 Comparison of homogeneous and heterogeneous catalysts.

	Homogeneous	Heterogeneous
<i>Effectivity</i>		
Active centers	All metal atoms	Only surface atoms
Concentration	Low	High
Selectivity	High	Lower
Diffusion problems	Practically absent	Present (mass-transfer-controlled reaction)
Reaction conditions	Mild (50–200 °C)	Severe (often >250 °C)
Applicability	Limited	Wide
Activity loss	Irreversible reaction with products (cluster formation); poisoning	Sintering of the metal crystallites; poisoning
<i>Catalyst properties</i>		
Structure/stoichiometry	Defined	Undefined
Modification possibilities	High	Low
Thermal stability	Low	High
<i>Catalyst separation</i>	Sometimes laborious (chemical decomposition, distillation, extraction)	Fixed-bed: unnecessary suspension: filtration
Catalyst recycling	Possible	Unnecessary (fixed-bed) or easy (suspension)
Cost of catalyst losses	High	Low

The most prominent feature of homogeneous transition metal catalysts is the high selectivities that can be achieved. Homogeneously catalyzed reactions are controlled mainly by kinetics and less by material transport, because diffusion of the reactants to the catalyst can occur more readily. Owing to the well-defined reaction site, the mechanism of homogeneous catalysis is relatively well understood. Mechanistic investigations can readily be carried out under reaction conditions by means of spectroscopic methods. In contrast, processes occurring in heterogeneous catalysis are often obscure.

Owing to the thermal stability of organometallic complexes in the liquid phase, industrially realizable homogeneous catalysis is limited to temperatures below 200 °C. In this temperature range, homogeneous catalysts can readily be stabilized or modified by the addition of ligands, and considerable solvent effects also occur.

In industrial use, both types of catalysts are subject to deactivation as a result of chemical or physical processes. Table 1.4 summarizes the advantages and disadvantages of the two classes of catalyst.

The major disadvantage of homogeneous transition metal catalysts is the difficulty of separating the catalyst from the product. Heterogeneous catalysts are either automatically removed in the process (e.g., gas-phase reactions in fixed-bed reactors) or can be separated by simple methods such as filtration

or centrifugation. In the case of homogeneous catalysts, more complicated processes such as distillation, liquid–liquid extraction, and ion exchange must often be used [3, 11].

The separability of homogeneous catalysts has been improved strongly by using organometallic complexes that are soluble in both organic and aqueous phases. These can readily be removed from the product stream at the reactor outlet by transferring them to the aqueous phase. This two-phase method has already been used successfully in large-scale industrial processes, for example,

- the Shell higher olefin process (SHOP) with nickel complex catalysts;
- the Ruhrchemie/Rhône-Poulenc oxo synthesis with soluble rhodium catalysts (see Section 3.2).

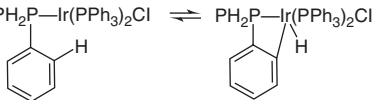
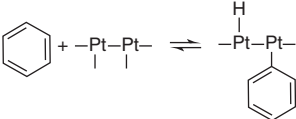
There are of course also parallels between homogeneous and heterogeneous transition metal catalysts. Many reaction mechanisms of homogeneous and heterogeneous catalysts exhibit similarities with regard to the intermediates and the product distribution.

Table 1.5 shows in more detail that the key reactions of homogeneous catalysis, such as hydride elimination and oxidative addition, correspond to dissociative chemisorption in heterogeneous catalysis (see Section 2.1) [13].

The hope of increasing the separability of homogeneous catalysts by, for example, fixing them on solid supports has not yet been realized. The aim of many research projects is to maintain the high selectivity of homogeneous catalysts while at the same time exploiting the advantages of easier catalyst separation. The main problems are still catalyst “bleeding” and the relatively low stability and high sensitivity to poisoning of the heterogenized complexes.

An interesting intermediate between homogeneous and heterogeneous catalysts is the metal cluster catalysts. In many reactions that require several active centers of the catalyst, it is found that heterogeneous catalysts are active, while homogeneous catalysts give zero conversion. The reason is that crystallites on a

Table 1.5 Comparison of the key reactions of homogeneous and heterogeneous transition metal catalysis [12].

Homogeneous phase Oxid reactions	Heterogeneous phase dissociative chemisorption
$\text{Ir}(\text{PPh}_3)_3\text{Cl} + \text{H}_2 \rightleftharpoons \text{H}-\text{Ir}(\text{PPh}_3)_3\text{Cl}$	$\text{H}_2 + \begin{array}{c} \quad \\ -\text{Pt}-\text{Pt}- \\ \quad \end{array} \rightleftharpoons \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{Pt}-\text{Pt}- \\ \quad \end{array}$
$\text{Pt}(\text{PPh}_3)_2 + \text{HC} \equiv \text{CR} \rightleftharpoons \text{Pt}(\text{H})(\text{C} \equiv \text{CR})(\text{PPh}_3)_2$	$\text{R}-\text{C} \equiv \text{CH} + \begin{array}{c} \quad \\ -\text{M}-\text{M}- \\ \quad \end{array} \rightleftharpoons \begin{array}{c} \text{H} \quad \text{C} \equiv \text{C}-\text{R} \\ \quad \\ -\text{M}-\text{M}- \\ \quad \end{array}$
$\text{PH}_2\text{P}-\text{Ir}(\text{PPh}_3)_2\text{Cl} \rightleftharpoons \text{PH}_2\text{P}-\text{Ir}(\text{PPh}_3)_2\text{Cl}$ 	$\text{C}_6\text{H}_6 + \begin{array}{c} \quad \\ -\text{Pt}-\text{Pt}- \\ \quad \end{array} \rightleftharpoons \begin{array}{c} \text{H} \\ \\ -\text{Pt}-\text{Pt}- \\ \quad \end{array}$ 

metal surface exhibit several active centers, while conventional soluble catalysts generally contain only one metal center.

In contrast, metal clusters have several active centers or can form multielectron systems. Metal clusters such as $\text{Rh}_6(\text{CO})_{16}$, $\text{Rh}_4(\text{CO})_{12}$, $\text{Ir}_4(\text{CO})_{12}$, $\text{Ru}_3(\text{CO})_{12}$, and more complex structures have been successfully tested in carbonylation reactions. Rhodium clusters catalyze the conversion of synthesis gas to ethylene glycol, albeit at very high pressures up to now.

With increasing size, the clusters become less soluble, and the precipitation of extremely small particles from solution is possible, that is, a transition from homogeneous to heterogeneous catalysis.

In conclusion, it can be stated that homogeneous and heterogeneous catalysts should be used to complement one another and not regarded as competitors, since each group has its special characteristics and properties.

Exercises

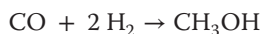
- 1.1 Classify the following reactions as homogeneous or heterogeneous catalysis and justify your answer:
 - (a) The higher reaction rate for the oxidation of SO_2 with O_2 in the presence of NO .
 - (b) The hydrogenation of liquid vegetable oil in the presence of a finely divided Ni catalyst.
 - (c) The transformation of an aqueous solution of D-glucose into a mixture of the D and L forms catalyzed by aqueous HCl .
- 1.2 Compare homogeneous and heterogeneous catalysis according to the following criteria:

	Heterogeneous catalysts	Homogeneous catalysts
Active center		
Concentration		
Diffusion problems		
Modifiability		
Catalyst separation		

- 1.3 Give four reasons why heterogeneous catalysts are preferred in industrial processes.
- 1.4
 - (a) Explain the difference between the activity and the selectivity of a catalyst.
 - (b) Name three methods for measuring the activity of catalysts.
- 1.5 Compare the key activation steps in the hydrogenation of alkenes with homogeneous and heterogeneous transition metal catalysts. What are the names of these steps?

Homogeneous catalysis	Heterogeneous catalysis
Activation of H ₂	
Activation of the olefin	

- 1.6** The methanol synthesis is carried out at 240 °C and 60 bar in a test reactor.



The flow rates at the reactor entrance under normal conditions are

22.4 l/h CO, 44.8 l/h H₂, 44.8 l/h N₂ (inert gas).

In the condenser, 6.8 g h⁻¹ liquid methanol is detected. The analysis of the gas phase shows the following results:

34.0 mol% H₂, 47.3 mol% N₂, 18.5 mol% CO

- Calculate the conversion referring to CO.
 - Calculate the composition of the gas phase at the reactor outlet.
 - Discuss the results.
- 1.7** The hydrogenation of benzaldehyde as a sequential reaction is examined in an autoclave with a supported Pd catalyst. From 0.7 mol benzaldehyde as starting material, 0.08 mol of benzyl alcohol and 0.32 mol of toluene are obtained.



- Find out the conversion of benzaldehyde in percentage.
- Which selectivity referring to toluene was achieved?

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