1
Introduction to Catalysis

Ask the average person in the street what a catalyst is, and he or she will probably tell you that a catalyst is what one has under the car to clean up the exhaust. Indeed, the automotive exhaust converter represents a very successful application of catalysis; it does a great job in removing most of the pollutants from the exhaust leaving the engines of cars. However, catalysis has a much wider scope of application than abating pollution.

Catalysis in Industry

Catalysts are the workhorses of chemical transformations in the industry. Approximately 85–90 % of the products of chemical industry are made in catalytic processes. Catalysts are indispensable in

- Production of transportation fuels in one of the approximately 440 oil refineries all over the world.
- Production of bulk and fine chemicals in all branches of chemical industry.
- Prevention of pollution by avoiding formation of waste (unwanted byproducts).
- Abatement of pollution in end-of-pipe solutions (automotive and industrial exhaust).

A catalyst offers an alternative, energetically favorable mechanism to the non-catalytic reaction, thus enabling processes to be carried out under industrially feasible conditions of pressure and temperature.

For example, living matter relies on enzymes, which are the most specific catalysts one can think of. Also, the chemical industry cannot exist without catalysis, which is an indispensable tool in the production of bulk chemicals, fine chemicals and fuels.

For scientists and engineers catalysis is a tremendously challenging, highly multidisciplinary field. Let us first see what catalysis is, and then why it is so important for mankind.

1.1
What is Catalysis?

A catalyst accelerates a chemical reaction. It does so by forming bonds with the reacting molecules, and by allowing these to react to a product, which detaches from the catalyst, and leaves it unaltered such that it is available for the next reaction. In fact, we can describe the catalytic reaction as a cyclic event in which the catalyst participates and is recovered in its original form at the end of the cycle.

Let us consider the catalytic reaction between two molecules A and B to give a product P, see Fig. 1.1. The cycle starts with the bonding of molecules A and B to the catalyst. A and B then react within this complex to give a product P, which is also bound to the catalyst. In the final step, P separates from the catalyst, thus leaving the reaction cycle in its original state.
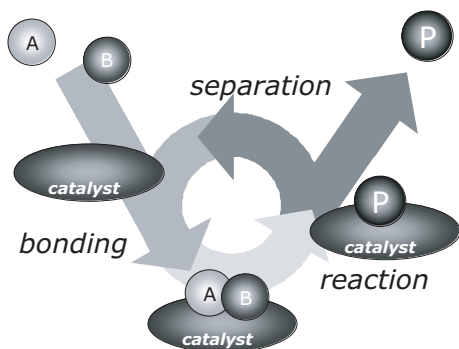

Figure 1.1.   Every catalytic reaction is a sequence of elementary steps, in which reactant molecules bind to the catalyst, where they react, after which the product detaches from the catalyst, liberating the latter for the next cycle.

To see how the catalyst accelerates the reaction, we need to look at the potential energy diagram in Fig. 1.2, which compares the non-catalytic and the catalytic reaction. For the non-catalytic reaction, the figure is simply the familiar way to visualize the Arrhenius equation: the reaction proceeds when A and B collide with sufficient energy to overcome the activation barrier in Fig. 1.2. The change in Gibbs free energy between the reactants, A + B, and the product P is ΔG.

The catalytic reaction starts by bonding of the reactants A and B to the catalyst, in a spontaneous reaction. Hence, the formation of this complex is exothermic, and the free energy is lowered. There then follows the reaction between A and B while they are bound to the catalyst. This step is associated with an activation energy; however, it is significantly lower than that for the uncatalyzed reaction. Finally, the product P separates from the catalyst in an endothermic step.
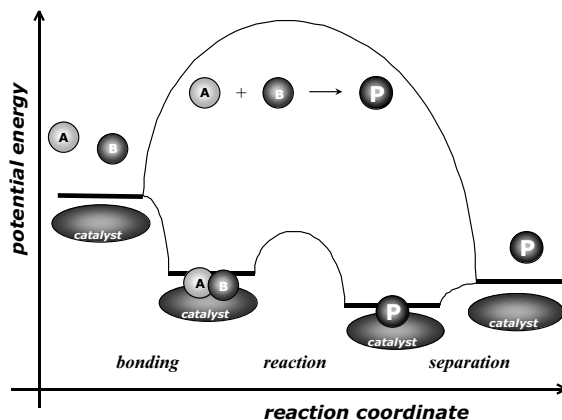
Figure 1.2. Potential energy diagram of a heterogeneous catalytic reaction, with gaseous reactants and products and a solid catalyst. Note that the uncatalyzed reaction has to overcome a substantial energy barrier, whereas the barriers in the catalytic route are much lower.

The energy diagram of Fig. 1.2 illustrates several important points:

- The catalyst offers an alternative path for the reaction, which is obviously more complex, but energetically much more favorable.
- The activation energy of the catalytic reaction is significantly smaller than that of the uncatalyzed reaction; hence, the rate of the catalytic reaction is much larger (we explain this in greater detail in Chapter 2).
- The overall change in free energy for the catalytic reaction equals that of the uncatalyzed reaction. Hence, the catalyst does not affect the equilibrium constant for the overall reaction of A + B to P. Thus, if a reaction is thermodynamically unfavorable, a catalyst cannot change this situation. A catalyst changes the kinetics but *not* the thermodynamics.
- The catalyst accelerates both the forward and the reverse reaction to the same extent. In other words, if a catalyst accelerates the formation of the product P from A and B, it will do the same for the decomposition of P into A and B.

Thus far it is immediately evident that there are also cases in which the combination of catalyst with reactants or products will not be successful:

- If the bonding between reactants and catalyst is too weak, there will be hardly any conversion of A and B into products.
- Conversely if the bond between the catalyst and one of the reactants, say A, is too strong, the catalyst will be mostly occupied with species A, and B is not available to form the product. If A and B both form strong bonds with the catalyst, the intermediate situation with A or B on the catalyst may be so stable that reaction becomes unlikely. In terms of Fig. 1.2, the second level lies so deep that the activa-

tion energy to form P on the catalyst becomes too high. The catalyst is said to be poisoned by (one of) the reactants.

- In the same way, the product P may be too strongly bound to the catalyst for separation to occur. In this case the product poisons the catalyst.

Hence, we intuitively feel that the successful combination of catalyst and reaction is that in which the interaction between catalyst and reacting species is not too weak, but also not too strong. This is a loosely formulated version of Sabatier's Principle, which we encounter in a more precise form in Chapter 2 and in detail in Section 6.5.3.5.

Until now, the catalyst has been an unspecified, abstract body, so let us first look at what kind of catalysts exist.

1.2
## Catalysts Can Be Atoms, Molecules, Enzymes and Solid Surfaces

Catalysts come in a multitude of forms, varying from atoms and molecules to large structures such as zeolites or enzymes. In addition they may be employed in various surroundings: in liquids, gases or at the surface of solids. Preparing a catalyst in the optimum form and studying its precise composition and shape are an important specialism, which we describe in later chapters.

It is customary to distinguish the following three subdisciplines in catalysis: homogeneous, heterogeneous and bio catalysis. We illustrate each with an example.

1.2.1
Homogeneous Catalysis

In homogeneous catalysis, both the catalyst and the reactants are in the same phase, i.e. all are molecules in the gas phase, or, more commonly, in the liquid phase. One of the simplest examples is found in atmospheric chemistry. Ozone in the atmosphere decomposes, among other routes, via a reaction with chlorine atoms:

$$Cl + O_3 \rightarrow ClO_3$$
$$ClO_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$

or overall

$$O_3 + O \rightarrow 2O_2$$
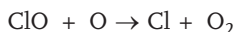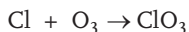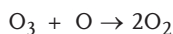
Ozone can decompose spontaneously, and also under the influence of light, but a Cl atom accelerates the reaction tremendously. As it leaves the reaction cycle unaltered, the Cl atom is a catalyst. Because both reactant and catalyst are both in the same phase, namely the gas phase, the reaction cycle is an example of homogeneous

catalysis. (This reaction was historically important in the prediction of the ozone hole.)

Industry uses a multitude of homogenous catalysts in all kinds of reactions to produce chemicals. The catalytic carbonylation of methanol to acetic acid

$$CH_3OH + CO \rightarrow CH_3COOH$$
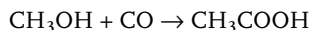
by $[Rh(CO)_2I_2]^-$ complexes in solution is one of many examples. In homogeneous catalysis, often aimed at the production of delicate pharmaceuticals, organometallic complexes are synthesized in procedures employing molecular control, such that the judicious choice of ligands directs the reacting molecules to the desired products.

1.2.2
Biocatalysis

Enzymes are nature's catalysts. For the moment it is sufficient to consider an enzyme as a large protein, the structure of which results in a very shape-specific active site (Fig. 1.3). Having shapes that are optimally suited to guide reactant molecules (usually referred to as substrates) in the optimum configuration for reaction, enzymes are highly specific and efficient catalysts. For example, the enzyme catalase catalyzes the decomposition of hydrogen peroxide into water and oxygen

$$2H_2O_2 \xrightarrow{\text{catalase}} H_2O \ + \ O_2$$
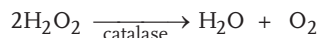
at an incredibly high rate of up to 10^7 hydrogen peroxide molecules per second!
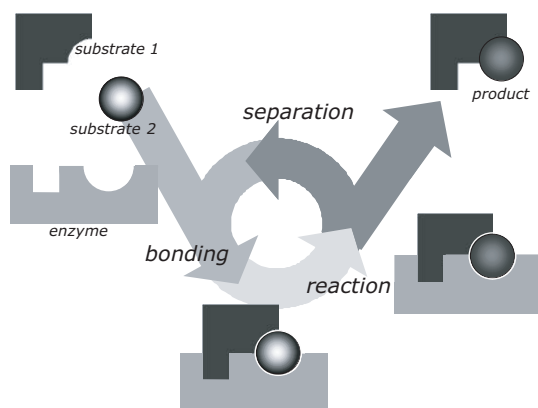

Figure 1.3. Schematic representation of an enzyme-catalyzed reaction. Enzymes often match the shape of the substrates they bind to, or the transition state of the reaction they catalyze. Enzymes are highly efficient catalysts and represent a great source of inspiration for designing technical catalysts.

Enzymes allow biological reactions to occur at the rates necessary to maintain life, such as the build up of proteins and DNA, or the breakdown of molecules and the storage of energy in sugars. An example with, perhaps, some special appeal to students is the breakdown of alcohol to acetaldehyde inside the body by the enzyme alcohol dehydrogenase. The acetaldehyde in turn is converted into acetate by aldehyde hydrogenase. Some people cannot tolerate alcohol (as revealed by facial flushing after drinking a small amount) because they lack the form of the enzyme that breaks down acetaldehyde.

1.2.3
Heterogeneous Catalysis

In heterogeneous catalysis, solids catalyze reactions of molecules in gas or solution. As solids – unless they are porous – are commonly impenetrable, catalytic reactions occur at the surface. To use the often expensive materials (e.g. platinum) in an economical way, catalysts are usually nanometer-sized particles, supported on an inert, porous structure (see Fig. 1.4). Heterogeneous catalysts are the workhorses of the chemical and petrochemical industry and we will discuss many applications of heterogeneous catalysis throughout this book.
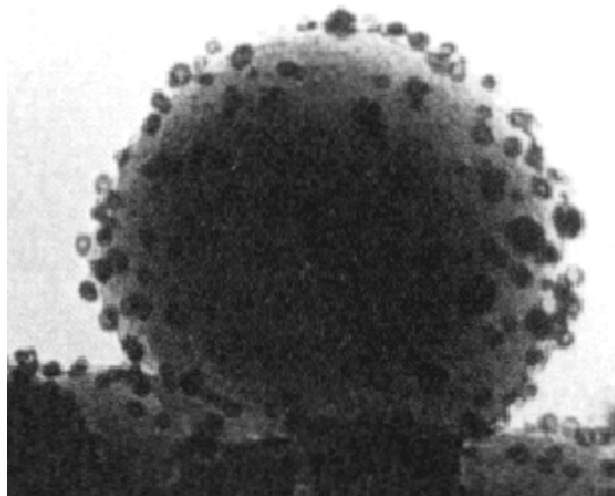
Figure 1.4. Catalysts are nanomaterials and catalysis is nanotechnology. If we define nanotechnology as the branch of materials science aiming to control material properties on the nanometer scale, then catalysis represents a field where nanomaterials have been applied commercially for about a century. Many synthetic techniques are available to produce small particles for heterogeneous catalysts, and to keep them sufficiently stable so that they can withstand the often hostile conditions of an industrial reactor. Modern catalysis is preeminently nanotechnology. (Adapted from A.K. Datye and N.J. Long, *Ultramicroscopy* 25 (1988) 203).

As an introductory example we take one of the key reactions in cleaning automotive exhaust, the catalytic oxidation of CO on the surface of noble metals such as platinum, palladium and rhodium. To describe the process, we will assume that the metal surface consists of active sites, denoted as "$_*$" We define them properly later on. The catalytic reaction cycle begins with the adsorption of CO and O_2 on the surface of platinum, whereby the O_2 molecule dissociates into two O atoms (X^* indicates that the atom or molecule is adsorbed on the surface, i.e. bound to the site $_*$):

$$O_2 + 2^* \rightleftharpoons 2O^*$$
$$CO +^* \rightleftharpoons CO^*$$
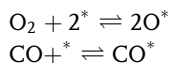
The adsorbed O atom and the adsorbed CO molecule then react on the surface to form CO_2, which, being very stable and relatively unreactive, interacts only weakly with the platinum surface and desorbs almost instantaneously:

$$CO^* + O^* \rightleftarrows CO_2 + 2^*$$
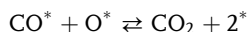
Note that in the latter step the adsorption sites on the catalyst are liberated, so that these become available for further reaction cycles. Figure 1.5 shows the reaction cycle along with a potential energy diagram.

Where in this cycle is the essential influence of the catalyst? Suppose we carry out the reaction in the gas phase without a catalyst. The reaction will proceed if we raise the temperature sufficiently for the O_2 molecule to dissociate into two O atoms (radicals). Once these radicals are available, the reaction with CO to CO_2 follows instantaneously. The activation energy of the gas phase reaction will be roughly equal to the energy required to split the strong O–O bond in O_2, i.e. about 500 kJ mol^{-1}. In the catalytic
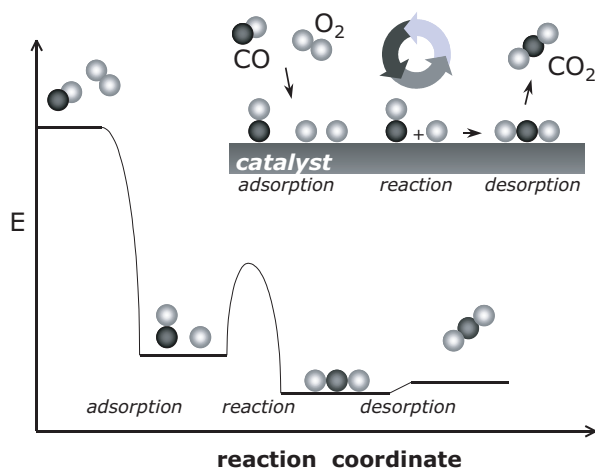

Figure 1.5. Reaction cycle and potential energy diagram for the catalytic oxidation of CO by O_2.

reaction, however, the O_2 molecule dissociates easily – in fact without an activation energy – on the surface of the catalyst. The activation energy is associated with the reaction between adsorbed CO and O atoms, which is of the order of 50–100 kJ mol^{-1}. Desorption of the product molecule CO_2 costs only about 15–30 kJ mol^{-1} (depending on the metal and its surface structure). Hence if we compare the catalytic and the uncatalyzed reaction, we see that the most difficult step of the homogeneous gas phase reaction, namely the breaking of the O–O bond is easily performed by the catalyst. Consequently, the ease with which the CO_2 molecule forms determines the rate at which the overall reaction from CO and O_2 to CO_2 proceeds. This is a very general situation for catalyzed reactions, hence the expression: A catalyst breaks bonds, and lets other bonds form. The beneficial action of the catalyst is in the dissociation of a strong bond, the subsequent steps might actually proceed faster without the catalyst (which is a hypothetical situation of course). In Chapter 6 we analyze in detail how a surface induces the breaking of intramolecular bonds.

1.3
Why is Catalysis Important?

The chemical industry of the 20th century could not have developed to its present status on the basis of non-catalytic, stoichiometric reactions alone. Reactions can in general be controlled on the basis of temperature, concentration, pressure and contact time. Raising the temperature and pressure will enable stoichiometric reactions to proceed at a reasonable rate of production, but the reactors in which such conditions can be safely maintained become progressively more expensive and difficult to make. In addition, there are thermodynamic limitations to the conditions under which products can be formed, e.g. the conversion of N_2 and H_2 into ammonia is practically impossible above 600 °C. Nevertheless, higher temperatures are needed to break the very strong N≡N bond in N_2. Without catalysts, many reactions that are common in the chemical industry would not be possible, and many other processes would not be economical.

Catalysts accelerate reactions by orders of magnitude, enabling them to be carried out under the most favorable thermodynamic regime, and at much lower temperatures and pressures. In this way efficient catalysts, in combination with optimized reactor and total plant design, are the key factor in reducing both the investment and operation costs of a chemical processes. But that is not all.

1.3.1
Catalysis and Green Chemistry

Technology is called "green" if it uses raw materials efficiently, such that the use of toxic and hazardous reagents and solvents can be avoided while formation of waste or undesirable byproducts is minimized. Catalytic routes often satisfy these criteria. A good example is provided by the selective oxidation of ethylene to ethylene epox-

ide, an important intermediate towards ethylene glycol (antifreeze) and various poly-ethers and polyurethanes (Fig. 1.6).
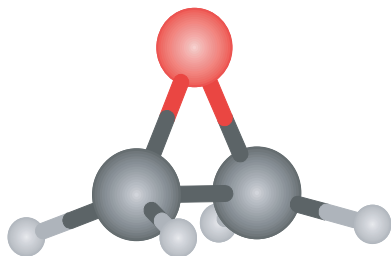

Figure 1.6. Ethylene epoxide, an important intermediate in the chemical industry.

The old, non-catalytic route (called the epichlorohydrine process) follows a three-step synthesis:

$$Cl_2 + NaOH \rightarrow HOCl + NaCl \tag{1}$$

$$C_2H_4 + HOCl \rightarrow CH_2Cl–CH_2OH \quad \text{(epichlorohydrine)} \tag{2}$$

$$CH_2Cl–CH_2OH + {}^1\!/_2Ca(OH)_2 \rightarrow {}^1\!/_2CaCl_2 + C_2H_4O + H_2O \tag{3}$$

or in total:

$$Cl_2 + NaOH + {}^1\!/_2Ca(OH)_2 + C_2H_4 \rightarrow C_2H_4O + {}^1\!/_2CaCl_2 + NaCl + H_2O$$
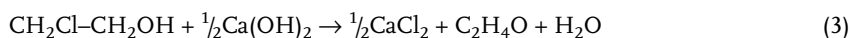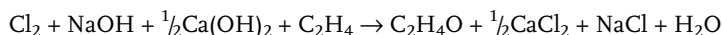
Hence, for every molecule of ethylene oxide, 1 molecule of salt is formed, creating a waste problem that was traditionally solved by dumping it in a river. Such practice is of course now totally unacceptable.

The catalytic route, however, is simple and clean, although it does produce a small amount of CO_2. Using silver, promoted by small amounts of chlorine, as the catalyst, ethylene oxide is formed directly from C_2H_4 and O_2 at a selectivity of around 90 %, with about 10 % of the ethylene ending up as CO_2. Nowadays all production facilities for ethylene oxide use catalysts.

1.3.2
Atom Efficiency, *E* Factors and Environmental Friendliness

Numerous organic syntheses are based on stoichiometric oxidations of hydrocarbons with sodium dichromate and potassium permanganate, or on hydrogenations with alkali metals, borohydrides or metallic zinc. In addition, there are reactions such as aromatic nitrations with H_2SO_4 and HNO_3, or acylations with $AlCl_3$ that generate significant amounts of inorganic salts as byproducts.

Fine chemicals are predominantly (but not exclusively!) the domain of homogeneous catalysis, where solvents present another issue of environmental concern. According to Sheldon, the best solvent is no solvent, but if a solvent is unavoidable, then water is a good candidate. [R.A. Sheldon, *J. Chem. Tech. Biotechnol.* **68** (1997) 381].
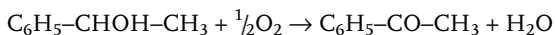
Sheldon has introduced several indicators to measure the efficiency and environmental impact of a reaction. The atom efficiency is the molecular weight of the desired product divided by the total molecular weight of all products. For example the conventional oxidation of a secondary alcohol

$$3C_6H_5-CHOH-CH_3 + 2CrO_3 + 3H_2SO_4 \rightarrow 3C_6H_5-CO-CH_3 + Cr_2(SO_4)_3 + 6H_2O$$
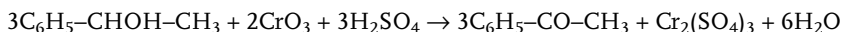
has an atom efficiency of 360/860 = 42 %. By contrast, the catalytic route

$$C_6H_5-CHOH-CH_3 + \tfrac{1}{2}O_2 \rightarrow C_6H_5-CO-CH_3 + H_2O$$

offers an atom efficiency of 120/138 = 87 %, with water as the only byproduct. The reverse step, a catalytic hydrogenation, proceeds with 100 % atom efficiency:

$$C_6H_5-CO-CH_3 + H_2 \rightarrow C_6H_5-CHOH-CH_3$$
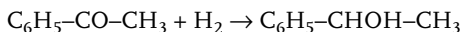
as does the catalytic carbonylation of this molecule:

$$C_6H_5-CHOH-CH_3 + CO \rightarrow C_6H_5-CH(CH_3)COOH$$
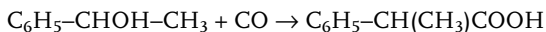
Another useful indicator of environmental acceptability is the *E* factor – the weight of waste or undesirable byproduct divided by the weight of the desired product. As Table 1.1 shows, the production of fine chemicals and pharmaceuticals generate the highest amounts of waste per unit weight of product. Atom efficiencies and *E* factors can be calculated from each other, but in practice *E* factors can be higher due to yields being less than optimum and reagents that are used in excess. Also, loss of solvents should be included, and perhaps even the energy consumption with the associated generation of waste CO_2.

Table 1.1. Environmental acceptability of products in different segments of the chemical industry. (From R.A. Sheldon, *Chem. Ind.* (1997) 12 and (1992) 903).

Industry segment	Product tonnage	*E* factor kg waste/kg product
Oil refining	10^6–10^8	<0.1
Bulk chemicals	10^4–10^6	<1 – 5
Fine chemicals	10^2–10^4	5–50
Pharmaceuticals	10–10^3	25–>100

To express that it is not just the amount of waste but rather its environmental impact, Sheldon introduced the environmental quotient *EQ* as the *E* factor multiplied by an unfriendliness quotient, *Q,* which can be assigned a value to indicate how undesirable a byproduct is. For example, $Q = 0$ for clean water, 1 for a benign salt, NaCl, and 100–1000 for toxic compounds. Evidently, catalytic routes that avoid waste formation are highly desirable, and the more economic value that is placed on, for example, the unfriendliness quotient, the higher the motivation to work on catalytic alternatives. Waste prevention is much to be preferred over waste remediation.

1.3.3
The Chemical Industry

Catalysts accelerate reactions and thus enable industrially important reactions to be carried out efficiently under practically attainable conditions. Very often, catalytic routes can be designed such that raw materials are used efficiently and waste production is minimized. Consequently, the chemical industry is largely based upon catalysis: Roughly 85–90 % of all products are made in catalytic processes, and the percentage is increasing steadily.

Tables 1.2 and 1.3 give an impression of the most important industrial chemicals and processes; Table 1.4 and Figure 1.7 show the top 50 of the chemical industry by company and country respectively.

Table 1.2. Largest processes based on heterogeneous catalysis.

Reaction	Catalyst
Catalytic cracking of crude oil	Zeolites
Hydrotreating of crude oil	Co–Mo, Ni–Mo, Ni–W (sulfidic form)
Reforming of naphtha (to gasoline)	Pt, Pt–Re, Pt–Ir
Alkylation	H_2SO_4, HF, solid acids
Polymerization of ethylene, propylene, a.o.	Cr, $TiCl_x/MgCl_2$
Ethylene epoxidation to ethylene oxide	Ag
Vinyl chloride (ethylene + Cl_2)	Cu (as chloride)
Steam reforming of methane to $CO + H_2$	Ni
Water-gas shift reaction	Fe (oxide), Cu–ZnO
Methanation	Ni
Ammonia synthesis	Fe
Ammonia oxidation to NO and HNO_3	Pt–Rh
Acrylonitrile from propylene and ammonia	Bi–Mo, Fe–Sb (oxides)
Hydrogenation of vegetable oils	Ni
Sulfuric acid	V (oxide)
Oxidation of CO & hydrocarbons (car exhaust)	Pt, Pd
Reduction of NOx (in exhaust)	Rh, vanadium oxide

Evidently, every chemistry student who is interested in a career in the chemical industry, or in chemical design in general, should know what catalysis is. This is why the authors teach catalysis early on in the chemistry curriculum of their respective universities.

Table 1.3a. Organic chemical production in the USA (2005) along with average annual change over the ten years 1995–2005. (Source: *Chemical Engineering News*, July 10, 2006).

Organic chemicals	ktons	% Change
Ethylene	23974	1.2
Propylene	15333	2.8
Ethylene dichloride	11308	3.7
Urea	5801	−2.4
Ethylbenzene	5251	−1.6
Styrene	5042	−0.2
Cumene	3509	3.2
Ethylene oxide	3166	−0.9
1,3-Butadiene	2046	2.1
Vinyl acetate	1327	0.1
Acrylonitrile	1323	−0.9
Aniline	964	4.3
Benzene (1000 liters)	7574	−0.8

Table 1.3b. Inorganic chemical production in the USA (2005) along with average annual change over the ten years 1995–2005. (Source: *Chemical Engineering News*, July 10, 2006).

Inorganic chemicals	ktons	% Change
Sulfuric acid	36520	−1.6
Phosphoric acid	11599	−0.3
Chlorine	10175	−1.0
Ammonia	9775	−4.7
Sodium hydroxide	8384	−2.1
Ammonium nitrate	6353	−1.9
Nitric acid	6328	−2.3
Hydrochloric acid	4406	2.2
Ammonium sulfate	2578	0.7

Table 1.3c. Polymers and plastics produced in the USA (2005) along with average annual change over the ten years 1995–2005. (Source: *Chemical Engineering News*, July 10, 2006).

Polymers, plastics	ktons	% Change
Polyethylene, low density	3558	0.3
Polyethylene, linear low density	5395	8.5
Polyethylene, high density	7328	3.7
Polypropylene	8149	5.1
Polystyrene	2855	1.1
Styrene polymers (ABS, etc.)	1413	0.3
Polyamine, nylons	568	2.1
Polyvinyl chloride & copolymers	6921	2.2

Table 1.4. World Top 50 of Chemical Producers. (Source: *Chemical Engineering News*, July 2006).

Rank 2005	2004	2001	1998	Company	Country	Total sales (million $)	Chemicals (million $)	Chemicals (%)
1	1	1	4	Dow Chemical	USA	46,307	46,307	100
2	2	3	1	BASF	Germany	53,271	43,682	82
3	4	7	5	Royal Dutch Shell	UK/Netherlands	318,145	34,996	11
4	5	6	8	Exxon Mobil	USA	259,883	31,186	12
5	6	5	–	Total	France	173,713	27,794	16
6	3	2	2	DuPont	USA	28,144	25,330	90
7	9	26	–	China Petroleum & Chemical	China	100,576	21,121	21
8	8	4	3	Bayer	Germany	33,859	20,654	61
9	7	9	11	BP	UK	257,838	20,627	8
10	11	18	30	SABIC	Saudi Arabia	20,821	18,947	91
11	13	30	46	Formosa Plastics	Taiwan	31,775	18,747	59
12	–	50	–	Lyondell Chemical	USA	18,606	18,606	100
13	10	14	31	Mitsubishi Chemical	Japan	21,884	17,945	82
14	12	8	35	Degussa	Germany	14,630	14,630	100
15	16	13	43	Mitsui Chemicals	Japan	13,372	13,372	100
16	15	12	29	Huntsman Corp.	USA	12,962	12,962	100
17	32	42	–	Ineos Group	UK	12,400	12,400	100

Table 1.4 (continued)

Rank				Company	Country	Total sales (million $)	Chem- icals (million $)	Chem- icals (%)
2005	2004	2001	1998					
18	14	11	19	AKZO Nobel	Netherlands	16,107	11,758	73
19	19	20	13	Sumitomo Chemical	Japan	14,146	11,458	81
20	17	22	25	Air Liquide	France	12,941	11,388	88
21	20	31	24	Toray Industries	Japan	12,985	11,297	87
22	24	23	47	Chevron Phillips	USA	10,707	10,707	100
23	18	10	6	ICI	UK	10,583	10,583	100
24	−	−	−	Basell	Netherlands	10,582	10,582	100
25	25	37	–	Shin-Etsu Chemicals	Japan	10,244	10,244	100
26	21	19	12	DSM	Netherlands	10,202	10,202	100
27	23	15	17	Dainippon Ink & Chemicals	Japan	9,126	9,126	100
28	27	−	−	Lanxess	Germany	8,901	8,901	100
29	30	34	27	BOC	UK	8,385	8,385	100
30	28	24	–	PPG Industries	USA	10,210	7,964	78
31	29	35	41	Asahi Kasei	Japan	13,667	7,927	58
32	40	41	26	Solvay	Belgium	10,585	7,833	74
33	34	46	33	ENI	Italy	86,522	7,787	9
34	31	29	36	Air Products	USA	8,151	7,743	95
35	35	36	32	Praxair	USA	7,656	7,656	100
36	42	−	−	Yara	Norway	7,168	7,168	100
37	41	40	44	Rohm and Haas	USA	8,027	7,064	88
38	36	33	34	Eastman Chemical	USA	7,059	7,059	100
39	37	38	22	Reliance Industries	India	18,661	6,718	36
40	26	16	14	General Electric	USA	165,150	6,606	4
41	33	27	15	Clariant	Switzerland	6,566	6,566	100
42	39	−	−	Sasol	South Africa	10,912	6,547	60
43	38	21	−	Rhodia	France	6,330	6,330	100
44	43	32	−	Syngenta	Switzerland	8,086	6,307	78
45	49	44	−	Celanese	USA	6,070	6,070	100
46	45	48	48	Borealis	Denmark	5,992	5,992	100

Table 1.4 (continued)

Rank				Company	Country	Total sales (million $)	Chemicals (million $)	Chemicals (%)
2005	2004	2001	1998					
47	46	45	21	Ciba Specialties	Switzerland	5,955	5,955	100
48	48	–	–	Nova Chemicals	Canada	5,617	5,617	100
49	47	28	–	Tejin	Japan	8,486	5,516	65
50	42	–	–	LG Cheme	South Korea	7,291	5,468	75

2001

2005

Japan 13% Other 6% USA 33%

Europe 48%

US$ 404,4 billion

Japan 13% Other 13% USA 29%

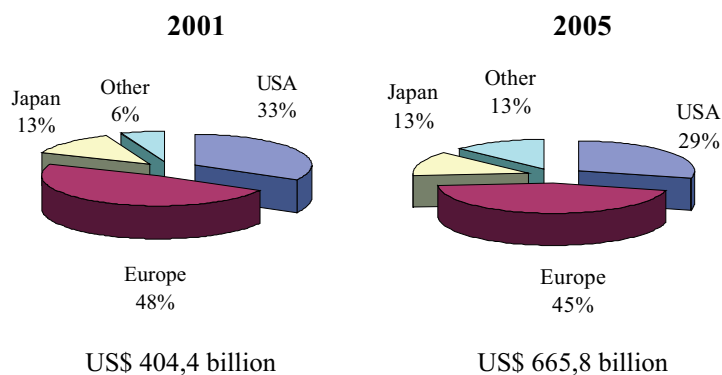Europe 45%

US$ 665,8 billion

Figure 1.7. Europe is the largest producer of bulk chemicals.

1.4
Catalysis as a Multidisciplinary Science

1.4.1
The Many Length Scales of a "Catalyst"

Catalysis is a very broad field of study that is closely interwoven with numerous other scientific disciplines. This becomes immediately evident if we realize that catalysis as phenomenon encompasses many length scales. Figurwe 1.8 illustrates this for the case of heterogeneous catalysis.

For the examples given above, the bonding of reactant molecules to a catalyst to give a reactive complex and the final separation of catalyst and product is catalysis on the molecular level. For heterogeneous, homogeneous or enzymatic catalysis, this is the level on which the chemistry takes place. Understanding reactions at the elementary level of the rupture of bonds in reactants and the formation of bonds in products is at the heart of the matter, and requires the most advanced experimental techniques and theoretical descriptions available. This is the domain of spectroscopy, computational chemistry and kinetics and mechanism on the level of elemen-
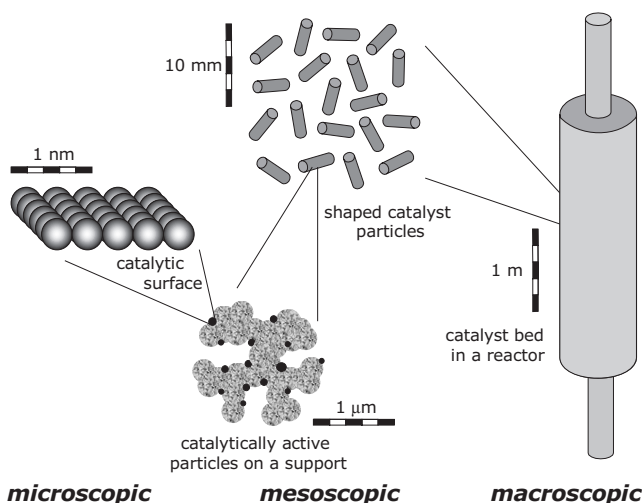
Figure 1.8. Relevant length scales in catalysis range from the subnano-
metre domain of the atomic and molecular level to the macroscopic
domain of an industrial reactor.

tary reaction steps. The length scales of interest are in the subnanometre region. Publications on research at the molecular scale are found predominantly in general journals in chemistry, physical chemistry and physics.

The next level is that of small catalytically active particles, with typical dimensions of between 1 and 10 nm, and inside the pores of support particles (ὄm range). The questions of interest are the size, shape, structure and composition of the active particles, in particular of their surfaces, and how these properties relate to catalytic reactivity. Although we will deal with heterogeneous catalysis, the anchoring of catalytic molecules or even enzymes to supporting structures is also of great interest in homogeneous and biocatalysis. This is the domain of catalyst preparation, characterization, testing on the laboratory scale, and mechanistic investigations. Transport phenomena such as the diffusion of molecules inside pores may affect the rate at which products form and become an important consideration on this level. Much academic research as well as exploratory work in industry occurs on this scale. Journals dedicated to catalysis deal largely with catalysis on this mesoscopic length scale.

The next level is that of shaped catalysts, in the form of extrudates, spheres, or monoliths on length scales varying from millimeters to centimeters, and occasionally even larger. Such matters are to a large extent the province of materials science. Typical issues of interest are porosity, strength, and attrition resistance such that catalysts are able to survive the conditions inside industrial reactors. This area of catalysis is mainly (though not exclusively) dealt with by industry, in particular by catalyst manufacturers. Consequently, much of the knowledge is covered by patents.

The macroscopic level is that of reactors, be it the 25 cm test reactor in the laboratory or the 10 m high reactor vessel in an industrial plant. The catalyst forms the heart of the reactor. Nevertheless catalysis as a discipline is only one of many other

aspects of reaction engineering, together with, for example, the design of efficient reactors that are capable of handling high pressure, offer precise control of temperature, enable optimized contact between reactants and catalyst and removal of products, are resistant to corrosion, make optimum use of energy resources, and are safe during operation. In describing the kinetics of catalytic reactions on the scale of reactors, extrinsic factors dealing with the mass and heat transport properties of reactants and products through the catalyst bed are as important as the intrinsic reactivity of the molecules reacting at the catalytic site. The catalyst's mechanical stability, sensitivity to trace impurities in the reactant feed, and degradation of particles, e.g. due to exposure to high temperatures, are important in addition to its intrinsic properties such as activity and selectivity. Literature on these aspects of catalysis is largely found in chemical engineering journals and patents.

1.4.2
Time Scales in Catalysis

The characteristic times on which catalytic events occur vary more or less in parallel with the different length scales discussed above. The activation and breaking of a chemical bond inside a molecule occurs in the picosecond regime, completion of an entire reaction cycle from complexation between catalyst and reactants through separation from the product may take anywhere between microseconds for the fastest enzymatic reactions to minutes for complicated reactions on surfaces. On the mesoscopic level, diffusion in and outside pores, and through shaped catalyst particles may take between seconds and minutes, and the residence times of molecules inside entire reactors may be from seconds to, effectively, infinity if the reactants end up in unwanted byproducts such as coke, which stay on the catalyst.

1.5
The Scope of This Book

The emphasis of this book is on the fundamental level of catalytic reactions on the molecular and the mesoscopic scale. Dealing with the acceleration of reactions, catalysis is a kinetic phenomenon. Hence, we start with a chapter on kinetics to describe how the rate of the catalytic reaction cycle depends on the main external process variables by which reactions can be influenced: concentration, pressure and temperature. Next is a chapter on the theory of reaction rates, which aims to make the connection between the properties of reactant molecules and their reactivity. To make the connection between fundamental catalysis and real life, we also describe what catalysts look like on the mesoscopic level, how they are made and how they are characterized. Owing to the spectacular advances in theoretical chemistry and computational facilities over the last decade it is now possible to predict reaction rates from first principles, albeit for idealized cases only. We intend to provide the reader with the necessary background to have at least a feeling for what fundamental catalysis currently means. Consequently, we describe phenomena such as adsorption and reaction on surfaces, along

with the tools needed to investigate this. Finally, we describe a number of industrially important catalytic processes, from both applied and fundamental points of view. The emphasis is on concepts and general trends rather than on specific details, and the aim has been to provide students with the necessary background to appreciate the more specialized literature on fundamental catalysis. The literature section gives references to a number of general books in catalysis and related disciplines.

1.6
Catalysis in Journals

The results of research in catalysis are published in a wide range of general and more specialized journals. This reflects the highly multidisciplinary nature of the field. Referring to the different length scales in Fig. 1.8, research in the microscopic domain, dealing with the fundamentals of adsorbed molecules and elementary reaction steps is often reported in general journals, such as the *Journal of Chemical Physics*, the *Journal of Physical Chemistry, Physical Chemistry-Chemical Physics, Surface Science, Langmuir* and *Physical Review*, and sometimes even *Science* and *Nature*. Also, the specialized *Journal of Catalysis* and *Catalysis Letters* publish articles in this area.

The mesoscopic domain of real catalysts is mostly covered by the typical catalysis periodicals, such as *Applied Catalysis*, the *Journal of Catalysis, Catalysis Letters, Topics in Catalysis, Catalysis Today, Microporous Materials* and *Zeolites*, although occasionally articles also appear in *Journal of Physical Chemistry* and *Physical Chemistry-Chemical Physics*, and many others.

The macroscopic domain is largely covered by journals dedicated to chemical engineering: *Chemical Engineering Science, Industrial & Engineering Chemistry Research*, and the *Journal of the American Institute of Chemical Engineers* (*AIChE Journal*) are some of the best known in this field.

Exciting, new results that may not yet be fully understood but for which it is important that the catalysis community learns about them, are published in the form of Letters, Notes and Rapid Communications. Specialized "Letter Journals" are *Chemical Communications, Catalysis Letters, Chemical Physics Letters* and *Physical Review Letters*, while several regular journals have sections for letters, such as the Priority Communications in the *Journal of Catalysis*.

In addition, there are the highly appreciated review journals, which publish overviews of the status of certain topics of interest in the field. *Advances in Catalysis, Catalysis Reviews*: *Science & Engineering* and *Catalysis, Specialist Periodical Reports* publish the most exhaustive reviews. *CaTTech* is a colorful magazine that publishes shorter reviews along with news from the catalysis community. Also the News Brief section of *Applied Catalysis* fulfills this important role.

As in all scientific fields, conferences are frequently followed up by a book of proceedings, containing short accounts of the presentations. However, proceedings are becoming less popular among scientists. As refereeing procedures tend to be less strict, and the amount of information that can be included is usually limited, the quality of these proceedings is not always what it should be. Often, work published

in expensive proceedings is also published in regular papers, rendering proceedings too often a waste of effort and money.

Midway between conference proceedings, reviews and regular research papers are the topical issues published by *Catalysis Today* and *Topics in Catalysis*. Rather than publishing the proceedings of an entire conference, the editor makes a selection of particularly interesting contributions and invites the presenters to write a not too short article about their work. Such topical issues often give a valuable overview of the status of a certain field, while the quality of the publications is much higher than that of the average conference proceedings.

To get an impression of which journals are the most read and cited, the Institute of Scientific Information (Philadelphia, PA, USA) provides two interesting indicators (*Journal Citation Reports, Science Edition*). The impact factor for a given journal is the number of citations in that year to articles published by the journal in the two previous years. Thus, if each article published in, for example, either 1998 or 1999 is cited exactly once in 2000, the journal will have an impact factor of 1 in that year. Authors use impact factors to decide where to submit their publications. For specialized journals, e.g. those focusing on catalysis, impact factors of 3 and higher are considered high. Review journals usually have higher impact factors, whereas letter journals usually score lower.

A much less appreciated but in fact highly informative parameter and indicator of quality is the citation half-life of a journal. This is the period in years (going back from the current year) during which cited papers were published, from which it received half of all the citations in the current year. A long citation half-life indicates that the journal has published quality articles that have long kept their value to the scientific community. Care should be exercised with these numbers, as relatively young journals need years before they can reach an appreciable citation half-life to prove that they indeed published papers of long lasting value. Table 1.5 lists the impact factor and citation half life for several relevant journals.

Table 1.5. Impact factors and citation half-lives for selected journals. (Source: Institute for Scientific Information (ISI), Philadelphia, PA, USA).

Journal	Impact factor					Citation half life (years)
	2001	2002	2003	2004	2005	2005
Catalysis Reviews	8,471	6,455	5,708	8,000	5,312	10
Journal of Catalysis	3,293	3,118	3,276	4,063	4,780	8,4
Chemical Communications	3,902	4,038	4,031	3,997	4,426	5,9
Journal of Physical Chemistry (B)	3,379	3,611	3,679	3,834	4,033	4,2
Applied Catalysis B Environmental	3,643	2,866	3,476	4,042	3,809	4,6
Microporous Materials	2,497	1,990	2,701	2,093	3,355	4,6
Advances in Catalysis	6,846	10,923	7,889	9,750	2,750	10
Applied Catalysis A General	2,258	1,915	2,825	2,378	2,728	4,9
Topics in Catalysis	2,136	1,648	2,187	2,493	2,547	4,4
Catalysis Today	2,333	2,146	2,627	3,108	2,365	6,1
Journal of Molecular Catalysis – A Chemical	1,520	1,729	2,264	2,316	2,348	4,5
Catalysis Communications				1,890	2,098	2,6
Catalysis Letters	1,852	1,559	1,581	1,904	2,088	6,5
AIChE Journal	1,793	1,626	1,667	1,761	2,036	10
Chemical Engineering Science	1,547	1,224	1,562	1,655	1,735	8,7
Journal of Molecular Catalysis – B Enzymatic	1,408	1,451	1,475	1,547	1,685	4,2
Industrial & Engineering Chemistry Research	1,351	1,247	1,317	1,424	1,504	6,6
Reaction Kinetics and Catalysis Letters	0,475	0,398	0,603	0,618	0,670	7,5
Studies in Surface Science and Catalysis	1,265	3,468	–	0,489	0,307	7,9
JACS	6,079	6,201	6,516	6,903	7,419	8,2
Phys Rev Lett	6,668	7,323	7,035	7,218	7,489	6,6
Phys Rev B	3,070	3,327	2,962	3,075	3,185	7,7
Science	23,329	28,956	29,781	31,853	30,927	7,3
Nature	27,955	30,432	30,979	32,182	29,273	7,5
Nature Materials	–	–	10,770	13,531	15,941	2,2
Angewandte Chemie	8,255	7,671	8,427	9,161	9,596	5,2

Arranged in order of 2005 impact factor, except for the general journals in the lower part of the table.

1.7
General References to Textbooks in Catalysis

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