

## Chapter 1

### Introduction to Catalysis

Ask the average person in the street what a catalyst is, and they will very likely tell you that it is part of a car. Indeed, the automotive exhaust converter represents a very successful application of catalysis; it effectively removes most of the pollutants that leave the engines of cars through exhausts. However, catalysis has a much wider scope of application than abating pollution alone [1–11].

#### Catalysis in Industry

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

- Production of transportation fuels in 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 for the noncatalytic reaction, thus, enabling processes to be carried out at industrially feasible conditions of pressure and temperature.

The economical importance is immediately evident from the estimate that industrial catalysis contributes about one quarter to the gross domestic product of developed countries. Around 2000, the catalyst world market was estimated to be about 10 billion US\$, about equally distributed over refining, polymerization, chemicals, and environmental applications. The products of these processes, however, were valued at 200–300 times that of the catalyst [12].

Outside science and technology, the word catalyst is often used in the sense of ‘enabler’ for all kinds of processes in society.

Catalysis also plays a key role in nature [13]. Living matter relies on enzymes, which are the most abundant catalysts to be found. Photosynthesis generates sugars and oxygen from carbon dioxide and water by using chlorophyll as the catalyst and is probably the largest catalytic process in nature. Finally, the chemical indus-

try relies heavily on catalysis, which is an indispensable tool in the production of bulk and fine chemicals, as well as fuels. In fact, energy technology also depends largely on catalysts, not only in the processing of conventional fuels, but also in emerging forms of renewable energy, for instance, where hydrogen is produced via photocatalytic or electrocatalytic routes [14, 15].

For scientists and engineers, catalysis is a tremendously challenging and highly multidisciplinary field. To better understand it, let us first see what catalysis is before we proceed to its importance and functionality for mankind.

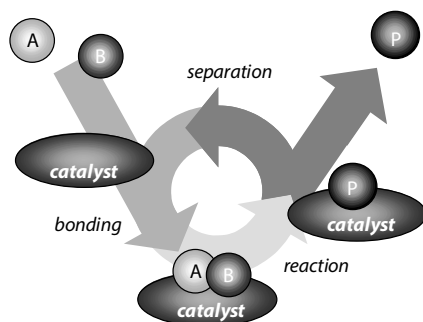
## 1.1

### What Is Catalysis?

In simple terms, a catalyst accelerates a chemical reaction. It does so by forming bonds with reacting molecules, allowing these to react to form a product, which then detaches from the catalyst (leaving 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 a product P, see Figure 1.1. The cycle starts with the bonding of molecules A and B to the catalyst. The next step is that A and B react, by ways of the catalyst, to create product P. In the final step, product P separates from the catalyst, thus, leaving the reaction cycle in its original state.

In order to see how the catalyst accelerates the reaction, we need to look at the potential energy diagram in Figure 1.2. To fully appreciate such diagrams, it is important to realize that lower energies imply more stable situations. It compares the noncatalytic and the catalytic reaction. For the former, 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  $\Delta E$  in



**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.

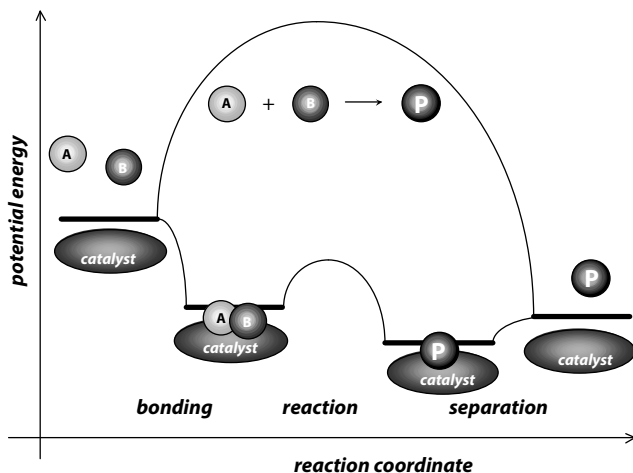
Figure 1.2. The change in Gibbs free energy between the reactants, A + B, and the product P is  $\Delta G$ , and the change in enthalpy is  $\Delta H$ .

The catalytic reaction starts by the bonding of reactants A and B to the catalyst, in a spontaneous reaction. Thus, the formation of this complex is exothermic, which in turn means that energy is lowered. Next comes the reaction between A and B while they are bound to the catalyst. This step is associated with an activation energy,  $\Delta E_{\text{cat}}$ . However, it is significantly lower than for the uncatalyzed reaction. Eventually, product P separates from the catalyst in an endothermic step.

The diagram of Figure 1.2 illustrates several important points, in terms of the enthalpy changes in the course of the reaction:

- 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 changes in enthalpy and also 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.

In addition to the enthalpy,  $H$ , one should also consider the entropy,  $S$ . Together they determine the free energy,  $G = H - TS$ . Hence, we can also draw Figure 1.2 in



**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.

terms of changes in free energy. While a reaction releasing heat is called *exothermic* ( $\Delta H < 0$ ), one that produces free energy is *exergonic* ( $\Delta G < 0$ ). Spontaneous processes are exergonic, and in catalysis, adsorption is an example. Conversely, a reaction that consumes heat is *endothermic* ( $\Delta H > 0$ ), while a reaction for which the free energy increases is *endergonic* ( $\Delta G > 0$ ). The final state of a process – for example of the reaction  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$  – is dictated by the equilibrium, and the process can be manipulated to become more exergonic by choosing optimal conditions, in case of the ammonia synthesis low temperature and high pressure. A catalyst only affects the way in which the reaction reaches its final state, and conversions can never lead to product concentrations exceeding those dictated by equilibrium.

Hence, in order to predict whether a reaction will proceed, one needs to consider the free energy, rather than the enthalpy. Doing this on the level of the elementary steps of a catalytic reaction requires that one knows both  $\Delta H$  and  $\Delta S$ , which has only recently become possible with the advent of computational chemistry. We discuss this in detail in Chapters 3 and 7.

With our current knowledge of catalytic reactions from Figure 1.2, we can already understand that there will be cases in which the combination of catalyst with reactants or products is not successful:

- If the bonding between reactants and catalyst is too weak, there will hardly be any conversion of A and B into products.
- If the bond between the catalyst and one of the reactants, say A, is too strong, the catalyst will mostly be occupied with species A, thus, not allowing B to form any product. Also, if both A and B 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 Figure 1.2, the second level lies so deep that the activation 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 catalytic surface 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.

The catalyst has thus far been an unspecified, abstract body, so let us now look at the different forms of catalysts that 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 as zeolites or enzymes. In addition, they may be employed in a variety of surroundings, in liquids, gases, or at the surface of solids. Preparing a

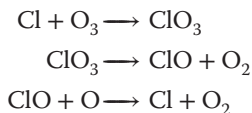
catalyst in the optimum form and studying its precise composition and shape are an important specialism, which we describe in later chapters.

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

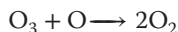
### 1.2.1

#### Homogeneous Catalysis

In homogeneous catalysis [16], the catalyst and the reactants are in the same phase, that is, 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:



or overall



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 the 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 homogeneous catalysts in all kinds of reactions to produce chemicals. The catalytic carbonylation of methanol to acetic acid

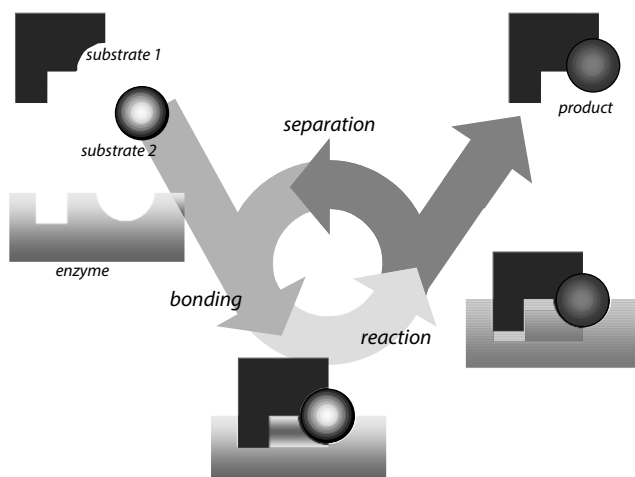


by  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  complexes in solution is one of many examples. In homogeneous catalysis, often aimed at the production of delicate pharmaceuticals, organometallic complexes are synthesized in procedures employing molecular control, such that the judicious choice of ligands directs the reacting molecules to the desired products.

### 1.2.2

#### Biocatalysis

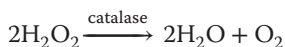
Enzymes are nature's catalysts [13, 17]. For the moment, it is sufficient to consider an enzyme as a large protein holding an active site within a very specific shape formed by the protein structure (see Figure 1.3). Having shapes that are optimally suited to guide reactant molecules (usually referred to as substrates)



**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 (TS) of the reaction

they catalyze. Enzymes are highly efficient catalysts and represent a great source of inspiration for designing technical catalysts.

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



at an incredibly high rate of up to  $10^7$  hydrogen peroxide molecules per second!

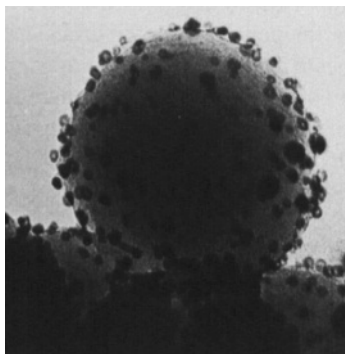
The enzyme catalase occurs in many living organisms. It consists of four polypeptide chains, each over 500 amino acids long, which all contain iron in a porphyrin heme group that is responsible for its catalytic activity. By decomposing hydrogen peroxide, it protects the cell against damage from reactive oxygen species.

Enzymes let biological reactions occur at rates which are necessary for the maintenance of life. For instance, the build up of proteins and DNA, or the breakdown of molecules, like  $\text{H}_2\text{O}_2$  or much larger ones, and the storage of energy in sugars. An example that especially appeals to students is the breakdown of alcohol to acetaldehyde inside the body by the enzyme alcohol dehydrogenase. The acetaldehyde in turn is converted to acetate by aldehyde hydrogenase. Some people cannot tolerate alcohol (as revealed by facial flushing) because they lack the form of the enzyme that breaks down the 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

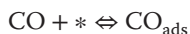


**Figure 1.4** Catalysts are nanomaterials and catalysis is, thus, nanotechnology. By defining nanotechnology as the branch of materials science aiming at control over material properties on the nanometer scale, then catalysis represents a field where nanomaterials have been applied commercially for about one century. Many synthetic techniques are available

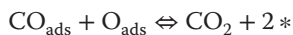
to produce small particles for heterogeneous catalysts and to keep them sufficiently stable that they can withstand the often hostile conditions under which they have to work inside an industrial reactor. Modern catalysis is pre-eminently nanotechnology (figure reproduced from Datye and Long [18] with permission of Elsevier).

reactions occur at the surface. In order 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 (Figure 1.4). Heterogeneous catalysts can be considered the workhorses of the chemical and petrochemical industry and we will discuss many applications of heterogeneous catalysis throughout this book.

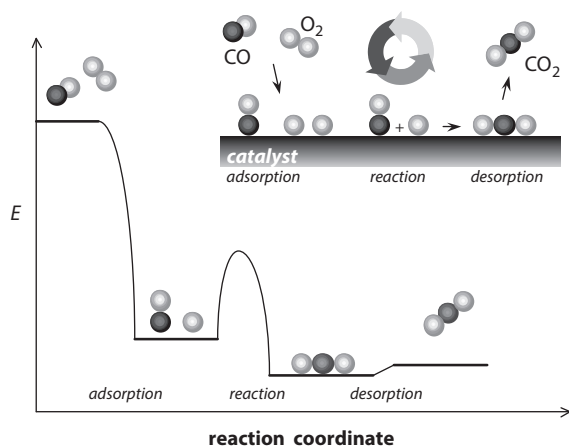
As an introductory example, we take one of the key reactions in cleaning automotive exhaust, the catalytic oxidation of CO on the surface of noble metals such as platinum, palladium, and rhodium. In order to describe the process, we will assume that the metal surface consists of active sites, denoted as “\*” (we define them properly later on). The catalytic reaction cycle begins with the adsorption of CO and O<sub>2</sub> on the surface of platinum, where the O<sub>2</sub> molecule dissociates into two separate O atoms (the subscript “ads” indicates that the atom or molecule is adsorbed on the surface, i.e., bound to the site \*):



Next, the adsorbed O atom and the adsorbed CO molecule react on the surface to form CO<sub>2</sub>, which being a very stable and relatively unreactive molecule, interacts only weakly with the platinum surface and desorbs almost instantaneously:



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.



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

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  $O_2$  of about 500 kJ/mol. In the catalytic reaction, however, the  $O_2$  molecule dissociates easily – in fact without activation energy – on the surface of the catalyst. The activation energy is associated with the reaction between adsorbed CO and O atoms, which is on the order of 50–100 kJ/mol. Desorption of the product molecule  $CO_2$  costs only about 15–30 kJ/mol (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. As a consequence, the ease at 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 in catalyzed reactions, hence the saying: “a catalyst breaks bonds, and lets other bonds form.” The beneficial action of the catalyst is in the dissociation of a strong bond; the following 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?

It is impossible to imagine how the chemical industry of the twentieth century could have developed to its present form without catalysis (i.e., on the basis of noncatalytic, stoichiometric reactions alone). Reactions in general can be controlled on the basis of temperature, concentration, pressure, and contact time. Raising 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, for example, conversion of  $\text{N}_2$  and  $\text{H}_2$  to ammonia is practically impossible above  $600^\circ\text{C}$ . Nevertheless, higher temperatures are needed to be able to break the very strong N–N bond in  $\text{N}_2$ . Without catalysts, many reactions that are now common in the chemical industry would not be possible, and many other processes would not be economical.

Catalysts accelerate reactions by orders of magnitude, thus, enabling reactions to be carried out in the thermodynamically most favorable regime, and at much milder conditions of temperature and pressure. 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 chemical processes. But that is not all.

#### 1.3.1

##### Catalysis and Green Chemistry

Technology is termed “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.

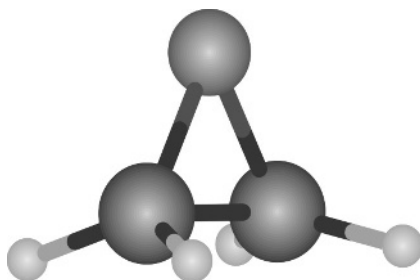
A good example is provided by the selective oxidation of ethylene to ethylene epoxide, an important intermediate towards ethylene glycol (antifreeze) and various polyethers and polyurethanes (Figure 1.6). The old, noncatalytic route (called the epichlorohydrin process) follows a three-step synthesis:

1.  $\text{Cl}_2 + \text{NaOH} \longrightarrow \text{HOCl} + \text{NaCl}$
2.  $\text{C}_2\text{H}_4 + \text{HOCl} \longrightarrow \text{CH}_2\text{Cl}-\text{CH}_2\text{OH}$  (epichlorohydrin)
3.  $\text{CH}_2\text{Cl}-\text{CH}_2\text{OH} + 1/2\text{Ca}(\text{OH})_2 \longrightarrow 1/2\text{CaCl}_2 + \text{C}_2\text{H}_4\text{O} + \text{H}_2\text{O}$

or in total:



Hence, for every molecule of ethylene oxide,  $1\frac{1}{2}$  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.



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

The catalytic route, on the other hand, is simple and clean (although it does produce a small amount of  $\text{CO}_2$ ). By using silver promoted by small amounts of chlorine as the catalyst, ethylene oxide is directly formed from  $\text{C}_2\text{H}_4$  and  $\text{O}_2$  at a selectivity of around 90% (with about 10% of the ethylene ending up as  $\text{CO}_2$ ). Nowadays all production facilities for ethylene oxide use catalysts.

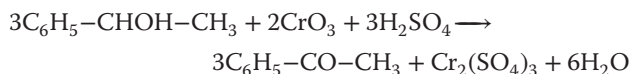
### 1.3.2

#### Atom Efficiency, E Factors, and Environmental Friendliness

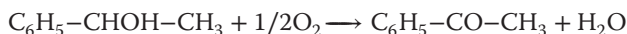
Organic chemistry is full of synthesis routes that are based on either stoichiometric oxidations of hydrocarbons with sodium dichromate and potassium permanganate, or on hydrogenations with alkali metals, borohydrides, or metallic zinc. In addition, there are reactions such as aromatic nitrations with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , or acylations with  $\text{AlCl}_3$  that generate significant amounts of inorganic salts as byproducts.

Fine chemicals are predominantly (although not exclusively) the domain of homogeneous catalysis, where solvents present another issue of environmental concern. According to Sheldon [19]: “The best solvent is no solvent, but if a solvent is unavoidable, then water is a good candidate.”

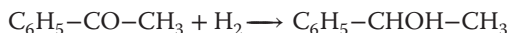
Sheldon has introduced several indicators to measure the efficiency and environmental impact of a reaction [20]. The atom efficiency is the molecular weight of the desired product divided by the total molecular weight of all products. For example, the conventional oxidation of the secondary alcohol



has an atom efficiency of  $360/860 = 42\%$ . By contrast, the catalytic route



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:



as does the catalytic carbonylation of this molecule:



**Table 1.1** Environmental acceptability of products in different segments of the chemical industry [20].

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

Another useful indicator of environmental acceptability is the E factor, which is the weight of waste or undesirable byproduct divided by the weight of the desired product. As Table 1.1 shows, 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 alongside each other; however, in practice, E factors tend to be higher due to the yields being less than optimum and reagents that are used in excess. Also, loss of solvents should be included, and perhaps even energy consumption with the associated generation of waste  $\text{CO}_2$ .

To stress the environmental impact rather than the amount of waste, Sheldon introduced an environmental quotient EQ. This is the E factor multiplied by an unfriendliness quotient,  $Q$ , which assigns a value indicating how undesirable a byproduct is. For example,  $Q = 0$  for clean water, 1 for a benign salt as NaCl, and 100–1000 for toxic compounds. Evidently, catalytic routes that avoid waste formation are highly desirable, and placing more weight on the economic value of environmental acceptability will spark greater motivation towards catalytic alternatives. After all – and economics permitting – waste prevention is in principle 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 to ensure that raw materials are used efficiently, thus, minimizing waste production. As a consequence, the chemical industry heavily relies on catalysis, roughly 85–90% of all products are made in catalytic processes [12].

The chemical industry produces a large range of base, middle, and end products. The main subsectors are

- Base chemicals, including organic and inorganic chemicals, polymers and plastics, dyes and pigments. Table 1.2 lists the most important ones, but there are many more in each category. Polymers have become enormously important in

**Table 1.2** Some of the most important base chemicals and polymers.

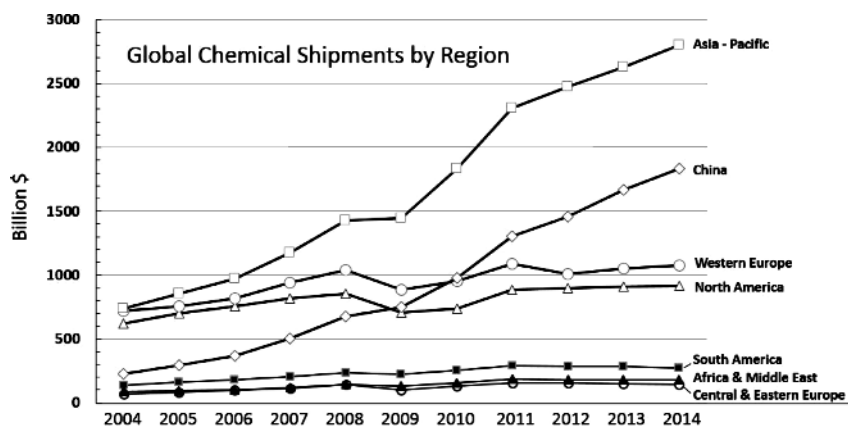
Inorganic chemicals	Organic chemicals	Polymers and plastics
Sulfuric acid	Ethylene	Polyethylene
Ammonia	Propylene	– high density
Chlorine	Ethylene chloride	– linear low density
Phosphoric acid	Urea	– low density
Sodium hydroxide	Ethylbenzene	Polypropylene
Nitric acid	Styrene	Polyvinyl chloride
Ammonium nitrate	Ethylene oxide	Polystyrene
Hydrochloric acid	Cumene	Styrene polymers (e.g., ABS)
Ammonium sulfate	1,3-Butadiene	Polyamines, nylons
Titanium oxide	Acrylonitrile	
Aluminum sulfate	Benzene and aromatics	
N <sub>2</sub> , O <sub>2</sub> , H <sub>2</sub> gas	Aniline	
Sodium chlorate and sulfate		

replacing traditional materials in the automotive, construction, and packaging markets.

- Specialty chemicals, such as paints and coatings, adhesives, plastic additives, and also catalysts. These are performance-oriented products that are usually sold including technical services for customers.
- Agricultural chemicals, for farming and food processing.
- Pharmaceuticals, including diagnostics, drugs, vaccines, vitamins, etc., for humans or animals.
- Consumer products, such as soaps, detergents, cleaners, toiletries, and cosmetics.

Although catalysis is vitally important in all subsectors, in this book we limit ourselves to catalysts in the production of fuels and base chemicals. Figure 1.7 shows where chemicals are produced in the world. Where Western Europe and the USA largely dominated the market in the twentieth century, nowadays the Asia–Pacific region, and notably China, is the largest producer of chemicals in the world.

Some of the largest catalytic processes in this sector are listed in Table 1.3; Tables 1.4 and 1.5 list the top 50 of the chemical industry and the largest companies in the petroleum sector, respectively.



**Figure 1.7** China and the Asia-Pacific region (including large producers in Japan, Korea, and India) dominate the chemicals market these days (data from the American Chemistry Council, [www.americanchemistry.com](http://www.americanchemistry.com)).

**Table 1.3** Selection of the 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 <sub>2</sub> SO <sub>4</sub> , HF, solid acids
Polymerization of ethylene, propylene, and others	Cr, TiCl <sub>x</sub> /MgCl <sub>2</sub>
Ethylene epoxidation to ethylene oxide	Ag
Vinylchloride (ethylene + Cl <sub>2</sub> )	Cu (as chloride)
Steam reforming of methane to CO + H <sub>2</sub>	Ni
Water-gas shift reaction, and reverse	Fe (oxide), Cu-ZnO
Methanation	Ni
Ammonia synthesis	Fe
Ammonia oxidation to NO and HNO <sub>3</sub>	Pt-Rh
Methanol synthesis	Cu/ZnO/Al <sub>2</sub> O <sub>3</sub>
Fischer-Tropsch synthesis	Fe, Co
Acrylonitrile from propylene and ammonia	Bi-Mo, Fe-Sb (oxides)
Hydrogenation of vegetable oils	Ni
Sulfuric acid	V (oxide)
Oxidation of CO and hydrocarbons (car exhaust)	Pt, Pd
Reduction of NO <sub>x</sub> (in exhaust)	Rh, Pd, vanadium oxide

**Table 1.4** World top 50 of chemical producers [21].

Rank				Company	Country	Chemical sales (million \$)	Chemicals (%)
2014	2010	2005	2001				
1	1	2	3	BASF	Germany	78 698	80
2	2	1	1	Dow Chemical	USA	58 167	100
3	3	7	26	Sinopec	China	57 953	13
4	7	10	18	SABIC	Saudi Arabia	43 341	86
5	4	4	6	ExxonMobil	USA	38 178	10
6	6	11	30	Formosa Plastics	Taiwan	37 059	60
7	9	12	50	LyondellBasell Industries	Netherlands	34 839	76
8	8	6	2	DuPont	USA	29 945	86
9	11	17	42	Ineos	Switzerland	29 652	100
10	13	8	4	Bayer	Germany	28 120	50
11	10	13	14	Mitsubishi Chemical	Japan	26 342	76
12	5	3	7	Royal Dutch Shell	Netherlands	24 607	6
13	18	50	–	LG Chem	South Korea	21 456	100
14	26	–	–	Braskem	Brazil	19 578	100
15	19	20	22	Air Liquide	France	19 210	94
16	14	18	11	AkzoNobel	Netherlands	19 011	100
17	22	–	–	Linde	Germany	18 539	82
18	16	19	20	Sumitomo Chemical	Japan	17 833	79
19	15	15	13	Mitsui Chemicals	Japan	17 201	100
20	17	14	8	Evonik Industries (< 2007: Degussa)	Germany	17 177	100
21	21	21	31	Toray Industries	Japan	17 006	89
22	20	39	38	Reliance Industries	India	15 870	26
23	29	36	–	Yara	Norway	15 141	100
24	23	30	24	PPG Industries	USA	14 250	93
25	33	32	41	Solvay	Belgium	14 134	100
26	45	–	–	Lotte Chemical	South Korea	14 121	100
27	28	22	23	Chevron Phillips	USA	13 416	100
28	25	26	19	DSM	Netherlands	12 344	100
29	30	35	36	Praxair	USA	12 273	100
30	–	–	–	SK Innovation	South Korea	12 011	19
31	24	25	37	Shin-Etsu Chemical	Japan	11 874	100
32	32	16	12	Huntsman Corp.	USA	11 578	100
33	34	44	32	Syngenta	Switzerland	11 286	75
34	37	46	48	Borealis	Austria	11 076	100
35	31	28	–	Lanxess	Germany	10 646	100
36	27	31	35	Asahi Kasei	Japan	10 628	55
37	43	42	–	Sasol	South Africa	10 299	55
38	36	34	29	Air Products & Chemicals	USA	9 989	96

Table 1.4 (Continued).

Rank					Country	Chemical sales (million \$)	Chemicals (%)
	2014	2010	2005	2001			
39	48	38	33	Eastman Chemical	USA	9 527	100
40	–	–	–	PTT Global Chemical	Thailand	9 522	54
41	44	–	–	Mosaic	USA	9 056	100
42	35	27	15	DIC (Dainippon Ink & Chemicals)	Japan	8 218	100
43	38	–	–	Arkema	France	7 915	100
44	40	–	–	Tosoh	Japan	7 657	100
45	–	–	–	Hanwha Chemical	Korea	7 655	100
46	–	–	–	Siam Cement	Thailand	7 617	51
47	–	–	–	Indorama	Thailand	7 514	100
48	–	9	9	BP	UK	7 284	2
49	–	–	–	Ecolab	USA	7 215	51
50	–	23	10	Johnson Matthey	UK	7 203	43
> 50	12	5	5	Total	France	7 570	3
> 50	39	33	46	ENI	Italy	7 397	5

Table 1.5 The world's largest petroleum companies.

Company			Product sales (barrels/day)			Company			Distillation capacity (barrels/day)		
1	Royal Dutch Shell	6 235 000	1	ExxonMobil	5 375 000	2	Sinopec	5 239 000	3	CNPC	4 421 000
2	ExxonMobil	6 174 000	2	Sinopec	5 239 000	3	CNPC	4 421 000	4	Royal Dutch Shell	3 360 000
3	BP	5 657 000	3	CNPC	4 421 000	4	Royal Dutch Shell	3 360 000	5	PDV	2 822 000
4	Sinopec	3 548 000	4	Royal Dutch Shell	3 360 000						
5	Total	3 403 000	5	PDV	2 822 000						

BP: British Petroleum; CNPC: China National Petroleum Company; PDV: Petroleos de Venezuela. Data from Energy Intelligence, <http://www2.energyintel.com/>.

Every chemistry student who is interested in a career in the chemical industry, or in chemical design in general, should know and understand what catalysis is and does. This is the reason that the authors and many of their colleagues teach catalysis in early stages of the chemistry curriculum of their respective universities.

## 1.4

## Catalysis as a Multidisciplinary Science

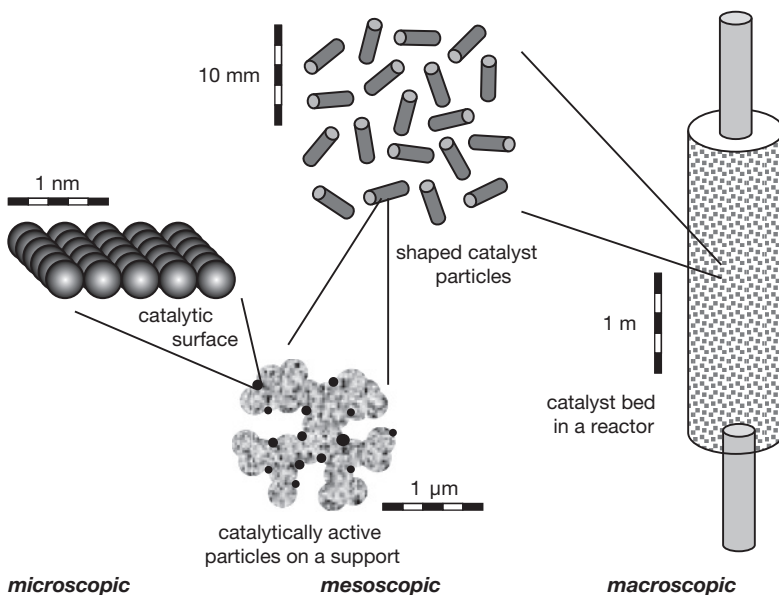
## 1.4.1

## The Many Length Scales of a “Catalyst”

Catalysis as a field of study is very broad and is closely interwoven with numerous other scientific disciplines. This becomes immediately evident if we realize that catalysis is a phenomenon encompassing many length scales. Figure 1.8 illustrates this for the case of heterogeneous catalysis [22].

When we introduced the cycle of catalysis in Figures 1.1, 1.2, and 1.5, we dealt with 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 on the way to 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 elementary reaction steps. The length scales of interest are in the subnanometer region. Publications and research at the molecular scale are predominantly found in academic journals specialized in chemistry, physical chemistry, and physics.

The next level is that of small catalytically active particles, with typical dimensions between 1 and 10 nm. These particles exist within the pores of support par-



**Figure 1.8** The relevant length scales in catalysis range from the subnanometer domain of the atomic and molecular level to the macroscopic domain of an industrial reactor.



ticles in the micrometer range. The key interests at this level are the size, shape, structure, and composition of the active particles, and in particular 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 are largely dealing with phenomena on this length scale.

The mesoscopic 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. This field is to a large extent materials science. Typical points of interest are porosity, strength, and attrition resistance which enable catalysts to survive the conditions inside industrial reactors. This part of catalysis is mainly (though not exclusively) covered 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 a 10 cm test reactor in a laboratory or a 50-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 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. For the catalyst, matters as mechanical stability, sensitivity to trace impurities in the reactant feed, and degradation of the particles (e.g., due to exposure to high temperatures) are essential in addition to intrinsic properties 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 that we 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 the pores, and through shaped catalyst particles may vary between seconds and minutes. Fur-

thermore, residence times of molecules inside entire reactors may vary from seconds to infinity. This happens if 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. In simple terms, catalysis is a kinetic phenomenon which deals with the acceleration of reactions. 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, namely concentration, pressure, and temperature. Next is a chapter on the theory of reaction rates, which is meant to bridge the connection between the properties of reactant molecules and their reactivity. Owing to the spectacular advances in theoretical chemistry and computational facilities of the last decades, it has become possible to predict reaction rates from first principles (be it for idealized cases only). We intend to provide the reader with the necessary background to help understand the current possibilities of catalysis anno 2016. Consequently, we will describe phenomena such as adsorption and reaction on surfaces, while providing the tools needed to investigate and conduct research. In order to ensure a practical knowledge of catalysts, we will describe what catalysts look like on the mesoscopic level, how they are made, and how they are characterized. Finally, we will 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, while the aim is 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

### Appendix: 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 Figure 1.8, research in the microscopic domain (which deals with the fundamental level in which adsorbed molecules and elementary reaction steps take place) 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 occasionally in the *Journal of the American Chemical Society*, *Angewandte Chemie*, *Energy & Environmental Science*, *Nature*, and its daughters *Nature Chemistry* and *Nature Materials*, and *Science*. Also the more specialized

*Journal of Catalysis*, *ACS Catalysis*, *ChemCatChem*, 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*, *ACS Catalysis*, *Catalysis Science and Technology*, *Catalysis Structure and Reactivity*, the *Journal of Catalysis*, *Catalysis Letters*, *Topics in Catalysis*, *Catalysis Today*, *Microporous Materials*, and *Zeolites*. However, occasionally articles appear in *Angewandte Chemie*, *Journal of Physical Chemistry*, and *Physical Chemistry Chemical Physics*, and many others.

The macroscopic domain of reactors and transport processes is largely covered by journals from the chemical engineering field such as *Chemical Engineering Science*, *Industrial & Engineering Chemistry Research*, and the *Journal of the American Institute of Chemical Engineers (AIChE Journal)* which are some of the best-known periodicals in this field.

Exciting new results, which are not fully understood but are nevertheless important, are published in the form of Letters, Notes, and Rapid Communications. Specialized “Letter Journals” are *Chemical Communications*, *Catalysis Letters*, *Catalysis Communications*, *Chemical Physics Letters*, and *Physical Review Letters*, while several regular journals have sections for letters, such as the Communications and Research Notes in the *Journal of Catalysis*.

In addition, there are the highly appreciated review journals. These 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.

As in all scientific fields, conferences are frequently followed up by a book of proceedings, containing short accounts of the presentations. However, these books of 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 satisfactory. Midway between conference proceedings, reviews, and regular research papers, there are also 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 noteworthy contributions. Presenters are then invited to write a short article about their findings. Such topical issues often give a valuable overview of the status of a certain field, while the quality of the publications is better guaranteed by adequate review procedures.

In order to get an impression which journals are best read and cited, the *Journal Citation Reports*® provides interesting indicators: 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 either 2013 or 2014 is cited exactly once in 2015, the journal will have an impact factor of 1 in that year. Publishers use impact factors to monitor the success of their journals, while authors use them as a guide as to where to submit their work. For specialized journals, for example, those focusing on catalysis, impact factors of 5 and higher are considered high. Review journals usually have higher impact factors, whereas letters 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 1.6 lists the impact factor and citation half-life for several journals in the field. Almost all journals have seen a significant increase in citations over the period 2001–2014, reflecting the growing research activity and increased use of scientific journals in the world. The number of publications in the field of catalysis has worldwide gone up substantially, with the emerging countries contributing most to the growth. Another factor of importance is that nowadays articles are available on line, and accessing them has become very easy. Also, several publishers have changed from subscriptions to individual titles to arrangements where groups of institutions subscribe to access to all journals in certain domains, which has facilitated the access to journals greatly. Also the requirement of some universities for PhD students to have journal publications before they can graduate has contributed substantially to the increased volume of publications, and higher impact factors.

The down side is that some scientists (or their universities) regard publishing as a competition, where the reputation of a journal is almost seen as more important than the quality of the article.

One should realize that the impact of the journal is only of immediate interest in the first one or two years after publication, where the title of the journal could indicate an expected impact. But in the end, it is the impact of the published results that counts. Hence, there are many examples of highly cited papers in low impact journals, as well as little cited articles in high impact titles.

Similarly one should be aware that among different fields of science there are large variations in citation practices. Medical journals, for example, in general receive more citations than those in catalysis, physical chemistry, or surface science.

In choosing where to publish, one should realize that each journal has its own characteristic scope, and prospective authors should therefore always consult the guide for authors of a journal, and check if their subject fits.

**Table 1.6** Impact factors and citation half-lives for selected journals (source: Journal Citation Reports®, Thomson Reuters, New York, USA).

	Impact factor				$t_{1/2}$ 2015 (years)
	2015	2010	2005	2001	
<b>Catalysis journals</b>					
<i>ACS Catalysis</i>	9.307	–	–	–	2.4 <sup>a)</sup>
<i>Applied Catalysis B – Environmental</i>	8.328	4.749	3.809	3.643	5.2
<i>Catalysis Reviews – Science and Engineering</i>	7.526	7.000	5.312	8.471	> 10.0
<i>Journal of Catalysis</i>	7.354	5.415	4.780	3.293	> 10.0
<i>Catalysis Science &amp; Technology</i>	5.287	–	–	–	2.6 <sup>a)</sup>
<i>ChemCatChem</i>	4.724	3.345	–	–	2.9 <sup>a)</sup>
<i>Advances in Catalysis</i>	4.500	8.167	2.750	6.846	> 10.0
<i>Catalysis Today</i>	4.312	2.993	2.365	2.333	8.1
<i>Applied Catalysis A – General</i>	4.012	3.384	2.728	2.258	8.4
<i>Journal of Molecular Catalysis A</i>	3.958	2.872	2.348	1.520	8.7
<i>Catalysis Communications</i>	3.389	2.827	2.098	–	5.6 <sup>a)</sup>
<i>Catalysts</i>	2.964	–	–	–	2.5 <sup>a)</sup>
<i>Chinese Journal of Catalysis</i>	2.628	0.752	0.665	–	3.3
<i>Topics in Catalysis</i>	2.355	2.359	2.547	2.136	6.9
<i>Catalysis Letters</i>	2.294	1.907	2.088	1.852	9.1
<i>Catalysis Surveys of Asia</i>	2.038	2.432	1.236	–	7.7
<b>Engineering journals</b>					
<i>Chemical Engineering Journal</i>	5.310	3.074	2.034	0.847	3.9
<i>AIChE Journal</i>	2.980	2.030	2.036	1.793	> 10.0
<i>Chemical Engineering Science</i>	2.750	2.379	1.735	1.547	10.0
<i>Industrial &amp; Engineering Chemistry Research</i>	2.567	2.072	1.504	1.351	6.8
<b>General journals</b>					
<i>Nature Materials</i>	38.891	29.920	15.941	–	6.3
<i>Nature</i>	38.138	36.104	29.273	27.955	> 10.0
<i>Science</i>	34.661	31.377	30.927	23.329	> 10.0
<i>Nature Chemistry</i>	27.893	17.927	–	–	3.8 <sup>a)</sup>
<i>Energy &amp; Environmental Science</i>	25.427	9.488	–	–	3.3 <sup>a)</sup>
<i>Journal of the American Chemical Society</i>	13.038	9.023	7.419	6.079	8.0
<i>Angewandte Chemie – International Edition</i>	11.709	12.730	9.596	8.255	5.8
<i>Journal of Physical Chemistry Letters</i>	8.539	–	–	–	3.0 <sup>a)</sup>
<i>Physical Review Letters</i>	7.645	7.622	7.489	6.668	9.4
<i>Chemical Communications</i>	6.567	5.787	4.426	3.902	4.6
<i>Chemistry – A European Journal</i>	5.771	5.476	4.907	4.614	4.6
<i>Journal of Physical Chemistry C</i>	4.509	4.524	–	–	4.7 <sup>a)</sup>
<i>Physical Chemistry Chemical Physics</i>	4.449	3.454	2.519	1.787	4.1
<i>Langmuir</i>	3.993	4.269	3.705	2.963	7.6
<i>Journal of Physical Chemistry B</i>	3.187	3.603	4.033	3.379	9.8
<i>ChemPhysChem</i>	3.138	3.340	3.607	4.271	5.5

a) Note that a number journals have not existed long enough to establish a meaningful citation half-life; such values are indicated with a footnote.

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