1

Definition, Variants and Examples

What Actually Is Catalysis?

Learning Objectives

By the end of this chapter, you will be able to …

- name the today's definition of catalysis.
- describe the different variants of catalysis.
- explain the steering possibilities offered by catalysis.
- check the information sources on catalysis.

1.1 Definition of Catalysis

Let us consider a reversible chemical reaction between the educts A and B, which leads to the products C and D (Eq. 1.1).

$$A + B \rightleftharpoons C + D \qquad (1.1)$$

A typical example is the esterification of a carboxylic acid with an alcohol yielding an ester and water. The steady state of this reaction – depending on pressure and temperature – is controlled by Nature and determined by the thermodynamics (Chapter 10). The rate at which equilibrium is achieved is described by kinetics (Chapter 11).

As is well known from organic chemistry, the esterification of a carboxylic acid with an alcohol requires a small amount of a catalyst, typically a proton H^+ provided by a Brønsted acid. The catalytic esterification only appears to be a single reaction as shown in Eq. (1.1). On the molecular level, it proceeds as a series of successive partial reactions with different intermediates (Figure 1.1a). In the first step, the carboxylic acid is protonated, forming a carbocation (step **1**). In the second step, the alcohol attacks this carbocation (step **2**). In the intermediate thus formed, a proton migration proceeds (step **3**). Next, water is released, again forming a carbocation (step **4**). In the final step, the proton is restored releasing the ester product (step **5**). This series of reaction can then be restarted, a catalytic mechanism can be postulated, which is usually depicted as a **cycle** (Figure 1.1b).

This step-by-step process is typical for all types of catalysis. Consider, for example, the reverse reaction of the example in Figure 1.1: two stable molecules, an ester and water, should be reacted with each other to form an alcohol and a carboxylic acid. This reaction does not take place 'voluntarily!' Only with the help of the catalyst the bonds between the atoms 'loosen' and via a (non-isolable) **transition state** an intermediate is formed, which then reacts further.

Catalysis is also well known in Nature. A peculiar example is the bombardier beetle (see Excursion 'Animal Catalysis').

Another example of catalysis is the highly exothermic reaction of the two gases hydrogen and oxygen. In a sealed vessel, they can be mixed to any ratio without reaction, but if a small amount of a platinum sponge is added to the mixture it reacts spontaneously. The catalyst, with its large surface area, initiates the so-called '**hydrogen–oxygen reaction**':

$$H_2 + {}^1/_2\, O_2 \rightleftharpoons H_2O \qquad (1.2)$$

The reaction heat indicates a thermodynamically permitted reaction that will proceed even at room temperature and at low pressure. At room temperature, this reaction also requires a catalyst – the transition metal platinum – to get it started: only the catalyst is able to run the reaction.

Applied Homogeneous Catalysis: A Tool for Sustainable Chemistry, Second Edition. Arno Behr, Thomas Seidensticker, and Dieter Vogt.

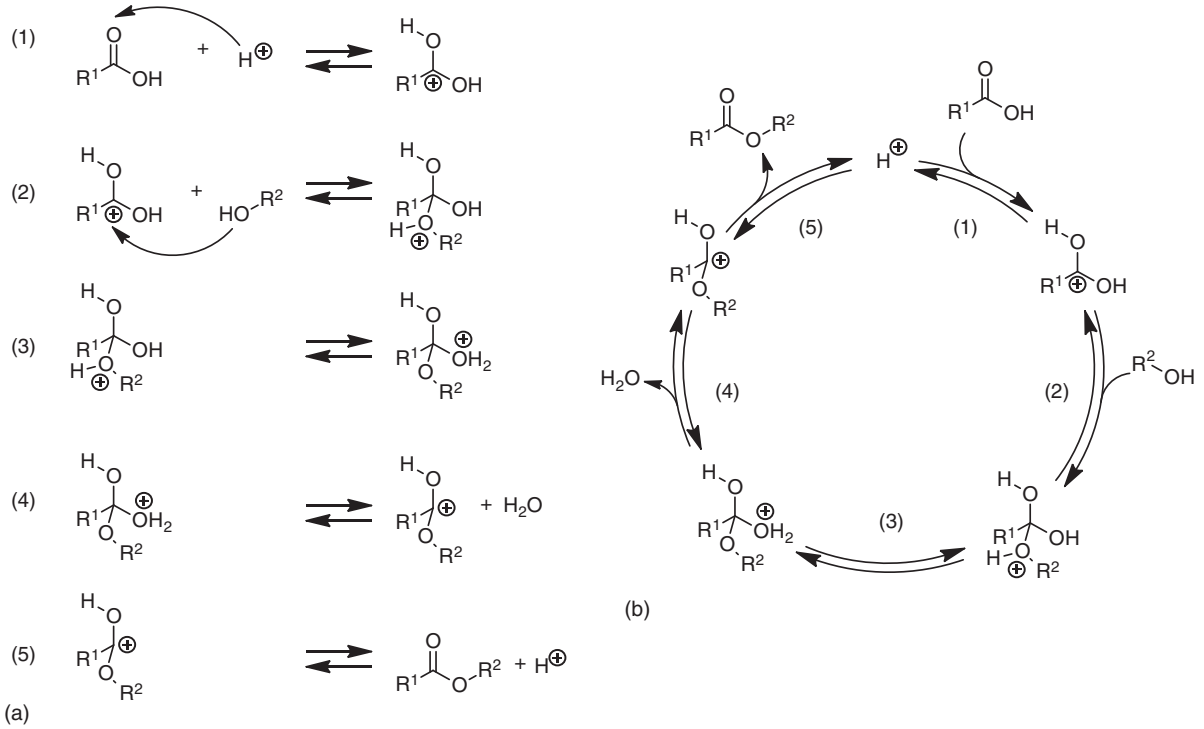


Figure 1.1 Reaction steps of the acid-catalysed esterification of a carboxylic acid and an alcohol (a) and the postulated mechanism (b).

EXCURSION: Animal Catalysis: The Bombardier Beetle

Catalysis is also well known in the animal kingdom: the small bombardier beetle (*Brachinus explodens*), only about 7 mm in size, can keep its predators, birds or frogs, at bay with the help of a violent catalytic reaction. It stores *p*-hydroquinone and hydrogen peroxide in a stable chitin shell. In case of danger, it opens a gland in its abdomen and injects these two reactants into an 'explosion chamber' in which two catalysts are located, catalase and peroxidase. These convert the H_2O_2 into water and oxygen and the hydroquinone into *p*-benzoquinone. These reactions are strongly exothermic, and the water evaporating at 100 °C builds up a strong pressure in the chamber. In case of danger, the beetle sprays its foul-smelling mixture towards the enemy with a loud bang. As it can turn its rear end by approx. 270°, it can precisely aim at its opponent. The enemy usually flees and vows not to put this type of beetle on its menu again.

PS: *You can find some great videos about the beetle on YouTube.*

The adjuvant effect of the platinum sponge was first discovered by *Johann Wolfgang Döbereiner* who, on the 27th of July 1823, used a platinum sponge to construct a gas lighter (see Excursion 'Light My Fire').

The **first definition of a catalyst** was provided in 1836 by the Swedish chemist *Jöns Jakob Berzelius* (Chapter 2) of the University of Stockholm, who noted that:

> '*The substances that cause the decomposition of H_2O_2 do not achieve this goal by being incorporated into the new compounds (H_2O and O_2); in each case*

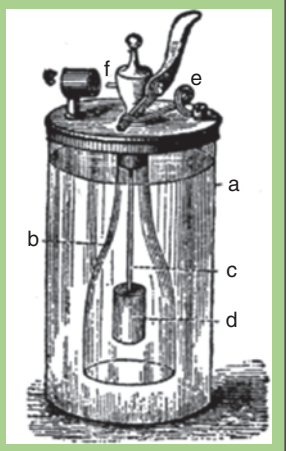
they remain unchanged and hence act by means of an inherent force whose nature is still unknown…'.

(*Berzelius* meant that, in the case of the hydrogen–oxygen reaction, the 'substance' – the platinum sponge – would wake up the 'dozing' gases hydrogen and oxygen. However, he was unclear about the details of the processes driven by the catalyst.)

Berzelius used the term '*katalysis*', which is derived from the Greek, meaning 'to untie', and on that basis he considered the bond-breaking stage to be the crucial step. In contrast, the Chinese took a somewhat different approach to catalysis; the Chinese character '*Chù Méi*' (Figure 1.2) means both catalysis and 'matchmaker,' with the emphasis being placed much more on the linking properties.

EXCURSION: Light My Fire: Döbereiner's Catalytic Lighter

Johann Wolfgang Döbereiner, born in 1780 in Hof, Bavaria, was a well-known chemist who was appointed Professor of Chemistry, Pharmacy and Technology at the University of Jena in 1810. He made numerous discoveries, including that of the 'platinum lighter' in 1823: this glass vessel contains sulphuric acid into which a piece of zinc can be dipped with the help of a lever. Hydrogen is produced, which mixes with the oxygen of the air at a nozzle. However, this 'oxyhydrogen mixture' does not ignite spontaneously. It is ignited by a piece of platinum sponge, that is, finely distributed platinum: a flame is formed that can be used to light a pipe. Only the catalyst platinum got the reaction going under ambient conditions!



PS: *In 1828,* **Döbereiner** *gave his friend* J.W. von Goethe *a sample of this lighter: after initial caution, the famous poet is said to have been quite enthusiastic about this useful invention.*

Figure 1.2 The Chinese character for catalysis and matchmaker ('*Chù Méi*').

The current **definition of catalysis** is as follows:

- A catalyst is a substance that increases the rate at which a chemical system reaches its equilibrium.
- A catalyst participates in a chemical reaction but is not consumed itself.

Although, in theory, a catalyst should be active 'forever', there is of course no ideal philosopher's stone'. Whilst each catalyst has a certain lifetime, during which it will catalyse a reaction in an economical fashion, its efficiency will decrease steadily until, ultimately, it is 'dead'. The lifetime of a catalyst may be very short, or it may be several years (this point is described in detail in Chapter 4).

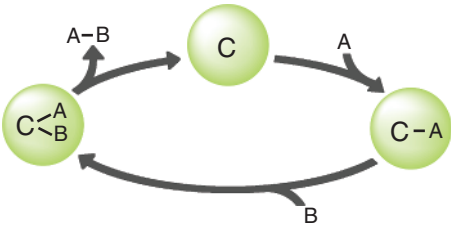


Figure 1.3 A general catalytic cycle.

One factor that all catalysts have in common is that, immediately after they have successfully catalysed a first reaction, they are available to catalyse another reaction. Moreover, this action can be repeated many thousands or even million times. The most commonly used method used to represent this behaviour graphically is a circle; this is often referred to as '**catalytic cycle**'. A generalised type of cycle incorporating the addition reaction $A + B \rightarrow A{-}B$, catalysed by the catalyst C, is shown in Figure 1.3.

Here, the catalyst C first adds reactant A and, subsequently, also reactant B. The two reactants are

united in the immediate vicinity of the catalyst (the 'matchmaker,') such that the product, A–B, is formed. The active catalyst is restored and, therefore, available for another cycle.

1.2 The Different Varieties of Catalysis

In the reaction in Figure 1.1, only liquid reactants are involved: a carboxylic acid and an alcohol yielding an ester and water. All components are soluble and, as there is only one homogeneous liquid phase in the vessel, this is referred to as ***homogeneous catalysis***.

In contrast, in Eq. (1.2) two gases react in the presence of a solid catalyst, the platinum sponge. In this type of catalysis there are two phases, and sometimes even three (gaseous, liquid and solid). Based on such heterogeneity, this variant is referred to as ***heterogeneous catalysis***.

Several subtypes of catalysis have emerged over time. The easiest way is to classify them according to the number of aggregate states during the reaction, that is, homogeneous (= one phase) or heterogeneous (two or more phases) catalysis. It is also possible to distinguish whether they operate **with a metal** (M) (as in *Döbereiner*'s lighter) or **without a metal** component (as in ester hydrolysis). Figure 1.4 attempts to overview the different variants of catalysis, most of which we will meet again in this book.

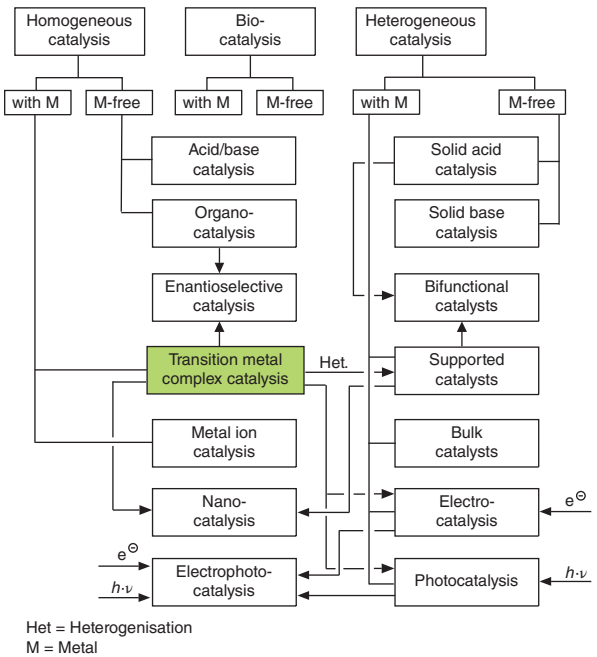


Figure 1.4 Overview of catalysis variants.

At the top of this overview stand the two large areas of homogeneous and heterogeneous catalysis. Some people also refer to **biocatalysis** (or **enzyme catalysis**) as a separate catalyst class. This is plausible, because biocatalysis does indeed have a number of special features that make it worth considering separately. However, if we again only look at the aggregate states, we can distinguish the biocatalysts into soluble (metal-containing or metal-free) homogeneous catalysts and insoluble, heterogeneous catalysts fixed to carriers. In Figure 1.4, biocatalysis thus stands at the top between homogeneous and heterogeneous catalysis. Since biocatalysis and heterogeneous catalysis represent special fields of catalysis, they will not be discussed in detail in the present book.

The focus of this book is homogeneous catalysis with an emphasis on **transition metal complex catalysis**, which is based on organometallic species. It provides excellent opportunities for both gentle and selective reactions (Principles of Green Chemistry **PGC6** and **PGC1**). This catalysis is in turn divided into different variants and partly overlaps with other branches. Therefore, this book also introduces some interesting peripheral areas, which are briefly explained in the following:

- The homogeneous metal-free **acid/base catalysts** are a major focus of organic synthesis and are discussed in detail in organic chemistry. In the present book, they are therefore only discussed for comparison purposes or in the chapter on tandem catalysis (Chapter 34). Their counterparts in heterogeneous catalysis, solid acid and solid base catalysis, play a major role in the chemical industry.
- **Organocatalysis** is a metal-free variant of homogeneous catalysis that strongly resembles mechanisms of biocatalysis. It has gained importance in the synthesis of active pharmaceutical ingredients (APIs) so that it is briefly introduced in Chapter 39.
- In **enantioselective catalysis**, one enantiomer can be formed in favour of the other. This selectivity can be achieved using both, organocatalysts and transition metal catalysts. Since it is also of great importance for the synthesis of pharmaceuticals and other fine chemicals, it is discussed in a separate chapter (Chapter 9) and in numerous other places in the book.
- Transition metal complex catalysts can be heterogenised on solids or membranes and thus become **supported catalysts**, which are often easier to handle in the industry (Chapter 16).
- **Transition metal salts** are also important as catalysts. We will meet them in particular in the oxidation reactions (Chapter 30).

Table 1.1 Comparison of homogeneous and heterogeneous catalysis.

Criterion	Heterogeneous catalysis	Homogeneous catalysis
Catalyst stoichiometry	Often undefined	Common
Catalyst structure	Often undefined	Common
Catalyst variability	Little	Very variable
Catalyst reproducibility	Often difficult	Very high
Mechanism knowledge	Often very little	Available
Number of active centres	Only surface atoms	All metal atoms
Catalyst activity	Different	High
Catalyst selectivity	Usually poor	Usually high
Diffusion problems	Present	Barely present
Conditions	Often harsh	Usually mild
Catalyst lifetime	Different	Different
Deactivation through poisoning	Common	Rarely
Separation and recycling	Usually easy	Difficult, but solvable

- Transition metals can form larger units, referred to as **nanocatalysts** (Chapter 35). They stand between homogeneous and heterogeneous catalysis.
- By using electric current, chemical reactions can be carried out by **electrocatalysis** (Chapter 36). One example is the fuel cell in which nanocatalysts are deposited on supports.
- In **photocatalysis** (Chapter 37), catalysts can be switched by photons into excited states and can then undergo uncommon reactions.
- Electrocatalysis and photocatalysis can also be combined to **electrophotocatalysis**.

In fact, homogeneous catalysis offers a range of benefits compared to heterogeneous catalysis (Table 1.1).

Unfortunately, however, homogeneous transition metal catalysis has one inherent disadvantage that derives from its definition; that is, as all of the reactants, catalysts and products are in the same homogeneous phase during reaction, any subsequent separation of the catalyst for its reuse can be very difficult. Catalyst separation is, nonetheless, essential as the typically very expensive transition metal catalyst must be recycled uncompromisingly for economic reasons, and not discharged with the product.

Likewise, for ecological reasons, neither the transition metal compounds nor any associated organic compounds must be released into the environment (**PGC1**). For example, although nickel is an important catalyst metal, many people will suffer an allergic response if they encounter it. Because of these problems, several chapters of this book relate to separation concepts associated with homogeneous catalysis (Chapters 14–18).

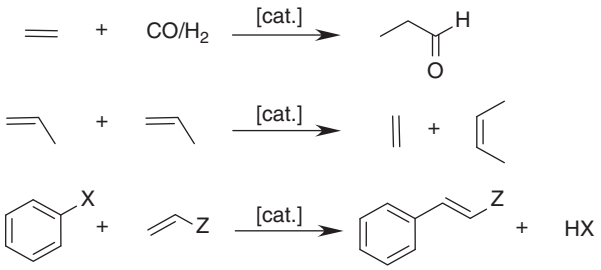
Homogeneous transition metal catalysts are usually well-defined compounds; typically, their chemical composition is well known, and their structure can be determined easily by using various spectroscopic methods (**PGC11**). Such catalysts can be synthesised according to definite, reproducible synthetic protocols.

A typical example of a homogeneous transition metal catalyst is **Wilkinson's catalyst** $[Rh(PPh_3)_3Cl]$, named after the Nobel prize laureate *Sir Geoffrey Wilkinson* (Chapter 6), from Imperial College, London. This catalyst can be easily and reproducibly prepared in high yields from rhodium trichloride hydrate and triphenylphosphine PPh_3 in ethanol. Furthermore, variations can easily be achieved in its electronic and steric properties, by using different phosphine ligands. Moreover, its functionality – for example, in the hydrogenation of olefinic double bonds – has been investigated thoroughly, mainly due to the good analytical tools available for homogeneous catalysts (Chapter 12).

A typical example of a *heterogeneous catalyst* is the '**ammonia catalyst**', which catalyses the conversion of hydrogen and nitrogen into ammonia. This catalyst was developed by the Nobel Prize laureate *Fritz Haber* (Chapter 2), at the Kaiser-Wilhelm-Institut in Berlin, and later applied to the industrial process by *Carl Bosch,* at BASF, who was also awarded the Nobel Prize. The ammonia catalyst consists mainly of iron in combination with various adjuvants and is very difficult to analyse during its application in the reactor. The structural conditions on the catalyst surface and in the pores during reaction are not exactly known. The production of heterogeneous catalysts is largely the domain of a few manufacturers that have an extensive, mostly empirically acquired, know-how of catalyst synthesis.

The optimal reaction conditions for the ammonia synthesis using this catalyst are quite harsh (350–520 °C, 30 MPa, **PGC6**). Moreover, the catalyst can be easily deactivated by catalyst 'poisons'such as carbon monoxide or sulphur compounds. The catalyst can be easily separated from the product; the solid catalyst remains in the reactor, while the gaseous ammonia is easily collected.

Homogeneous and heterogeneous catalysis have complementary positions in the chemical industry. For example, many major industrial products such as gasoline, sulphuric acid and nitric acid are produced via heterogeneous catalysis, whereas many basic



Hydroformylation of alkenes (1.3)

Alkene metathesis (1.4)

C–C coupling (Heck) (1.5)

Figure 1.5 Reactions, which are only possible with transition metal catalysis.

chemicals and fine chemicals, pharmaceuticals and agrochemicals are produced via homogeneous catalysis (Part III of this book). Transition metal catalysts enable reactions that, normally, cannot be carried out in any other way (Figure 1.5); examples include hydroformylations of alkenes (Eq. 1.3), alkene metathesis (Eq. 1.4) or C–C-coupling reactions like the "Heck-reaction" (Eq. 1.5). Each of these reactions is described in detail in the Chapters 21–34. In these descriptions, the abbreviation [cat.] is placed above the reaction's arrow to indicate that it must be catalysed; occasionally, other abbreviations such as [Pd] or [Rh] are also shown, to indicate palladium- or rhodium-catalysed reactions.

1.3 The Directing Effect of the Catalyst

Catalysts not only permit a reaction to proceed at all, but in most cases, they also direct the reaction selectively towards certain products. A typical example of this is the *various reaction possibilities of* **syngas** (a mixture of carbon monoxide and hydrogen), as shown in Figure 1.6:

- Aqueous iron/chromium or copper catalysts convert syngas and water to carbon dioxide and hydrogen.
- Iron- or cobalt-containing 'Fischer–Tropsch' catalysts lead to (depending on reaction conditions) alkanes, alkenes or long-chain alcohols.
- Copper/zinc catalysts lead almost exclusively to methanol.
- Ethylene glycol can be produced by using ruthenium catalysts.
- Nickel catalysts afford an entire methanisation to methane.

Hence, a wide product range of products is accessible from the same staring material, simply by selecting the most suitable catalyst. All these reactions are catalytic,

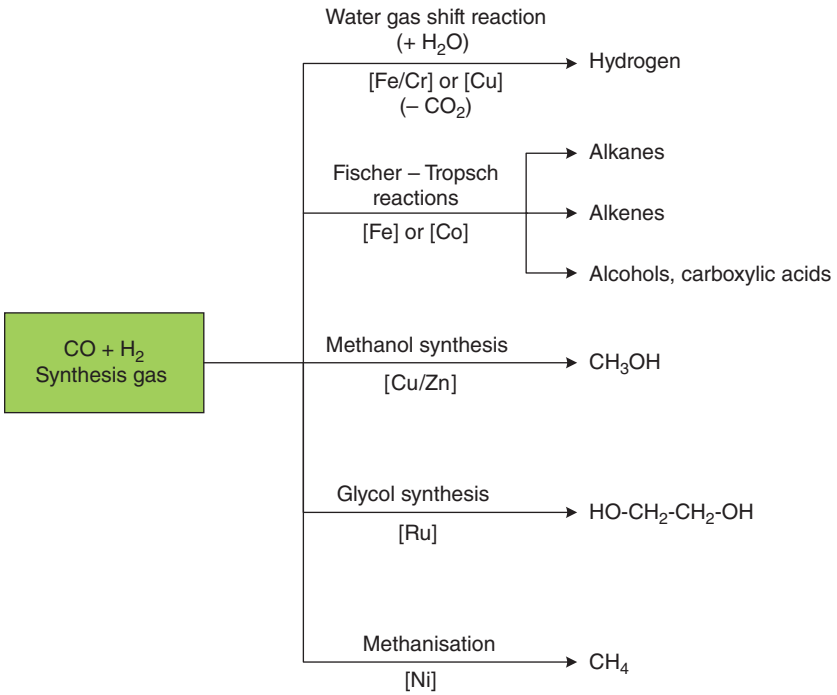


Figure 1.6 Selectivity controls of syngas reactions.

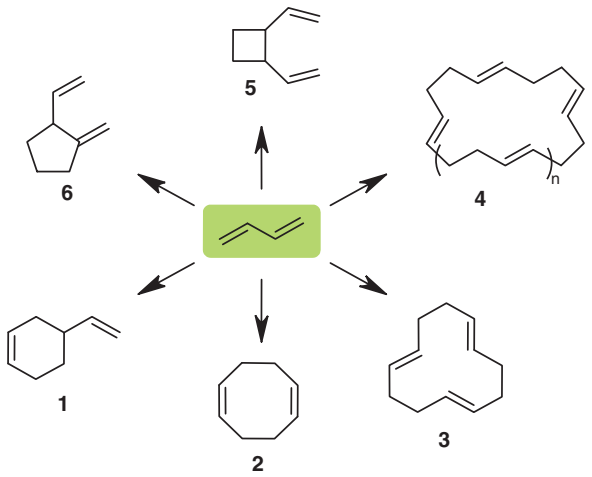


Figure 1.7 The cyclic oligomers of butadiene.

not stoichiometric (**PGC9**). No protecting groups are required (**PGC8**).

The examples in Figure 1.6 relate almost exclusively to heterogeneous catalysis (except for the example of glycol synthesis), which frequently employs different metals, or their combination. Homogeneous transition metal catalysts offer another possibility, namely the choice of different **complex ligands** (Chapter 7). This is illustrated in Figure 1.7 by the example of *butadiene cyclooligomerisation* (Chapter 24) whereby, using the same catalyst metal (that is, nickel) a diversity of butadiene oligomers can be produced, simply by altering the ligand sphere:

- Tricyclohexylphosphine (PCy_3) leads predominantly to 4-vinyl-1-cyclohexene (**1**).
- Triphenylphosphite ($P(OPh)_3$) produces the eight-membered ring 1,5-cyclooctadiene (**2**).
- A catalyst made from nickelbis(acrylonitrile) and triethylaluminium $AlEt_3$ yields the 12-membered ring (**3**).
- Nickel allyl complexes form the higher homologues (**4**).
- The palladium catalyst $Pd(ClO_4)_2$ can yield the four-membered ring (**5**).
- The five-membered ring (**6**) is formed when using (NiCl[*ortho*-tolyl][PEt_3]$_2$).

Again, several products can be derived from a single substrate, although the eight-and 12-membered rings are particularly important from an industrial aspect. The controlling possibilities of the ligands are discussed in detail in Chapters 7 and 9, while the monitoring of reactions is detailed in Chapter 4, which incorporates the 'target sizes' of catalytic reactions.

1.4 Sources of Information About Catalysis

When reading through this book, a **literature appendix** will be found at the end of each chapter, which cites a small selection of reasonable books, reviews and important reports. In the appendix of this chapter, details are provided of several well-known textbooks and reference books that will help to deepen the knowledge on homogeneous transition metal catalysis.

Today, the **search for the relevant literature** is, thanks to search engines and digital repositories, much more convenient than it was still at the beginning of the 21st century. For instance, alerts can be installed that keep you updated every time a new report is published that either deals with a certain topic (via keywords), comes from a relevant research group (via authors) or cites an original publication or a review that already was relevant. Such a service is offered, for instance, by SciFinder (from CAS), by Scopus (from Elsevier) or by Google Scholar. Novel programs for drawing chemical structures, for instance ChemDraw, have plugins to directly search for chemical substances and reactions in these online databases. Physical properties, analytical data and syntheses as well as reactions are thus accessible very conveniently. Publishers tend to publish literature only online and quit printing journals, the respective pdf of articles can be downloaded from their homepages. More and more research is published as open access, which makes it accessible also without institutional affiliation. Managing and storing of the articles' pdf files together with their bibliographic data for correct referencing in typesetting programs has also become very convenient using designated literature managing programs such as EndNote, Mendeley or Citavi. Plugins for web browsers and office programs are available, fetching all relevant data. Coworking with peers is also todays' standard using these programs. Additionally, you can follow individual researchers and their groups through scientific communities such as ResearchGate. The *Open Researcher Contributor Identification Initiative* (ORCID) was initiated in 2010 to resolve the author's name ambiguity problem in scholarly communications. Today, more than 13 million researchers use their unique identification number and others can thus follow their research.

In order to be kept up to date and to get new ideas, however, it is essential to monitor relevant '**catalysis journals**'. In the appendix, you will find a (surely not complete) list of catalysis journals recommended by the authors.

Today, as catalysis is used and explored so intensively by industry, much of the recently acquired information is not available in 'open access literature', but rather may be located (at least in part) in **patents**. Nonetheless, research details included in patents may be obtained from various patent databases that include:

- '*Espacenet*': This is a European network of patent databases, which can be accessed on the internet at www.espacenet.com. It includes more than 50 million patents from all around the world, which are frequently updated. A quick search can include keywords, inventors or companies; in an advanced search, the various search terms can be linked together. For first-time visitors 'An introduction to the database of ideas' is provided on the portal site.
- '*Depatisnet*': This is the database of the German Patent and Trade Mark Office (DPMA). It can be found at http://depatisnet.dpma.de. It is possible to choose between a 'Beginner's search' and an 'Expert search' or to search for patent families. When using the 'Assisted search', it is possible to forward requests to the German patent information system.
- The patent database of the US is administered by the 'United States Patent and Trademark Office' and is linked to http://patft.uspto.gov.
- Other important web addresses for patent databases include:
  - http://www.wipo.int/pctdb/en/index.jsp
  - http://pericles.ipaustralia.gov.au/ols/auspat
  - http://www.getthepatent.com
  - http://www.google.com/patents
  - http://www.freepatentsonline.com/search.html
  - http://www.ipo.gov.uk/types/patent.htm
  - http://www.irossco.com/patentsearching.htm

Take-Home Messages

- **Catalysts** increase the rate at which a chemical system reaches its equilibrium.
- In theory, catalysts are **not consumed** during catalytic reactions; in reality, they can be either destroyed or poisoned.
- The mechanisms of catalytic processes are usually presented as **catalytic cycles**.
- Catalysts can be divided into **homogeneous** and **heterogeneous** catalysts. Homogeneous catalysts can be dissolved in the reactants or solved via an additional solvent; heterogeneous catalysts form a second, usually solid, phase.
- Homogeneous catalysis can be further subdivided into: enzyme or biocatalysis; acid/base catalysis; organocatalysis and **transition metal catalysis**.
- Transition metal catalysis proceeds mainly via **organometallic intermediates**; in some cases also, transition metal salts are the active species.
- **Special variants** of homogeneous catalysis are nanocatalysis, electrocatalysis and photocatalysis. They represent the switch from homogeneous to heterogeneous catalysis.
- **Homogeneous transition metal catalysts** are characterised by high activities and high selectivities. Transition metal catalysts can be adapted to the synthetic demands by changing their **ligand field.**
- Homogeneous transition metal catalysts have **advantages** over the heterogeneous catalysts, because of their well-known molecular structure and their reproducible synthesis. As homogeneous catalysts are completely soluble, all metal atoms can be catalytically active. There are no diffusion problems involved in homogeneous catalysis.
- At first glance, the demanding **separability** appears to be a disadvantage of homogeneous catalysis. However, numerous possible approaches are available to resolve this problem.
- Homogeneous transition metal catalysis requires only mild conditions, and often allows the selective synthesis of a desired product in a few reaction steps, without creating by-products. Hence, homogeneous transition metal catalysis *is a cornerstone of* **Green Chemistry**.

Exercise Questions

1.1 Which catalyst did *Döbereiner* use in his gas lighter?

1.2 Draw a general catalytic cycle of the hydrogen–oxygen-reaction!

1.3 List five advantages of homogeneous catalysis in comparison to heterogeneous catalysis.

1.4 What is the main problem associated with homogeneous transition metal catalysis?

1.5 How can *Wilkinson*'s complex be synthesised?
1.6 Which products can be obtained catalytically from syngas?
1.7 Draw at least three cyclic butadiene oligomers. Note the correct position of the double bonds. What is their technical importance?
1.8 How can a homogeneous transition metal catalyst be varied relatively easily?
1.9 Why are there no diffusion problems in homogeneous catalysis?
1.10 Which principles of Green Chemistry are met by homogeneous transition metal catalysis?

… and as a reward for having answered all questions, a football quote:

'*I took a whack on my left ankle, but something told me it was my right*'.

Lee Hendrie

Literature

T. J. Colacot, C. Johansson Seechurn, *Organometallic Chemistry in Industry – A Practical Approach*, Wiley-VCH, 2020.

P. C. J. Kamer, D. Vogt, J. W. Thybaut, *Contemporary Catalysis – Science, Technology, and Applications*, Royal Society of Chemistry, 2017.

Further literature references can be found on the following website www.wiley.com/go/behr/AHC2!