Part I
Chemical Basics

Applied Homogeneous Catalysis, First Edition. Arno Behr and Peter Neubert.

1
Definition, Options, and Examples

What Actually Is 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:

$$A + B \leftrightarrows C + D \tag{1.1}$$

A typical example is the formation of an ester from a carboxylic acid and an alcohol, which involves the elimination of water, while the reverse reaction involves the hydrolysis of an ester to a carboxylic acid and an alcohol:

$$R-COOH + R'-OH \leftrightarrows R-COOR' + H_2O \tag{1.2}$$

The steady state of this reaction – depending on pressure and temperature – is controlled by Nature and determined by the thermodynamics (cf. Chapter 10). The rate at which equilibrium is achieved is described by kinetics (cf. Chapter 11). As is well known from organic chemistry, the reaction requires a small amount of sulfuric acid to get it started. Then, if the water produced is removed constantly from the reaction vessel, the ester can be obtained in quantitative amounts. In this case, the sulfuric acid serves as a "catalyst."

Another example 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"*:

$$H_2 + 0.5\,O_2 \leftrightarrows H_2O \tag{1.3}$$

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

The adjuvant effect of the platinum sponge was first discovered by *Johann Wolfgang Döbereiner* (Figure 1.1) who, on the 27th of July 1823, used a platinum sponge to construct a gas lighter (Figure 1.2). In the lighter, the crank, **e**, is used to dip a piece of zinc into a tank, **c**, which contains sulfuric acid; this leads to the formation of hydrogen (Eq. (1.4)):

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Figure 1.1 Johann Wolfgang Döbereiner.

$$Zn + 2H^{+} \rightarrow Zn^{2+} + H_2 \qquad (1.4)$$

The hydrogen is first collected in an upright pipe and then released from the pipe's upper end through a simultaneously opened valve. The hydrogen is mixed with oxygen from the ambient air and ignited by a piece of platinum sponge, **f**, attached immediately above the valve. The first automatic gas lighter had been invented! Döbereiner gave one of these lighters to his namesake, Goethe, who initially had problems using it. In 1828, Goethe wrote to Döbereiner:

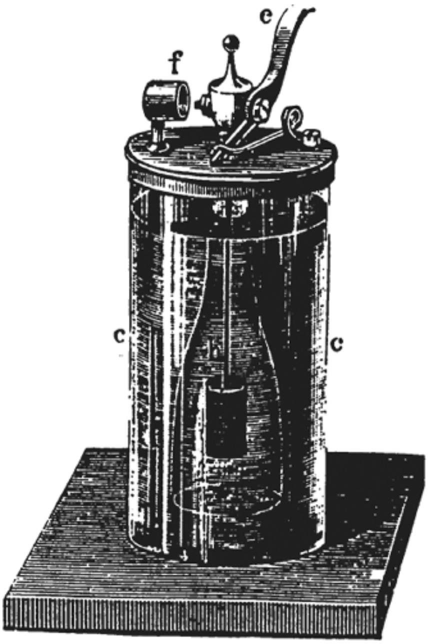

Figure 1.2 Döbereiner's gas lighter.

> *"Ew. Hochwohlgeboren haben die Gefälligkeit gehabt, einen dem Anblick und Zweck nach sehr anmutigen Apparat zuzusenden, aber ich will nur gestehen, daß ohngeachtet der genauen beigefügten Beschreibung ich doch das Experiment nicht zu unternehmen getraue."*

(Approximate English translation: Your honor has been so kind to send me the very charming apparatus; however, I have to admit that I don't feel able to carry out the experiment.)

However, some time later Goethe is said to have used the lighter on a regular basis.

The first definition of a catalyst was provided in 1836 by the Swedish chemist Jöns Jakob Berzelius (Figure 1.3) 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 waken the "dozing" gases hydrogen and oxygen.

Figure 1.3 Jöns Jakob Berzelius.

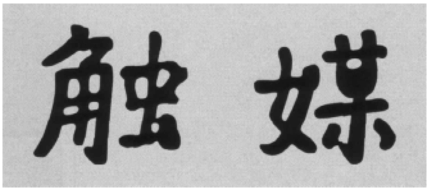

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Figure 1.4 The Chinese character for catalysis and matchmaker (“tschu mei”).

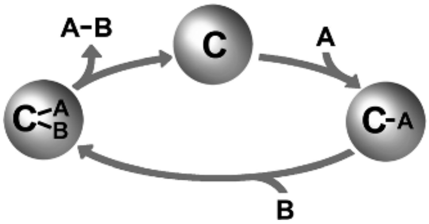


Figure 1.5 A general catalysis cycle.

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 “tschu mei” (Figure 1.4) means both catalysis and “marriage broker,” with the emphasis being placed much more on the linking properties.

When considering *today’s definition of a catalyst:*

- 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 itself consumed.

Although, in theory, a catalyst should be active “for ever,” there is of course no ideal “philosopher’s stone.” Whilst each catalyst has a certain lifetime, during which it will catalyze 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).

One factor that all catalysts have in common is that, immediately after they have successfully catalyzed a first reaction, they are available to catalyze another reaction.

Moreover, this action can be repeated many thousands or even millions of times. The most commonly used method used to represent this behavior graphically is a circle; this is often referred to as “*catalytic cycle.*” A generalized type of cycle incorporating the addition reaction $A + B \rightarrow A - B$, catalyzed by C, is shown in Figure 1.5.

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 “marriage broker”), such that a new product, A–B, is formed. The catalyst remains in the condition it was in at the start of the cycle and, therefore, is available for another cycle.

1.2
The Different Varieties of Catalysis

The reaction in Eq. (1.2) contains liquid reactants – carboxylic acid and alcohol – which are reacted to produce a liquid ester in the presence of liquid sulfuric acid. All of the components are completely soluble and, as there is only one homogeneous liquid phase in the vessel, this is referred to as *homogeneous catalysis.*

In contrast, in Eq. (1.3) two gases react in the presence of a solid catalyst, the platinum sponge. In this type of catalysis there are at least two phases, and sometimes even three (gaseous, liquid, and solid). Based on such heterogeneity, this variant is referred to as *heterogeneous catalysis.*

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 centers	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

There are, however, different subtypes of the two variants, depending on the type of catalyst being used.

Homogeneous catalysts These can be:

- soluble acids or bases ⇒ homogeneous acid/base catalysis
- organic compounds ⇒ homogeneous organocatalysis
- soluble enzymes ⇒ homogeneous enzyme or biocatalysis
- soluble transition metal salts or soluble transition metal complexes ⇒ *homogeneous transition metal catalysis.*

Heterogeneous catalysts These can be:

- insoluble acids or bases ⇒ heterogeneous acid/base catalysis
- solid immobilized enzymes ⇒ heterogeneous enzyme catalysis
- solid metals or metal oxides ⇒ heterogeneous metal catalysis.

The main subject of this book is *homogeneous transition metal catalysis*, which provides excellent opportunities for both gentle and selective reactions. In fact, such catalysis offers a range of benefits compared to heterogeneous catalysis (see 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. For example, although nickel is an important catalyst metal, many people will suffer an allergic response if they come into contact with it. Because of these problems, several chapters of this book relate to separation concepts associated with homogeneous catalysis (see Chapters 14 to 18).

Homogeneous transition metal catalysts are usually well-defined compounds; typically, their chemical composition is well known and their structure can be determined easily

Figure 1.6 Geoffrey Wilkinson.

by using various spectroscopic methods. Such catalysts can be synthesized according to definite, reproducible synthetic protocols. A typical example of a homogeneous transition metal catalyst is *Wilkinson's catalyst* [Rh(PPh$_3$)$_3$Cl], named after the Nobel prize laureate *Sir Geoffrey Wilkinson* (Figure 1.6), 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, due mainly to the good analytical options available during homogeneous catalysis (see Chapter 12).

Figure 1.7 Fritz Haber.

Figure 1.8 Carl Bosch.

A typical example of a *heterogeneous catalyst* is the "*ammonia catalyst*," which catalyzes the conversion of hydrogen and nitrogen into ammonia. This was developed by the Nobel prize laureate *Fritz Haber* (Figure 1.7), at the Kaiser-Wilhelm-Institut in Berlin, and later applied to the industrial process by *Carl Bosch*, at BASF (Figure 1.8), who was also awarded the Nobel prize. The ammonia catalyst consists mainly of iron in combination with various adjuvants, and is very difficult to analyze 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 catalyst are quite harsh (350–520 °C, 300 bar), and it can be easily deactivated by catalyst "poisons" such as carbon monoxide or sulfur compounds. The main advantage of the process, however, is the good separability of the product and catalyst; 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, sulfuric acid and nitric acid are produced via heterogeneous catalysis, whereas many basic chemicals and fine chemicals, phar-

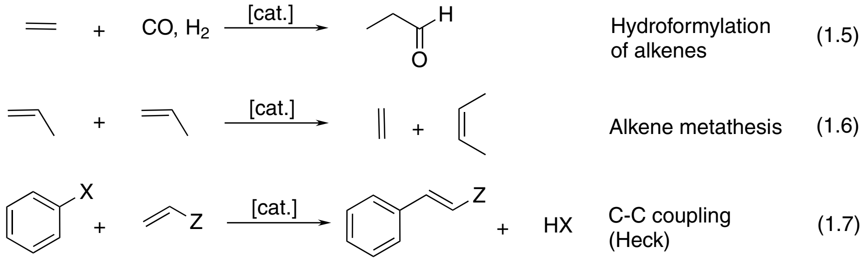


Figure 1.9 Reactions, which are only possible with transition metal catalysis.

maceuticals and agrochemicals are produced via homogeneous catalysis. Transition metal catalysts enable reactions that, normally, cannot be carried out in any other way; examples include hydroformylations (Eq. (1.5)), metathesis (Eq. (1.6)), or C—C-coupling reactions (Eq. (1.7)) (Figure 1.9). Each of these reactions is described in detail in Section 1.3 (see also Chapters 19–31). In these descriptions, the abbreviation [cat] is placed above the reaction's arrow to indicate that it must be catalyzed; occasionally, other abbreviations such as [Pd] or [Rh] are also shown, to indicate palladium- or rhodium-catalyzed reactions.

1.3
The Directing Effect of the Catalyst

The catalyst not only has the property to permit a reaction to proceed at all, but in most cases it also has the ability to direct the reaction towards certain products. A typical example of this is the "*various reaction possibilities of synthesis gas*" (a mixture of carbon monoxide and hydrogen), as shown in Figure 1.10:

- Aqueous iron/chromium or copper catalysts convert synthesis gas 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 methanization to methane.

Hence, the chemical industry is in the position to prepare a wide product range from the same material basis, simply by selecting the most suitable catalyst.

The examples in Figure 1.10 relate almost exclusively to heterogeneous catalysis (except for the example of glycol synthesis), which frequently employs different metals, or their combination. The homogeneous transition metal catalysis offers still another variation possibility, namely the choice of different complex ligands. This is illustrated in Figure 1.11 by the example of *butadiene cyclooligomerization* (cf. Chapter 22) whereby, using the same catalyst metal (i.e., 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 molecule 1,5-cyclooctadiene (**2**).

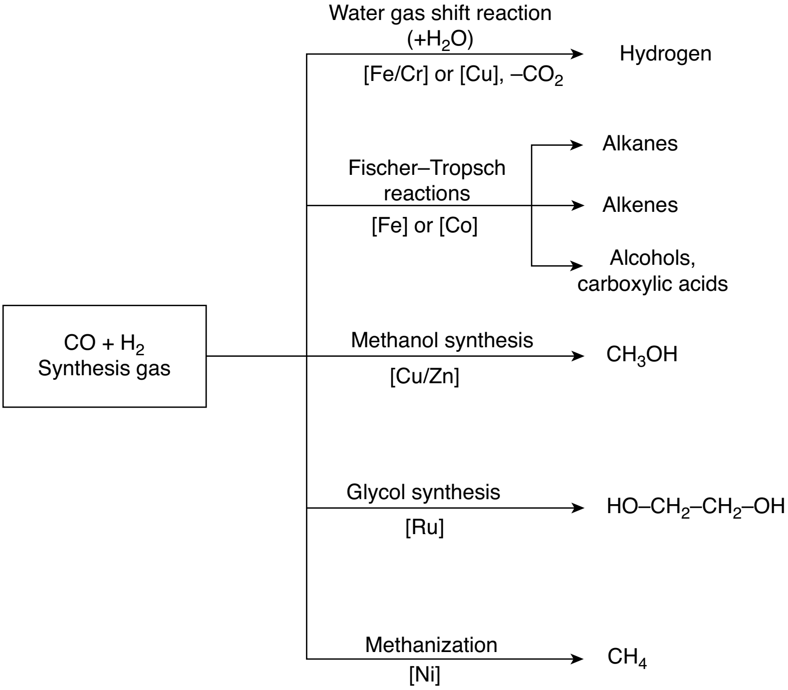


Figure 1.10 Catalytic control of synthesis gas reactions.

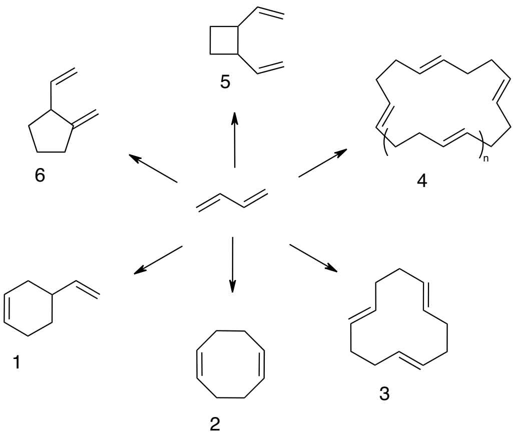


Figure 1.11 The cyclic oligomers of butadiene.

- With nickel bis(acrylonitrile) and aluminum triethyl $AlEt_3$ the 12-membered ring (**3**) is formed.
- 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 $[NiCl(\textit{ortho}\text{-tolyl})(PEt_3)_2]$.

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
Catalysis as a Part of "Green Chemistry"

As catalysis provides the ability to produce a desired product without unquestioned byproducts, it can be seen as a cornerstone of "*green chemistry*," the important principles of which include:

- The prevention of waste.
- The products shall contain the maximal proportion of reactants; that is, the reaction is to be "atom-economic."
- The reactions must function with increased energy efficiencies.
- The usage of renewable feedstocks is possible.
- Any derivatization reactions, such as the need for blocking or protecting groups, should be avoided.
- Catalytic agents are superior to stoichiometric agents.

Homogeneous transition metal catalysis, in particular, meets such demands, for example, it allows the direct C—C-bonding of different building blocks without any needless intermediate steps (see Chapter 19). Such catalysis usually functions under mild reaction conditions, such as low temperatures (room temperature to 150 °C) and low pressures. It is also suitable for the conversion of renewables (as will be described in Chapter 38).

An example from the chemical industry can be used to demonstrate the above-stated principles. After a heavy night's drinking, pills containing ibuprofen can help in the recovery from a hangover. Ibuprofen is conventionally synthesized from isobutylbenzene in a six-step synthesis (Figure 1.12, left); three of the six steps involve Brønsted or Lewis acids, while the two other steps require bases. This leads inevitably to the production of large quantities of salts, the disposal of which may create an unnecessary burden on the environment. In contrast, a novel catalytic pathway of ibuprofen synthesis – as elaborated by Hoechst–Celanese (Figure 1.12, right) – contains only three reaction steps, without the formation of considerable quantities of salt:

- The first step – the acylation of isobutylbenzene in the *para* position – is still catalyzed by homogeneous acid catalysis.
- In the second step, the keto group is hydrogenated to an alcohol by heterogeneous catalysis. The catalyst used is recyclable palladium on carbon [Pd/C].
- The third step includes carbonylation of the hydroxyl group, leading to the carboxylic acid by means of carbon monoxide. The catalyst is a homogeneous palladium complex.

So, ibuprofen has been synthesized after only three steps, and all of the reactants used – except, of course, the catalysts! – are present in the final product.

1.5
Sources of Information about Catalysis

When working through this book, a *literature annex* 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, the details are provided of several well-known textbooks and reference books, that will help to deepen the knowledge of homogeneous transition metal catalysis.

In order to be kept up to date, however, it is essential to monitor relevant "*catalysis journals*," the following of which are recommended by the authors.

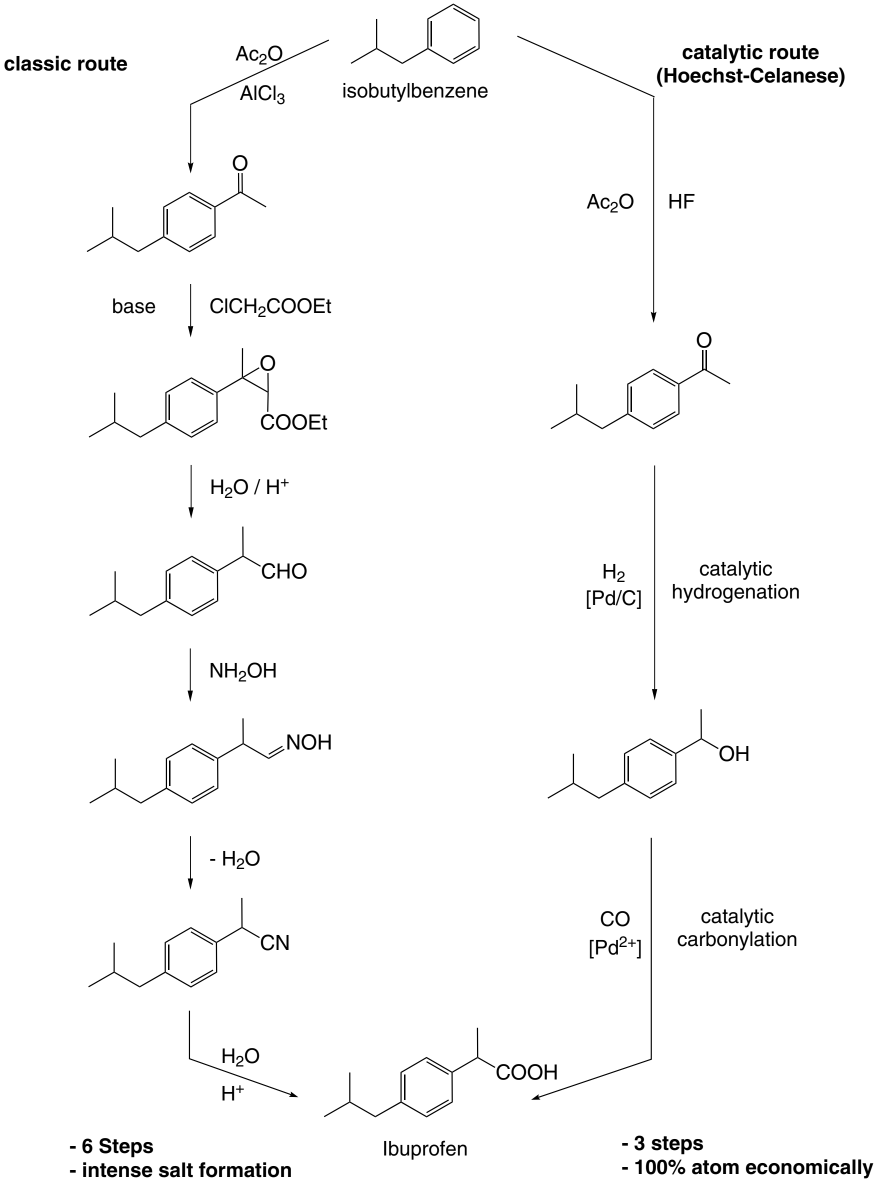


Figure 1.12 Comparison of synthesis methods of ibuprofen.

Homogeneous transition metal catalysis:

- *Journal of Molecular Catalysis A: Chemical*
- *Advanced Synthesis and Catalysis*

Organometallic chemistry and homogeneous transition metal catalysis:

- *Journal of Organometallic Chemistry*
- *Applied Organometallic Chemistry*
- *Organometallics*

- *Transition Metal Chemistry*
- *Advances in Organometallic Chemistry*
- *Topics in Organometallic Chemistry*
- *Coordination Chemistry Reviews*

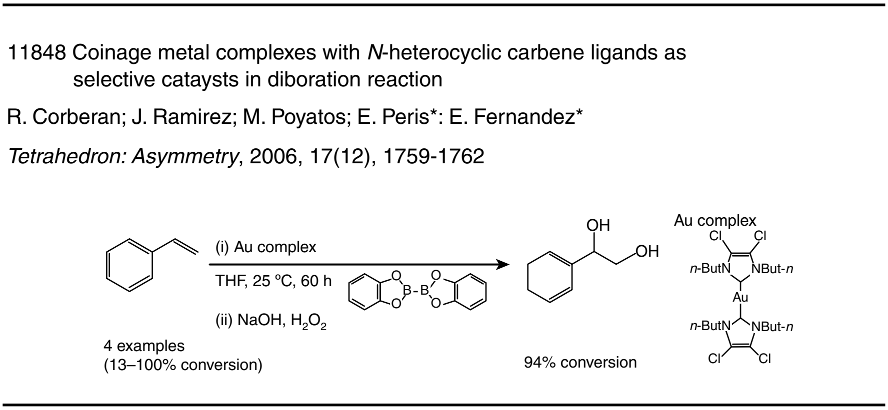
Catalysis (general, but especially heterogeneous):

- *ACS Catalysis*
- *Catalysis Science & Technolog Today*
- *Advances in Catalysis*
- *Applied Catalysis A: General*
- *Catalysis Letters*
- *Catalysis Reviews: Science and Engineering*
- *ChemCatChem*
- *Catalysis Communications*

Journals which often also report on catalysis:

- *Angewandte Chemie*
- *Chemistry – A European Journal*
- *Journal of the American Chemical Society*
- *Chemical Communications*
- *Green Chemistry*
- *Chemical Reviews*
- *Synthesis*
- *Organic Letters*
- *Tetrahedron*
- *Tetrahedron Letters*
- *Platinum Metals Reviews* (online: www.platinummetalsreview.com)
- *Accounts of Chemical Research*
- *Journal of Organic Chemistry*
- *Chemie-Ingenieur-Technik*
- *Science*
- *ChemSusChem*
- *Dalton Transactions*
- *Chimia*

To ensure that no important findings are be missed, it is useful to subscribe to "*Catalysts and Catalyzed Reactions,*" which is published by the Royal Society of Chemistry (see: www.rsc.org/catalysts). This abstract journal is published 12 times each year in both print and electronic format, and contains (very short!) summaries of recent key publications on catalysis. A general example is given in Figure 1.13, which contains only the title, authors and source, besides a typical reaction, the catalyst, and important reaction conditions and results. If an article is interesting, of course, the original report must also be considered. The abstracts are indexed by type of reaction, comparable to Part III of this book. So, if the details of only certain reactions are being sought, it is possible to examine the relevant subsections in selective fashion.



11848 Coinage metal complexes with *N*-heterocyclic carbene ligands as selective cataysts in diboration reaction

R. Corberan; J. Ramirez; M. Poyatos; E. Peris*: E. Fernandez*

Tetrahedron: Asymmetry, 2006, 17(12), 1759-1762

Figure 1.13 Constitution of a graphical abstract in "*Catalysts and Catalyzed Reactions.*"

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 USA is administered by the "United States Patent and Trademark Office," and is linked under 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.
- Catalytic processes are usually presented in *catalytic cycles*.
- Catalysts can be divided into homogeneous and heterogeneous catalysts. Homogeneous catalysts can be dissolved in the reaction solvent; heterogeneous catalysts form a second, usually solid, phase.
- Homogeneous catalysis can be further subdivided into: acid/base catalysis; enzyme or biocatalysis; and transition metal catalysis.
- *Homogeneous transition metal catalysts* are characterized 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 byproducts. Hence, *it is a cornerstone of "green chemistry."*

Exercise Questions

1.1 Which catalyst did Döbereiner use in his gas lighter?
1.2 Draw a general catalyst cycle of the Knallgas 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 synthesized?
1.6 Which products can be obtained catalytically from synthesis gas?
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?

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