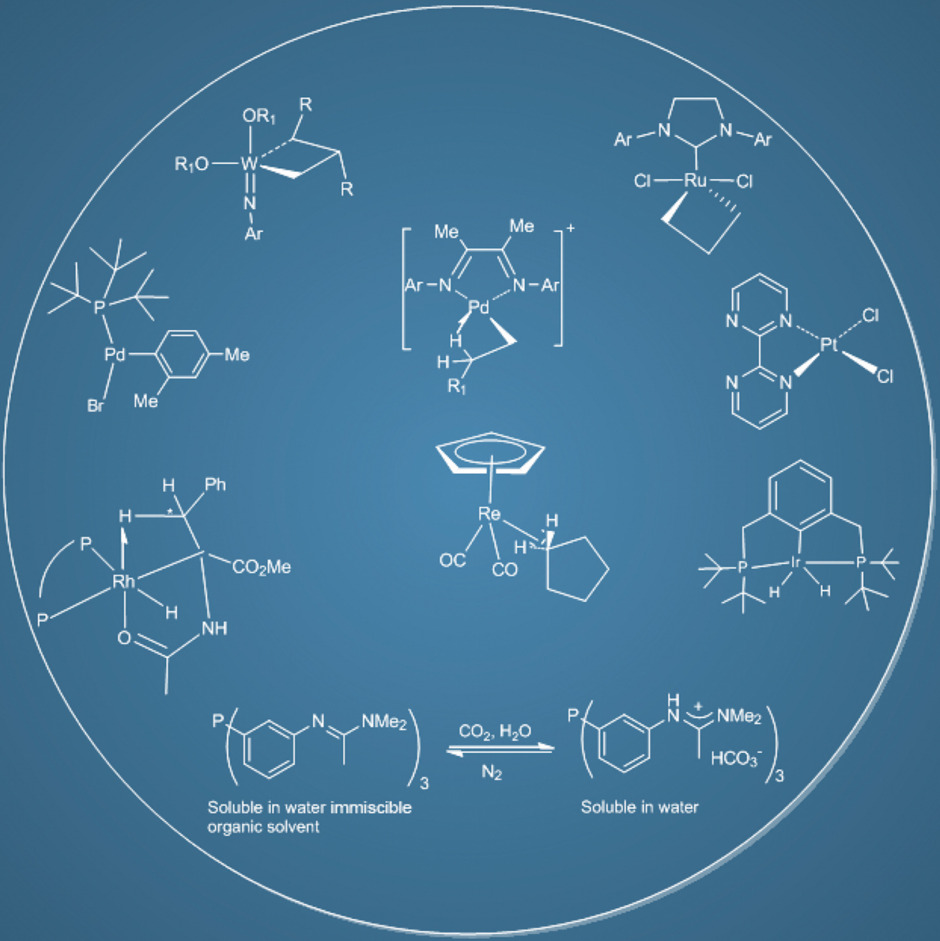
Homogeneous Catalysis

Mechanisms and Industrial Applications

Sumit Bhaduri • Doble Mukesh

SECOND EDITION



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Preface

In the preface to the first edition of this book published in 2000, we said "Industrial applications of homogeneous catalysis are proven, and a much wider application in the future is anticipated." Growth in the area of homogeneous catalysis with transition metal over the last 12 years has been phenomenal, and the innumerable number of patent applications and successful commercialization of selected processes in sectors as diverse as bulk chemicals, specialty polymers, and pharmaceutical intermediates have validated our anticipation.

This new edition has been comprehensibly revised and reorganized, with new drawings and new information. The problems given at the end of each chapter and bibliography are also new and, unlike the earlier edition, a few selected representative patents are included in the bibliography. Because of the spectacular advances in the application of spectroscopy and computational methods in mechanistic studies, a new chapter solely devoted to such studies has been added in the revised edition. A deliberate attempt has been made to keep the book at a manageable size. To achieve this, and based on student feedback, some of the outdated information of the earlier edition has been removed.

The philosophy behind the revised edition however, remains unchanged. The revision has been carried out from a pedagogical point of view to highlight the synergy that exists between path breaking academic research and significant industrial applications of organometallic chemistry. After all, three Nobel Prizes in the first decade of this century in chemistry were awarded for academic research in this area. Finally, many people have helped in various ways in the preparation of the revised edition. Sumit Bhaduri gratefully acknowledges invitations from Northwestern University over the last several years for teaching a course on homogeneous catalysis that made the revision a practical proposition.

CHAPTER 1

Chemical Industry and Homogeneous Catalysis

Homogeneous Catalysis: Mechanisms and Industrial Applications, Second Edition.
Sumit Bhaduri and Doble Mukesh.

The chemical industry manufactures a very large number of products for different uses. In industrial parlance, the products are often classified under different categories such as polymers and resins, fine chemicals, flavors and fragrances, and pharmaceutical intermediates. Some of these such as plastics are produced in millions of tons, while some others less than a few tons per year. As we will see, homogeneous catalysis plays an important role at both these extremes.

It is estimated that the chemical industry contributes about 10% to the world's total trade and about 5% to the total income. It employs about 10 million employees and generates a combined turnover of more than 3 trillion dollars including from pharmaceuticals. The manufacturing processes of many of the products mentioned are critically dependent on the use of catalysts. In recent years, catalytic research has gained additional momentum for two main reasons.

First, many existing chemical products and processes have been found to have adverse effects on the environment and this has spurred search for alternatives that are more environment friendly. In this approach, catalysis plays a pivotal role. Second, catalysts help to save energy and to avoid the formation of unwanted products. Thus the use of catalysts for new chemical processes makes them commercially attractive.

1.1 FEEDSTOCKS, FUELS, AND CATALYSTS

The manufacture of all organic chemicals and carbon-based polymers requires a carbon-containing precursor, i.e., a feedstock. The main feedstocks of the chemical industry are *crude* **oil**, other oils that are difficult to process, coal, and natural gas. These feedstocks are also used to meet much of today's worldwide energy requirements. To emphasize their geological origin and finite availability, crude oil, coal, etc., are referred to as *fossil* **fuels**.

Crude oil is currently the main feedstock used by the oil industry to manufacture processed petroleum products such as petrol, diesel, kerosene, and aviation fuel. Of the total amount of available crude oil, only about 10% is used for the manufacture of chemicals and the rest are used as fuels. Basically, crude oil is a complex physical mixture of many hydrocarbons where the number of carbon atoms per molecule could be as high as 60 or more.

The phenomenological definition of a **catalyst** is a substance that accelerates a chemical reaction but in the process does not undergo any chemical change itself. Catalysis plays a critical role not just in the oil and chemical industries but also in the manufacture of many inorganic chemicals, pollution abatement, and fuel cells. At a rough estimate, more than 75% of all existing industrial chemical transformations and 90% of newly developed processes involve the use of catalysts.

In most of these applications, the catalysts are insoluble solids and are called **heterogeneous** catalysts. In this book we deal almost exclusively with **homogeneous** catalytic processes. These are processes in which soluble catalysts are used and the catalytic reactions take place in the liquid phase. However, both heterogeneous and homogeneous catalysts operate by reducing the energy required to bring about the reorganization and changes of *molecular structures* of the reactants.

At a molecular level, most homogeneous catalysts are well characterized in terms of their chemical composition and structure. As all the molecules of a given homogeneous catalyst have the same structure, they facilitate breaking, forming, and reorganization of chemical bonds of the reactants in an identical manner. In contrast, in heterogeneous catalytic processes the molecules of the gaseous or liquid reactants are adsorbed on the *surfaces of the solid* catalysts. Unlike homogeneous catalysts, solid surfaces consist of an infinite array of ions or atoms with different types of local structures, i.e., potential reaction **sites**. To emphasize the homogeneity at a molecular level, some homogeneous catalysts are also called **single site** catalysts.

1.2 CRUDE OIL TO GASOLINE AND BASIC BUILDING BLOCKS BY HETEROGENEOUS CATALYSTS

To put the importance of homogeneous catalysis in perspective, we first present a very brief summary of the basic processes of the petrochemical industry. Most of these processes are catalytic, and the goal is to convert crude oil to gasoline, other fuels, and basic building blocks for downstream chemicals.

Crude oil is composed of many hydrocarbons that differ in the number of carbon atoms per molecule. As the number of carbon atoms increases, the boiling point (BP) also increases. The BP and the number of carbon atoms per molecule in crude oil typically range from <30°C to >610°C and 1 to >60, respectively. By subjecting crude oil to fractional distillation, the major components such as crude gasoline (~5–12), naphtha (~8–12), kerosene (~11–13), and diesel (~13–17) are separated. The approximate number of carbon atoms of the hydrocarbons present in these components is given in the parentheses.

As shown in Figure 1.1, in the oil and petrochemical industry, the catalytic conversion of crude oil to hydrogen, usable grades of fuel, and small organic molecules is very important. Hydrogen is produced by a reaction called *steam reformation* (see Section 1.6.4) and the mixture of CO and H_2 is called **synthesis gas**. Small molecules such as ethylene, propylene, and benzene are produced by subjecting naphtha to catalytic **cracking**.

The small organic molecules, aromatics, and the mixture of CO and hydrogen, or synthesis gas, are the **base chemicals** or basic building blocks for most chemicals. The production of high octane gasoline and/or diesel with low sulfur involves distillation followed by two *heterogeneous* catalytic reactions: **hydrodesulfurization (HDS)** and **reformation**. Because of their enormous importance in the chemical industry, brief descriptions of cracking and HDS reactions are given.

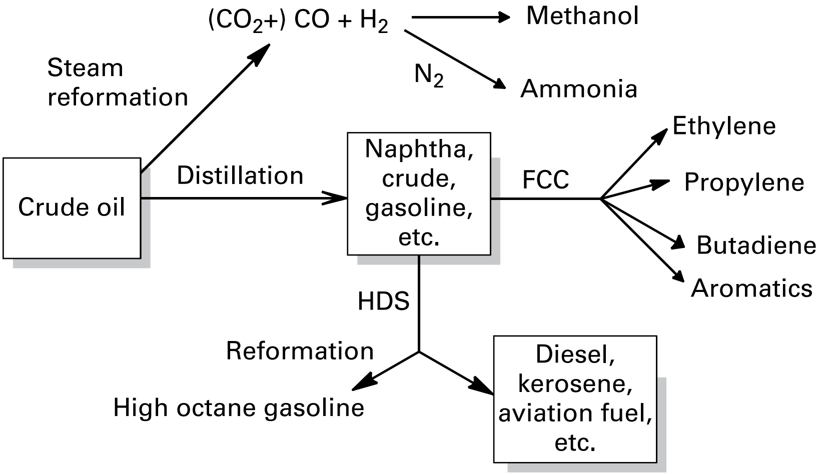


Figure 1.1 Conversion of crude oil to gasoline, other fuels, and basic building blocks for most chemicals.

1.2.1 Cracking Reactions

As the name suggests, in cracking, high molecular weight organic molecules are broken down into molecules of low molecular weights. Cracking could be induced thermally, but when catalysts are used the amount of gasoline produced increases significantly.

Fluid catalytic cracking or **FCC** is a widely used technology where the reactor is a vertical or upward sloped pipe. In the reactor, finely powdered heterogeneous catalyst particles are brought into contact with crude oil for a short time and at a high temperature (>650°C). This is achieved by spraying the crude oil upward through the catalyst bed. On contact with the hot catalyst particles, the oil vaporizes and the cracking reactions start.

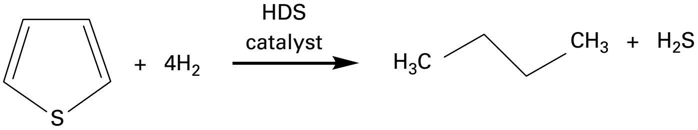
For cracking reactions, combinations of zeolites, alumina, clay, and silica are used as the catalyst. These acidic materials, which contain both BrØnstead and Lewis acidic sites, initiate a complex set of *carbonium*- and *carbenium* ion–based reactions. Note that carbonium ions are protonated alkyl groups (e.g., $C_2H_6^+$), while carbenium ions refer to alkyl cations (e.g., $C_2H_5^+$). To enhance the acidic properties, rare earth ions such as La^{3+} and Ce^{3+} are often incorporated in the zeolites by ion exchange. FCC catalysts must have high acidity, and their bulk density, particle size distribution, porosity, structural strength, etc., must meet stringent specifications.

During the cracking reaction, coke, which is basically a complex mixture of hydrocarbons with very high carbon content, is deposited on the catalyst particles. This reduces the activity and selectivity of the catalyst very significantly. The catalyst is regenerated by burning the deposited coke with oxygen or air. As cracking is an endothermic reaction, the energy obtained by burning coke is used to supply the heat for the cracking reaction. A variant of catalytic cracking is hydrocracking where hydrogen is mixed with crude oil.

1.2.2 Hydrodesulfurization Reactions

In crude oil, along with the hydrocarbons, small amounts of sulfur- and nitrogen-containing organic compounds are also present. Typically, the nitrogen and sulfur contents in terms of elemental composition range from ~0.2–3% to 0.5–6%, respectively.

Hydrodesulfurization belongs to the general catalytic process called **hydrotreatment** where heteroatoms are removed from the hydrocarbons of crude oil by reaction with hydrogen. Removal of sulfur from crude oil and its cracked products is extremely important for two reasons. First, on burning all sulfur-containing fuels produce sulfur dioxide, which is highly detrimental to the environment. Second, sulfur-containing compounds even in very low concentrations poison Pt- and Re-containing reformation catalysts. Hydrodesulfurization is a catalytic process where sulfur removal takes place. Sulfur is removed as H_2S, which is then converted to elemental sulfur. An example of one of the many reactions that take place during HDS is given by reaction 1.2.2.1.



(1.2.2.1)

The most common HDS catalyst consists of 2- to 3-nm-wide, single-layered MoS_2 *nanoparticles*, promoted with cobalt or nickel and supported on alumina. Only the edges of the S–Mo–S layers are known to be active. Sophisticated surface science studies have shown that even in such a well-defined nanostructure, two different types of active sites are present. In the reformation step, the Pt–Re–alumina–based catalyst catalyzes dehydrogenation and isomerization reactions. High octane gasoline must be rich in aromatics and branched chain paraffins, and this is achieved by subjecting crude gasoline to these reactions.

1.3 BASIC BUILDING BLOCKS TO DOWNSTREAM PRODUCTS BY HOMOGENEOUS CATALYSIS

Although the fundamental processes for refining petroleum and its conversion to base chemicals are based on heterogeneous catalysts, many important value-added consumer products are manufactured by homogeneous catalytic processes. Some of these reactions are shown in Figure 1.2.

The filled arrows in Figure 1.2 are processes either based on homogeneous catalysts or having great relevance in homogeneous catalysis. Conversion of synthesis gas into methanol is achieved by a heterogeneous catalyst, while the manufacture of acetic acid is based on the homogeneous catalytic carbonylation of methanol. Similar carbonylation of methyl acetate, the ester of methanol and acetic acid, yields acetic anhydride. These reactions are discussed in Chapter 4.

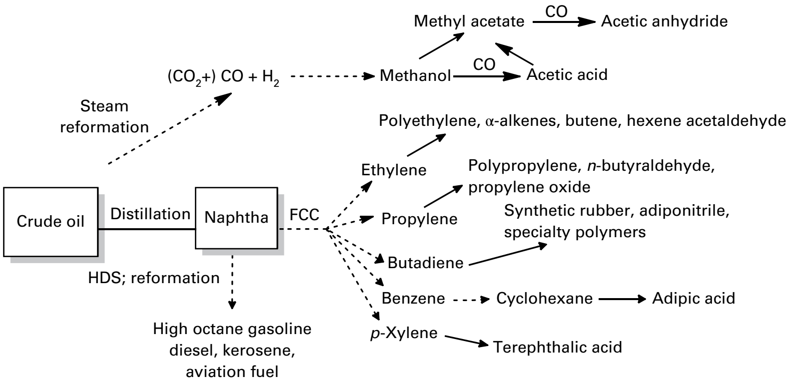


Figure 1.2 Applications of homogeneous catalysis in the chemical industry. The dashed arrows represent *heterogeneous* catalytic processes.

Propylene and α-alkenes can be reacted with synthesis gas to give *n*-butyraldehyde and alcohols, respectively. These reactions are called hydroformylation or oxo-reactions. The reaction between butadiene and hydrocyanic acid to obtain adiponitrile is called hydrocyanation. The mechanistic details and the relevance of hydroformylation and hydrocyanation reactions for the manufacture of consumer products are discussed in Chapter 5.

Polymerization of ethylene, propylene, and butadiene yields polyethylene, polypropylene, and polybutadiene, respectively. Although *heterogeneous* catalysts are mainly used in the industry, the mechanisms of these polymerization reactions are best understood by referring to well-established homogeneous catalytic systems. Selective conversions of ethylene to butene, or hexene, or a mixture of α-alkenes, are also achieved by homogeneous catalysts. Polymerization reactions are discussed in Chapter 6, while the selective conversions of ethylene to other alkenes are discussed in Chapter 7.

Oxidation of ethylene to acetaldehyde is one of the early examples of an industrial homogeneous catalytic process. Adipic acid and terephthalic acid are required for the manufacture of nylon and polyester, respectively. All these are produced by homogeneous catalyst-based oxidation reactions.

Selective epoxidation reactions, like the conversion of propylene to propylene oxide and allyl alcohol to glycidol, are also achieved by using homogeneous catalysts. These and a few other related reactions that are of relevance in the fine chemical industry are discussed in Chapter 8.

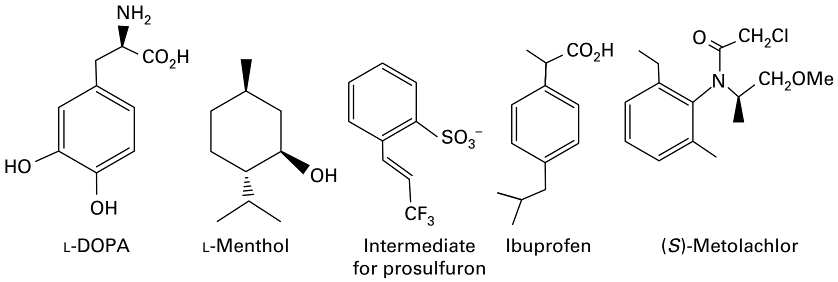


Figure 1.3 Examples of pharmaceuticals, flavoring agents, and herbicides whose synthesis involves homogeneous catalysis.

Apart from the chemicals and polymers listed in Figure 1.2, homogeneous catalysts play a very important role in the manufacture of many pharmaceuticals, specialty polymers, agrochemicals, flavors, etc. A few examples are shown in Figure 1.3. It is clear that many of these products are complex organic molecules.

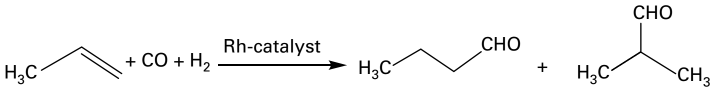
Thus L-DOPA is a drug used for Parkinson's disease, while ibuprofen is an analgesic. Both prosulfuron and (*S*)-metolachlor are herbicides, while L-menthol is a flavoring agent. As we will see later, the use of homogeneous catalysts in the manufacture of these chemicals eliminates the formation of unwanted products and increases the overall efficiencies with which the desired conversions are achieved.

1.4 COMPARISON AMONG DIFFERENT TYPES OF CATALYSIS

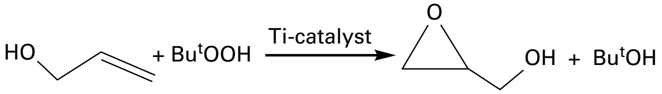
Heterogeneous catalysts are more widely used in industry than homogeneous catalysts because of their wider scope and higher thermal stability. There are no homogeneous catalysts as yet for cracking, reformation, ammonia synthesis, etc. The BP of the solvent and the intrinsic thermal stability of the catalyst limit the highest temperature at which a homogeneous catalyst may be used. The upper temperature limit of a homogeneous catalytic reaction is about 250°C, while heterogeneous catalysts routinely operate at higher temperatures.

The two most important characteristics of a catalyst are its **activity**, expressed in terms of **turnover number** (TON) or **turnover frequency** (TOF), and **selectivity**. The TON is the number of product molecules produced per molecule of the catalyst. The TOF is the TON per unit time. In general, when either type of catalyst can catalyze a given reaction, homogeneous or heterogeneous catalysts do not differ by an order of magnitude in their activities.

Selectivity could be of different types such as **chemoselectivity**, **regioselectivity**, **diastereoselectivity**, and **enantioselectivity**. Reactions 1.4.1–1.4.4 are representative examples where homogeneous catalysts are used. In all these reactions, the possibility of forming more than one product exists.



(1.4.1)



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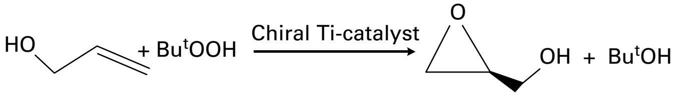

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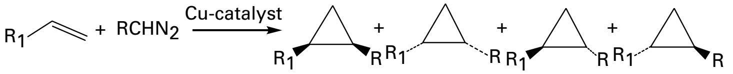


(1.4.4)

In reaction 1.4.1, a mixture of normal and isobutyraldehyde rather than propane, the hydrogenation product from propylene, is formed. This is an example of *chemoselectivity*. Furthermore, under optimal conditions using an Rh-based homogeneous catalyst, *n*-butyraldehyde may be obtained with more than 95% selectivity. This is an example of *regioselectivity*.

Similarly, in reaction 1.4.2, the alkene rather than the alcohol functionality of the allyl alcohol is selectively oxidized. However, the epoxide product is a mixture of two enantiomers. In reaction 1.4.3, only one enantiomer of the epoxide is formed. This is an example of an enantioselective reaction.

In reaction 1.4.4, a mixture of four diastereomers is formed. If one of the enantiomeric pair, let us say the first two enantiomers on the left, are selectively produced, then the reaction is diasteroselecive. Notice that in this reaction if a chiral catalyst is used, two enantiomers may not be produced in equal quantities. In other words, in such a situation both enantioselectivity and diastereoselectivity have to be measured.

Chemo-, regio-, and diastereoselectivity are usually expressed as a percentage of the amount of the desired product(s) in the total product(s) formed. A different formula is used for measuring enantioselectivity (see Section 3.6). Generally, by a choice of optimal catalyst and process conditions, it is possible to obtain high to very high selectivity in homogeneous catalytic reactions.

Another important aspect of any catalytic process is the ease with which the products could be separated from the catalyst. For heterogeneous catalysts this is not a problem. A solid catalyst is easily separated from liquid products by filtration or decantation. In contrast, in homogeneous catalytic processes, *catalyst recovery* could be a serious problem. Separation of the catalyst from the solvent by distillation is more expensive than by filtration or decantation. Also, in distillation the thermal stability of the catalyst may be a point of concern. In general, catalyst recovery in homogeneous catalytic processes requires careful consideration.

These factors—activity, selectivity, and catalyst recovery—are the ones on which comparisons between homogeneous and heterogeneous catalysts are usually made. Other important issues are catalyst life, susceptibility toward poisoning, diffusion, and, last but probably most important, control of performance through mechanistic understanding.

The life of a homogeneous catalyst is usually shorter than that of a heterogeneous one. In practical terms, this adds to the cost of homogeneous catalytic processes, as the metal has to be recovered and converted back to the active catalyst. Although homogeneous catalysts are thermally less stable than heterogeneous ones, they are less susceptible to poisoning by sulfur-containing compounds. Another important difference between the two types of catalysis is that *macroscopic* diffusion plays an important role in heterogeneous catalytic processes, but is usually less important for the homogeneous ones. In the terminology of chemical engineering, this is called **mass transfer**.

Mass transfer basically means the net movement of mass of a species from one phase to another. It occurs in many processes such as evaporation, adsorption, drying, precipitation, and distillation. Consider the reaction of a gas with a liquid in the presence of a solid insoluble heterogeneous catalyst. In such a catalytic system, mass transfer would refer to the dissolution of the gas in the liquid and transfer of the dissolved gas and the liquid to the active sites of the catalyst particles.

Finally, for an overall perspective on catalysis of all types, here are a few words about biochemical catalysts, namely, enzymes. In terms of activity, selectivity, and scope, enzymes score very high. A large number of reactions are catalyzed very efficiently, and the selectivity is very high. For chiral products, enzymes routinely give 100% enantioselectivity.

However, large-scale application of enzyme catalysis in the near future is difficult for many reasons. Isolation of a reasonable quantity of pure enzyme is often very difficult and expensive. Most enzymes are fragile and have poor thermal stability. Separation of the enzyme after the reaction is also a difficult problem. However, in the near future, catalytic processes based on thermostable enzymes may be adopted for selected products.

The biggest advantage of homogeneous catalysis is that the performance of the catalyst can be explained and understood at a molecular level. This is because the molecular species in a homogeneous catalytic system are spectroscopically easier to identify than in a heterogeneous one (see Chapter 3). The techniques available for studying adsorbed molecules on solid surfaces are more complex, and the results are less unequivocal. Based on a mechanistic understanding, the behavior of a homogeneous catalyst can be fine-tuned by optimal selection of the metal ion, ligand environment (see Section 2.1), and process conditions.

To summarize, both heterogeneous and homogeneous catalysts play important roles in the chemical industry. Roughly 85% of all catalytic processes are based on heterogeneous catalysts, but homogeneous catalysts, owing to their high selectivity, are becoming increasingly important for the manufacture of specialty polymers, fine chemicals, pharmaceutical intermediates, etc. Table 1.1 gives a comparative summary of the essential characteristics of homogeneous and heterogeneous catalysts.

Table 1.1
Comparison between homogeneous and heterogeneous catalysis

	Homogeneous	Heterogeneous
Active centers	All molecules	Only surface atoms
Selectivity	High	Low
Mass transfer limitations	Very rare	Can be severe
Structure/mechanism	Well defined	Less well defined
Catalyst separation	Tedious/expensive (mainly distillation or extraction)	Easy
Applicability	Limited	Wide
Cost of catalyst losses	High	Low

1.5 CATALYST RECOVERY

The separation problem of homogeneous catalysts can be addressed in different ways. In this section, we discuss the established industrial methods. One of the earliest forms of homogeneous catalyst recovery is by precipitating the metal as an insoluble salt, e.g., a hydroxide or a halide. The metal-containing precipitate is separated by filtration, converted to the active homogeneous catalyst, and then recycled. In many homogeneous catalytic processes, the *ligands* (see Section 2.1) present in the catalyst must be discarded or separated by some other method.

The most widely used industrial unit operation for the separation of a soluble catalyst from solution is distillation. Distillation could be of two types—flash distillation and distillation external to the reaction. In flash distillation, the reaction is carried out at elevated temperatures to continuously evaporate the products, while the catalyst remains in the solution. Thus the soluble catalyst always remains in the reactor and does not have to be recycled. The reactants that evaporate with the products can be reused by recycling them back to the reactor.

In distillation external to the reactor, a part of the solvent is evaporated together with the reactants and products, while the high boiling homogeneous catalyst solution is recycled via the bottom section of the distillation column. An obvious drawback of distillation is the decomposition of the homogeneous catalyst at elevated temperatures. The maximum temperatures of both flash and external distillations are limited by the temperature at which the homogeneous catalyst decomposes.

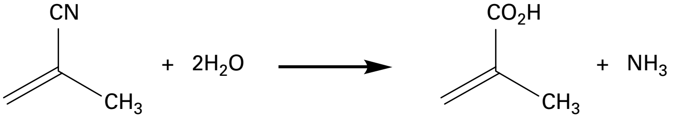
Another well-documented separation method is phase separation and/or extraction. In extraction, the differences in the solubilities of various compounds, and/or miscibilities of two liquids present in the reaction mixture, are exploited. Many organic liquids and water do not mix. This effect can be exploited if the products and reactants have very different solubilities in aqueous and organic phases. Recovery of homogeneous catalysts from a mixture of two immiscible liquids by phase separation is a relatively recent, successful industrial method. We discuss these and related methods in more detail in Chapter 5.

Finally, at a research level, **heterogenizations** of homogeneous catalysts have been extensively studied. The motivation behind this method is to combine the advantages of heterogeneous and homogeneous catalysts, i.e., easy separation with high selectivity. Basically, in this method the homogeneous catalyst is anchored to an insoluble support through chemical bonds. At the end of the catalytic reaction, the catalyst is separated by filtration and reused. Many different types of supports have been used, silica being one of the most common.

1.6 ENVIRONMENTAL ISSUES

The chemical industry manufactures a very large number (~30,000) of products through a variety of processes using fossil fuel as the source of carbon. The future of the chemical industry will be greatly influenced by three main environment-related issues. First, many chemicals and commonly used organic solvents are *toxic* and *hazardous* and may have a long-term detrimental effect on the environment. Consequently, minimum use or total avoidance of such chemicals is desirable. The use of volatile organic chemicals (**VOCs**) as solvents, for example, must be minimized or avoided wherever possible.

Second, in the manufacture of many chemicals, unwanted side products are generated. As an example, consider reaction 1.6.1, a common method for making a carboxylic acid.



(1.6.1)

In an industrial process, the ammonia generated in this reaction is neutralized with an acid such as H_2SO_4. The net result is the generation of a large amount of ammonium sulfate and bisulfate, which are unwanted solid wastes.

Finally, gases such as CO_2, methane, and nitrous oxide are called greenhouse gases (**GHGs**), because they are present in the earth's atmosphere, absorbing and emitting radiation within the thermal infrared range. The earth's surface temperature is therefore directly correlated to the concentrations of the GHGs. Due to indiscriminate fossil fuel burning, the concentration of CO_2 has increased to an alarming level.

Nitrous oxide and chlorinated fluorocarbons (CFCs) are also **ozone depleters**. As the ozone layer in the earth's atmosphere screens out the harmful part of ultraviolet radiation in sunlight, ozone depletion is a matter of serious concern. The chemical industry must therefore look for raw materials, end-products, and manufacturing processes that minimize or eliminate the adverse environmental impact of all these gases.

1.6.1 Background

The strategy for resolving the environmental issues mentioned earlier has been outlined in detail, in what is known as the 12 principles of **green chemistry**. In the context of homogeneous catalysis, these principles emphasize the need for the use of catalysts rather than stoichiometric reagents for the minimization of waste. They also underline the importance of biodegradable products, renewable raw materials, and the use of innocuous solvents rather than VOCs.

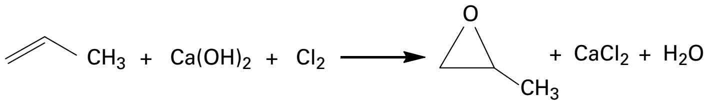
A simple definition of green chemistry is as follows. If there is an opportunity, then renewable raw materials must be used, and the generation of waste and the use of toxic and/or hazardous chemicals must be minimized. We first discuss the ways in which the waste generated by a given process is measured, and then how the correct choice of a catalyst and raw materials can bring it down.

There are two ways to estimate the environmental impact of a given manufacturing process. The methods are interrelated but in one case the **atom efficiency** (AE) or the **atom economy** of the process is calculated. In the other method, we calculate a parameter called the "*E* factor." In a given process if the molecular weight of the desired product is P and the total molecular weight of all the products is P_1, then AE and the *theoretical E* factor (E) are given by Equation 1.6.1.1.

$$\mathrm{AE} = \frac{P}{P_1}; \quad E = \frac{P_1 - P}{P} \qquad (1.6.1.1)$$

In E factor calculations the quantity $P_1 - P$ represents **waste**, and for an actual industrial process, the isolated yields must be taken into account. Also, any solvent or any other material loss must be added to $P_1 - P$.

If the AE for a given process is high, then the E factor would be low. As an example, consider two different manufacturing routes for propylene oxide where the overall stoichiometries are given by reactions 1.6.1.2 and 1.6.1.3.



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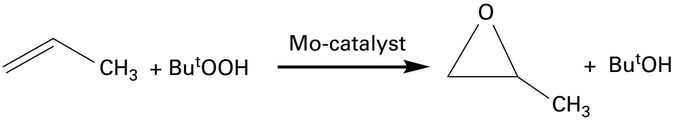

(1.6.1.3)

Reaction 1.6.1.2 refers to the overall reaction of an old *noncatalytic* process of multiple steps. Reaction of propylene with aqueous chlorine (HOCl) gives a chlorohydrin intermediate, which on treatment with calcium oxide gives propylene oxide and calcium chloride. The AE and the theoretical *E* factor for this process are 0.31 and 2.22, respectively.

Reaction 1.6.1.3 refers to a homogeneous catalyst-based process where a soluble molybdenum complex is used as the catalyst. The oxygen atom supplier in this case is tertiary butyl hydroperoxide. The AE and theoretical *E* factor are 0.43 and 1.27, respectively. The adverse environmental impact of the second process is therefore considerably less. In fact, if both tertiary butanol and propylene oxide are desired products, then the theoretical *E* factor is zero.

Different segments of the petrochemical industry have widely different scales of operations and associated *E* factors. Oil refining is carried out on a massive scale (~100 million tons) but on an average has a low *E* factor (~0.1). On the other hand, the manufacture of pharmaceuticals and their intermediates is carried out on a much smaller scale (~10–1000 tons), but has large *E* factors (~25–100). One of the reasons behind the rapid growth of homogeneous catalytic processes for the manufacturing of fine chemicals and pharmaceutical intermediates is that adoption of such processes reduces the *E* factors significantly.

1.6.2 Biofuel, Ethanol, and Glycerol

It has been argued that by replacing fossil fuels with biofuels, emission of CO_2 may be reduced. Here we consider the basic premises for this view. Later on in this book the utilization of CO_2 in homogeneous catalytic processes, either as a solvent or as a reactant, will be discussed (see Sections 4.7.3 and 4.7.4).

Fuels that come from plants are called **biofuels**. Two biofuels, ethanol and biodiesel, have received serious attention. As shown in Figure 1.4, once used as a fuel, the carbon in both fossil and biofuel gets converted to CO_2. As biofuels come from plants, and plants recycle CO_2 by photosynthesis, more extensive use of biofuels would add less CO_2 to the