

Homogeneous Catalysis

Mechanisms and Industrial Applications

Sumit Bhaduri and Doble Mukesh



Homogeneous Catalysis: Mechanisms and Industrial Applications
Sumit Bhaduri, Doble Mukesh
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HOMOGENEOUS CATALYSIS

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Mechanisms and Industrial Applications

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For
Vrinda Nabar—my severest critic and best friend
—Sumit Bhaduri

and

My dear wife Geetha
—Doble Mukesh

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PREFACE

This book has grown out of a graduate-level course on homogeneous catalysis that one of us taught at Northwestern University several times in the recent past. It deals with an interdisciplinary area of chemistry that offers challenging research problems. Industrial applications of homogeneous catalysis are proven, and a much wider application in the future is anticipated. Numerous publications and patent applications testify to the fact that in both the academic and industrial research laboratories the growth in research activity in this area in the past decade or so has been phenomenal.

Written mainly from a pedagogical point of view, this book is not comprehensive but selective. The material presented was selected on the basis of two criteria. We have tried to include most of the homogeneous catalytic reactions with proven industrial applications and well-established mechanisms. The basic aim has been to highlight the connections that exist between imaginative academic research and successful technology. In the process, topics and reports whose application or mechanism appears a little far-fetched at this point, have been given lower priority.

A chapter on the basic chemical concepts (Chapter 2) is meant for readers who do not have a strong background in organometallic chemistry. A chapter on chemical engineering fundamentals (Chapter 3) is included to give non-chemical engineering students some idea of the issues that are important for successful technology development. Because of the industrial mergers, acquisitions, etc., that have taken place over the past 10 years or so, the present names of some of the chemical companies today differ from their names as given in this book.

We have covered the literature up to the start of 1999. Recent publications that are particularly instructive or that deal with novel concepts are referred to

in the answers to problems given at the end of each chapter. The sources for the material presented are listed in the bibliography at the end of each chapter.

Many people have helped in various ways in the preparation of this book: Professor James A. Ibers; Professor Robert Rosenberg and Virginia Rosenberg; Professor Du Shriver; Suranjana Nabar-Bhaduri and Vrinda Nabar; R. Y. Nadkar and V. S. Joshi. Sumit Bhaduri gratefully acknowledges a sabbatical leave from Reliance Industries Limited, India, without which the book could not have been completed. More than anything else, it was the students at Northwestern University whose enthusiastic responses in the classroom made the whole enterprise seem necessary and worthwhile. The responsibility for any shortcomings in the book is of course only ours.

SUMIT BHADURI

DOBLE MUKESH

CHAPTER 1

CHEMICAL INDUSTRY AND HOMOGENEOUS CATALYSIS

1.1 FEED STOCKS AND DEFINITIONS

Most carbon-containing feed stock is actually used for energy production, and only a very small fraction goes into making chemicals. The four different types of feedstock available for energy production are crude oil, other oils that are difficult to process, coal, and natural gas. Currently, the raw material for most chemicals is crude oil. Since petroleum is also obtained from crude oil, the industry is called petrochemical industry. Of the total amount of available crude oil, about 90% are sold as fuels of various kinds by the petroleum industry. It is also possible to convert sources of carbon into a mixture of carbon monoxide and hydrogen ($\text{CO} + \text{H}_2$), commonly known as synthesis gas. Hydrogen by itself is a very important raw material (e.g., in the manufacture of ammonia). It is also required for the dehydrosulfurization of crude oil, a prerequisite for many other catalytic processing steps.

In this book we deal exclusively with *homogeneous* catalytic processes, that is, processes in which all the reactants are very often in gas–solution equilibrium. In other words, the catalyst and all the other reactants are in solution, and the catalytic reaction takes place in the liquid phase. In terms of total tonnage and dollar value, the contribution of homogeneous catalytic processes in the chemical industry is significantly smaller than that of *heterogeneous* catalytic reactions. All the basic raw materials or building blocks for chemicals are manufactured by a small but very important set of heterogeneous catalytic reactions. In these reactions gaseous reactants are passed over a solid catalyst. There are other reactions where liquid reactants are used with insoluble solid catalysts. These are also classified as heterogeneous catalytic reactions. Thus

in homogeneous catalytic reactions molecules of all the reactants, including those of the catalyst, are in the liquid phase. In contrast, in heterogeneous catalytic processes the molecules of the gaseous or liquid reactants are adsorbed on the surfaces of the solid catalysts. Unlike the discrete molecular structure of a homogeneous catalyst, a solid surface consists of an infinite array of ions or atoms.

1.2 FEED STOCK TO BASIC BUILDING BLOCKS BY HETEROGENEOUS CATALYSIS

To put the importance of homogeneous catalysis in perspective, we first present a very brief summary of the heterogeneous catalytic processes that are used to convert crude oil into the basic building blocks for chemicals. The heterogeneous catalytic reactions to which the feed stock is subjected, and the basic building blocks for chemicals that are obtained from such treatments, are shown in Fig. 1.1.

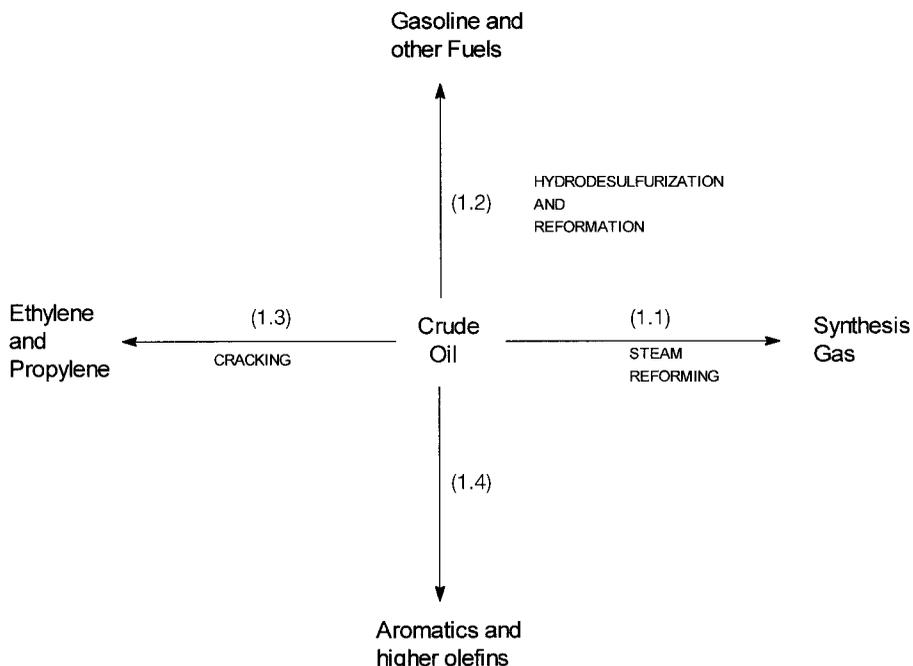


Figure 1.1 The basic building blocks for chemicals that are obtained from heterogeneous catalytic (and noncatalytic) treatment of crude petroleum.

Reaction 1.1 is known as steam reforming. The reaction conditions are fairly severe ($>1000^{\circ}\text{C}$), and the structural strength of the catalyst is an important point of consideration. The catalyst employed is nickel on alumina, or magnesia, or a mixture of them. Other non-transition metal oxides such as CaO , SiO_2 , and K_2O are also added.

Catalytic steam reforming could also be performed on natural gas (mainly methane) or the heavy fraction of crude oil called naphtha or fuel oil. The old method of producing synthesis gas by passing steam over red-hot coke was noncatalytic. Depending on the requirement for hydrogen, synthesis gas could be further enriched in hydrogen by the following reaction:



This is called the water gas shift reaction. We discuss this reaction in some detail in Chapter 4 (see Section 4.3). The heterogeneous catalysts used for the water gas shift reaction are of two types. The high-temperature shift catalyst is a mixture of Fe_3O_4 and Cr_2O_3 and operates at about 500°C . The low-temperature shift catalyst contains copper and zinc oxide on alumina, operates at about 230°C , and is more widely used in industry.

Step 1.2 involves separation of crude oil into volatile ($<670^{\circ}\text{C}$) and non-volatile fractions. On fractional distillation, the volatile part gives hydrocarbons containing four or fewer carbon atoms, light gasoline, naphtha, kerosene, etc. All these could be used as fuels for different purposes. From the point of view of catalysis, the modification of the heavier fractions to “high octane” gasoline is important.

The conversion of the heavier fractions into high-octane gasoline involves two catalytic steps: the reduction of the level of sulfur in the heavy oil by hydrodesulfurization, followed by “reformation” of the hydrocarbon mixture to make it rich in aromatics and branched alkanes. Hydrodesulfurization prevents poisoning of the catalyst in the reformation reaction, and employs alumina-supported cobalt molybdenum sulfide. In this reaction sulfur-containing organic compounds react with added hydrogen to give hydrogen sulfide and hydrocarbons. The reformation reaction also requires hydrogen as a co-reactant and is carried out at about 450°C . The reformation reaction involves the use of acidified alumina-supported platinum and rhenium as the catalyst.

Reaction 1.3 is often called a *cracking reaction* because high-molecular-weight hydrocarbons are broken into smaller fragments. The major processes used for cracking naphtha into ethylene and propylene are noncatalytic and thermal, and are carried out at a temperature of about 800°C . However, there are other cracking reactions that involve the use of acidic catalysts, such as rare earth exchanged zeolites or amorphous aluminosilicates, etc. In some cracking reactions hydrogen is also used as a co-reactant, and the reaction is then called a *hydrocracking reaction*. Step 1.4 may involve all the catalytic and noncatalytic processes discussed so far.

1.3 BASIC BUILDING BLOCKS TO DOWNSTREAM PRODUCTS BY HOMOGENEOUS CATALYSIS

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

The substances within the circles are the basic building blocks obtained from petroleum refining by processes discussed in the previous section. The products within the square are manufactured from these raw materials by homogeneous catalytic pathways. Except for 1.7, all the other four processes shown in Fig. 1.2 are large-tonnage manufacturing operations.

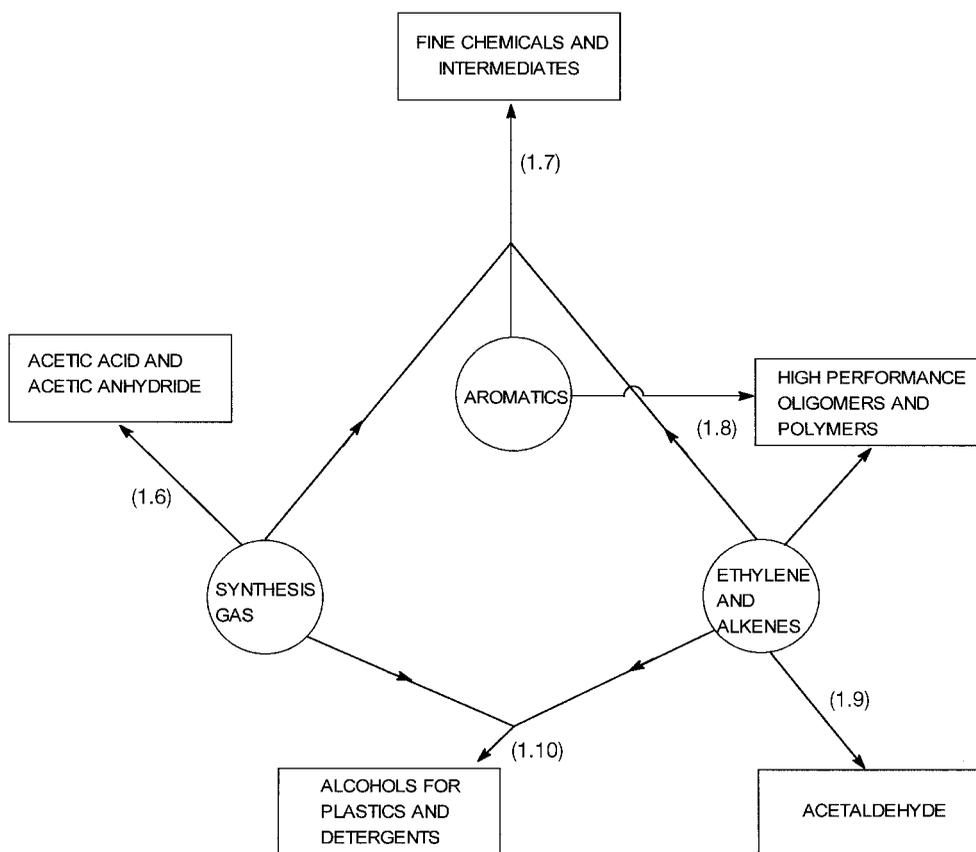


Figure 1.2 A few illustrative examples of chemicals and classes of chemicals that are manufactured by homogeneous catalytic processes. In 1.6 low-pressure methanol synthesis by a heterogeneous catalyst is one of the steps. In 1.9 it is ethylene that is converted to acetaldehyde. In 1.7 all the available building blocks may be used.

Step 1.6 involves the conversion of synthesis gas into methanol by a heterogeneous catalytic process. This is then followed by homogeneous catalytic carbonylation of methanol to give acetic acid. Similar carbonylation of methyl acetate gives acetic anhydride. These reactions are discussed in Chapter 4. Step 1.10 involves the conversion of alkenes and synthesis gas to aldehydes, which are then hydrogenated to give alcohols. These alcohols are used in plastics and detergents. The conversion of alkenes and synthesis gas to aldehydes is called an oxo or hydroformylation reaction and is discussed in Chapter 5. Step 1.9 is one of the early homogeneous catalytic processes and is discussed in Chapter 8. Steps 1.7 and 1.8 both represent the emerging frontiers of chemical technologies based on homogeneous catalysis. The use of metallocene catalysts in step 1.8 is discussed in Chapter 6.

As indicated by step 1.7, there are a number of small-volume but value-added fine chemicals, intermediates, and pharmaceuticals, where homogeneous catalytic reactions play a very important role. Some of these products, listed in Table 1.1, are optically active, and for these homogeneous catalysts exhibit almost enzymelike stereoselectivities. Asymmetric or stereoselective homogeneous catalytic reactions are discussed in Chapter 9.

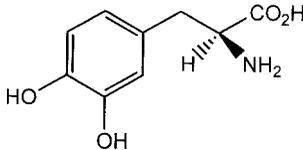
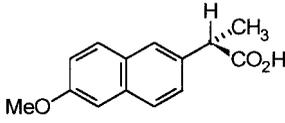
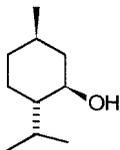
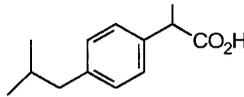
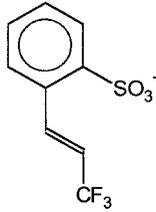
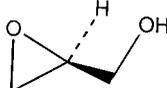
1.4 COMPARISON AMONG DIFFERENT TYPES OF CATALYSIS

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 boiling point of the solvent and the intrinsic thermal stability of the catalyst also 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 or frequency, and selectivity. The turnover number is the number of product molecules produced per molecule of the catalyst. The turnover frequency is the turnover number per unit time. In general, homogeneous and heterogeneous catalysts do not differ by an order of magnitude in their activities when either type of catalyst can catalyze a given reaction.

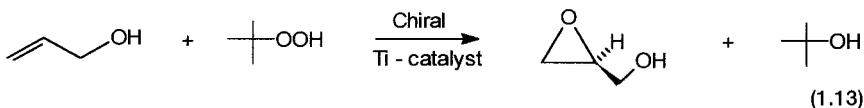
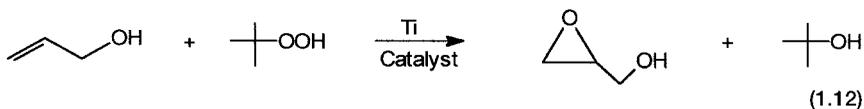
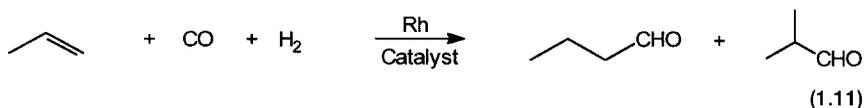
Selectivity could be of different type—chemoselectivity, regioselectivity, enantioselectivity, etc. Reactions 1.11–1.13 are representative examples of such selectivities taken from homogeneous catalytic processes. In all these reactions, the possibility of forming more than one product exists. In reaction 1.11 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 normal butyraldehyde may be obtained with more than 95% selectivity. This is an example of regioselectivity. Similarly, in reaction 1.12 the alkene rather than the alcohol functionality of allyl

TABLE 1.1 Products of Homogeneous Catalytic Reactions

| Structure | Name and use | Process |
|---|---|---|
|  | L-Dopa Drug for Parkinson's disease | Asymmetric hydrogenation |
|  R - Liver toxin S - Anti-inflammatory | Naproxen® Anti inflammatory drug | Asymmetric hydroformylation or hydrocyanation or hydrogenation! |
|  | L-Menthol Flavoring agent | Asymmetric isomerization |
|  | Ibuprofen Analgesic | Catalytic carbonylation |
|  | An intermediate for Prosulfuron Herbicide | C-C Coupling (Heck reaction) |
|  | r-Glycidol One of the components of a heart drug | Asymmetric epoxidation (Sharpless epoxidation) |

alcohol is selectively oxidized. However, the product epoxide, called glycidol, is a mixture of two enantiomers. In reaction 1.13 only one enantiomer of glycidol is formed in high yield. This is an example of an enantioselective reaction. Generally, by a choice of optimal catalyst and process conditions, it is possible to obtain very high selectivity in homogeneous catalytic reactions. This is one

of the main reasons for the commercial success of many homogeneous-catalyst-based industrial processes.



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, since a solid catalyst is easily separated from liquid products by filtration or decantation. In some of the homogeneous catalytic processes, catalyst recovery is a serious problem. This is particularly so when an expensive metal like rhodium or platinum is involved. In general, catalyst recovery in homogeneous catalytic processes requires careful consideration.

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 high. For chiral products enzymes routinely give 100% enantioselectivity. However, large-scale application of enzyme catalysis in the near future is unlikely 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 above-mentioned factors—activity, selectivity, and catalyst recovery—are the ones on which comparison between homogeneous and heterogeneous catalysts is normally based. Other important issues are catalyst life, susceptibility towards 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, since 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 dif-

fusion plays an important role in heterogeneous catalytic processes but is less important for homogeneous ones.

Finally, the biggest advantage of homogeneous catalysis is that, in most cases, 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 easier to identify than in a heterogeneous one. For soluble catalysts, there are many relatively simple spectroscopic and other techniques for obtaining accurate information at a molecular level (see Section 2.5). In contrast, the techniques available for studying adsorbed molecules on solid surfaces are more complex, and the results are often 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 and process conditions. As an example we refer back to reaction 1.11. In the absence of any phosphorus ligand and relatively high pressures, the ratio of the linear to the branched isomer is about 1:1. However, by using a phosphorus ligand and lower pressure, this ratio could be changed to >19:1. This change in selectivity can be explained and in fact can be predicted on the basis of what is known at a molecular level.

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 tailor-made plastics, fine chemicals, pharmaceutical intermediates, etc.

1.5 WHAT IS TO FOLLOW—A SUMMARY

In the following chapters we discuss the mechanisms of selected homogeneous catalytic reactions. Brief descriptions of some of these reactions, the metals involved, and the chapters where they are to be found are given in Table 1.2. The following points deserve attention: First, the names of five reactions (see the second to the sixth row) begin with the prefix “hydro.” In all these reactions a hydrogen atom and some other radical or group are added across the double bond of an alkene. Thus a “hydroformylation” reaction comprises an addition of H and CHO; “hydrocyanation,” an addition of H and CN, etc. Second, from the fourth column it is clear that complexes of a variety of transition and occasionally other metals have been successfully used as homogeneous catalysts. Third, the last row includes most of the reactions of the previous rows with an important modification, namely, the use of chiral metal complexes as catalysts. In the next two chapters we discuss some fundamental chemical and engineering concepts of homogeneous catalysis. These concepts will help us to understand the behavior of different homogeneous catalytic systems and their successful industrial implementation.