FUNDAMENTAL CONCEPTS IN HETEROGENEOUS CATALYSIS

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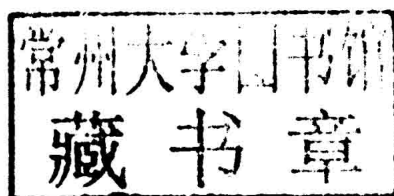
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PREFACE

The discovery and development of efficient chemical reactions and processes converting fossil resources into a broad range of fuels and chemicals is one of the most significant scientific developments in chemistry so far. The key to efficient chemical processes is the control of the rates of reaction. This control is usually provided by a catalyst—a substance that can facilitate a chemical reaction and determine the product distribution. The science of catalysis is the science of controlling chemical reactions.

There are many challenges to the science of catalysis that need to be met over the coming years. A sustainable future calls for the development of catalytic processes that do not rely on a net input of fossil resources. This can only be achieved if we discover new catalysts that can efficiently utilize the energy input from the sun or other sustainable sources to synthesize fuels as well as base chemicals for the production of everything from plastics to fertilizers. It also requires more selective processes with fewer waste products and catalysts made from Earth-abundant elements. This represents a formidable challenge. This textbook describes some of the fundamental concepts that will be needed to address this challenge.

Our basic assumption is that the discovery of new catalysts can be accelerated by developing a framework for understanding catalysis as a phenomenon and by pinpointing what are the most important parameters characterizing the chemical properties of the catalyst. We will concentrate in this book on heterogeneous catalysis, that is, catalysts where the processes take place at the surface of the solid. We will develop a systematic picture of the surface-catalyzed processes from the fundamental link to surface geometry and electronic structure to the kinetics of the network of elementary reactions that constitute a real catalytic process. The end result is a theory of variations in catalytic activity and selectivity from one catalyst to the next that will

allow the reader to understand the present literature and to make predictions of new catalysts. The latter is aided by the consistent involvement of public databases of surface chemical processes.

The text is aimed at senior undergraduate and graduate students but should be a good guide for any researcher interested in the science and technology of heterogeneous catalysis.

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HETEROGENEOUS CATALYSIS AND A SUSTAINABLE FUTURE

The processes that convert fossil resources into fuels and chemicals are essential to modern life. It is, however, also clear that these technologies result in an increased stress on the environment. Even the most efficient processes today result in pollution by by-products. While many chemical production processes have become "cleaner" over the past few decades, the world's consumption of fossil carbon resources has continued to increase. This has resulted in a sharp increase in atmospheric carbon dioxide levels, and because carbon dioxide is a greenhouse gas, the anthropogenic CO_2 emissions have been linked to global climate changes, increased temperatures, melting of the glaciers on all continents, rising sea water levels in the oceans, and the observation of more extreme weather variations across the globe. Since the global population is rapidly growing and many countries are becoming increasingly industrialized, the global energy demand will continue to rise over the next century.

There is a growing consensus that the world's increased demand for fuels and base chemicals will need to be met by more so-called "carbon-neutral" technologies. This calls for new catalytic processes and for catalytic technologies that focus on prevention rather than on remediation.

One central sustainable energy source, which we need to harvest much more efficiently and at a much larger scale than we do today, is sunlight. The annual global energy consumption could be covered by the sunlight striking the Earth within about 1 h assuming that the energy could be efficiently harvested. Consider therefore the
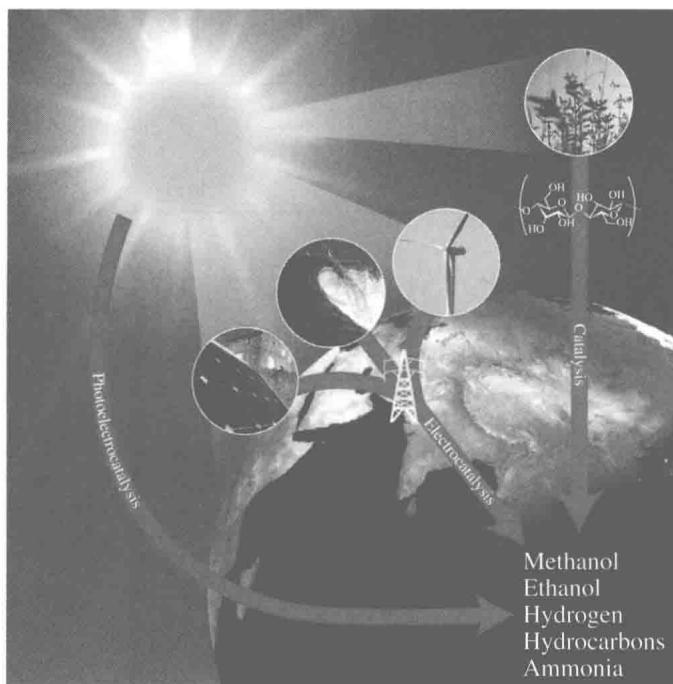
FIGURE 1.1   Illustration of the role of catalysis in providing sustainable routes to fuels and base chemicals. Whether the energy flux from sunlight is harvested through biomass, through intermediate electricity production from photovoltaics or wind turbines, or directly through a photoelectrochemical reaction, the process always requires an efficient catalyst, preferably made of earth-abundant materials. Taken from Nørskov and Bligaard (2013) with permission from Wiley. (*See insert for color representation of the figure.*)

challenge of turning the energy from sunlight into transportation fuels or base chemicals for industry (see Fig. 1.1). Irrespective of whether the sun's energy is harvested by photovoltaic cells, through the use of biomass, wind turbines, wave energy converters, or photoelectrochemical cells, one or more catalysts are needed in order to transform the harvested energy into a useful fuel or chemical. If the goal is to substitute a significant fraction of the global transportation fuel or of base chemicals for industry, the catalysts involved have to be made from elements that are abundant enough that large-scale implementation of the technology can be carried out at a reasonable level of resource utilization and cost.

Traditionally, the field of catalysis is divided into three areas: heterogeneous, homogeneous, and enzyme catalysis. Heterogeneous catalysts are present in a phase different from that of the reactants; typically, the reactants are in the gas or liquid phase, whereas the catalyst is a solid material. Homogeneous catalysts operate in the same phase as the reactants, and enzyme catalysts are specialized proteins. The chemically active part of enzymes is often a tiny part of the protein, and enzyme catalysis can be viewed as a special kind of heterogeneous catalysis.
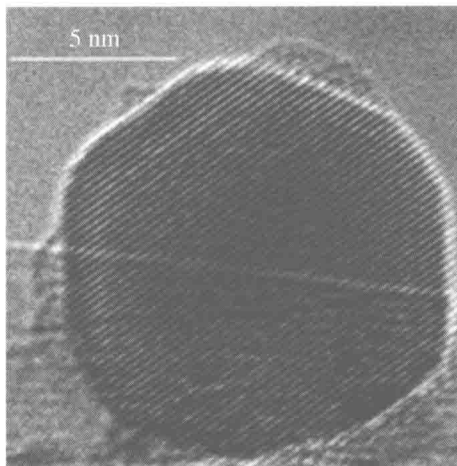
FIGURE 1.2 High-resolution transmission electron microscopy image of a supported Ru catalyst for ammonia synthesis recorded at 552°C and 5.2 mbar in a gas composition of 3:1 H_2/N_2. A Ru particle with a well-formed lattice and surface facets is seen on an amorphous support consisting of BN. A Ba–O promoter phase is observed on top of the Ru particle. Taken from Hansen et al. (2001) with permission from The American Association for the Advancement of Science.

Heterogeneous catalysts have the desirable property that after reaction they are easily separated from the reactants and products. This is an important reason why heterogeneous catalysts are often preferred in industry, in particular for high-volume products, for instance, in the energy sector. For heterogeneous catalysts, the chemical reactions take place at the surface of the material. For that reason, heterogeneous catalysts are typically extremely porous materials so that the surface area is large. In some cases, the catalytic material itself can be made with a high surface area. In other cases, a relatively inert material, the support, is used to stabilize nanoparticles (2–20 nm) of the active material (Fig. 1.2).

Homogeneous catalysts are typically relatively small molecules that are dissolved in the same solution as the reactants and products. Molecular catalysts are often simpler to study, since the active sites on the catalytic molecules can be synthesized with atomic-scale accuracy, and a very detailed understanding of many homogeneously catalyzed processes has therefore been developed.

The focus in the present textbook will be on the fundamental concepts that are needed to understand how solid surfaces act as catalysts. We will introduce a molecular-level understanding of the way surfaces catalyze chemical reactions, which allows the reader to understand why one material is a better catalyst than another for a given reaction. The aim is not to give a complete overview of the types of catalysts or catalytic processes or to give a detailed introduction to the experimental and computational methods that are used to study them. A number of recent textbooks cover these areas very well; see the "Further Reading" list at the end of the chapter. We will use a number of simple catalytic processes as examples throughout but only in order to develop the general rules according to which heterogeneous catalysis works.

SOLAR FUELS

Imagine that we could use renewable electricity, which could come from any of several sources (hydro, solar, wind, geothermal, and others), to directly reduce CO_2 to hydrocarbons and water. Then, we would have a renewable source of fuels for the transportation sector as well as a way of storing energy from intermittent resources. The problem is that there is presently no known catalyst that can do this efficiently. Metallic copper has been demonstrated to produce high (>50%) yields of hydrocarbons at reasonably high (5 mA cm²) current densities (Hori, 2008). But the electrochemical potential needed to make the process run is prohibitively high.

Electrical potential created by photon or from a renewable electricity source.

It turns out that each of the 8 electrons needed to reduce a CO_2 molecule to the simplest hydrocarbon, CH_4 ($CO_2 + 8(H^+ + e^-) \rightarrow CH_4 + 2H_2O$), need on the order of 1 V in extra potential relative to what is needed from a purely thermodynamic point of view in order to make the process run (Kuhl et al., 2012). That means that 8 eV per CO_2 molecule or ~800 kJ/mol is lost in the electrocatalytic reduction of CO_2. A much better catalyst is clearly needed.

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THE POTENTIAL ENERGY DIAGRAM

The central theme in catalysis is the effect of the catalyst on the rate of a chemical reaction or on the product distribution, which is given by the relative rates of different reaction pathways. You can say that catalysis is all about what determines the chemical kinetics. A good catalyst is typically one that gives a high rate and a high selectivity toward the desired product. The reaction rate constant, k, for an elementary reaction is often written as an Arrhenius expression in terms of a prefactor, v, and an activation energy, E_a:

$$k = v e^{-E_a/k_B T} \tag{2.1}$$

where k_B is the Boltzmann constant and T is the absolute temperature. Variations in the activation energy, when, for example, one catalyst or reactant is substituted with another or when a reaction proceeds through two different reaction mechanisms, are typically large (0.5–2 eV), while the thermal energy, $k_B T$, is small (typically ranges from $k_B T = 0.0257\,eV$ at $T = 298\,K$ to $k_B T = 0.1\,eV$ at $T = 1160\,K$). The rate constant is therefore very sensitive to the size of the activation energy. We will return with a more detailed discussion of how the Arrhenius expression comes about in Chapter 4. For now, it suffices to note that any discussion of reaction rates must start with a discussion of the origin of activation energies. For that reason, the starting point of this textbook is an understanding of the potential energy diagram (PED) for surface chemical transformations.