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 CO₂ 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
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 1.1 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.)
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.

**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.
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 CO₂ 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 cm⁻²) current densities (Hori, 2008). But the electrochemical potential needed to make the process run is prohibitively high.

It turns out that each of the 8 electrons needed to reduce a CO₂ molecule to the simplest hydrocarbon, CH₄ (CO₂ + 8(H⁺ + e⁻) → CH₄ + 2H₂O), 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 CO₂ molecule or ~800 kJ/mol is lost in the electrocatalytic reduction of CO₂. A much better catalyst is clearly needed.

REFERENCES


FURTHER READING


