Addition of hydrogen to a multiple bond is **hydrogenation**. It is applicable to almost all types of multiple bonds and is of great importance in synthetic chemistry, particularly in the chemical industry. Probably the most important technical example is production of ammonia by the hydrogenation of nitrogen:

\[
3\text{H}_2 + \text{N}_2 \rightleftharpoons 2\text{NH}_3 \quad \Delta H^\circ = -22.0 \text{ kcal (25\(^\circ\))}
\]

\[
\Delta G^\circ = -8.0 \text{ kcal (25\(^\circ\))}
\]

This may appear to be a simple process, but in fact it is difficult to carry out because the equilibrium is not very favorable. High pressures (150\(^-\)200 atm) are required to get a reasonable conversion, and high temperatures (430\(^-\)510\(^\circ\)) are necessary to get reasonable reaction rates. A catalyst, usually iron oxide, also is required. The reaction is very important because ammonia is used in ever-increasing amounts as a fertilizer either directly or through conversion to urea or ammonium salts.

Production of ammonia requires large quantities of hydrogen, most of which comes from the partial oxidation of hydrocarbons with water or oxygen. A simple and important example is the so-called “methane-steam gas” reaction, which is favorable only at very high temperatures because of the entropy effect in the formation of \(\text{H}_2\) (see Section 4-4B):

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \Delta H^\circ = +51.0 \text{ kcal (25\(^\circ\))}
\]

\[
\Delta G^\circ = +33.9 \text{ kcal (25\(^\circ\))}
\]

Therefore the fertilizer industry is allied closely with the natural gas and petroleum industries, and for obvious reasons ammonia and hydrogen often are produced at the same locations.

Alkenes and alkynes add hydrogen much more readily than does nitrogen. For example, ethene reacts rapidly and completely with hydrogen at ordinary pressures and temperatures in the presence of metal catalysts such as nickel, platinum, palladium, copper, and chromium:

\[
\text{CH}_2=\text{CH}_2 + \text{H}_2 \xrightarrow{\text{metal catalyst}} \text{CH}_3\text{CH}_3 \quad \Delta H^\circ = -32.7 \text{ kcal (25\(^\circ\))}
\]

\[
\Delta G^\circ = -24.1 \text{ kcal (25\(^\circ\))}
\]

These reactions are unlike any we have encountered so far. They are **heterogeneous** reactions, which means that the reacting system consists of two or more phases. Usually, the metal catalyst is present as a finely divided solid suspension in the liquid or solution to be reduced. Alternatively, the metal is deposited on an inert solid support such as carbon, barium sulfate, alumina (\(\text{Al}_2\text{O}_3\)), or calcium carbonate. Then the mixture of the liquid substrate and solid catalyst is shaken or stirred in a hydrogen atmosphere. However, then actual reaction takes place at the surface of the metal catalyst and is an example of **heterogeneous** or **surface catalysis**.

### 11-2A Mechanism of Hydrogenation

The exact mechanisms of heterogeneous reactions are difficult to determine, but much interesting and helpful information has been obtained for catalytic hydrogenation. The metal catalyst is believed to act by binding the reactants at the surface of a crystal lattice. As an example, consider the surface of a nickel crystal (Figure 11-1). The nickel atoms at the surface
have fewer neighbors (lower covalency) than the atoms in the interior of the crystal. The surface atoms therefore have residual bonding capacity and might be expected to combine with a variety of substances.

![Figure 11-1: Left: Schematic representation of a nickel crystal in cross section showing residual valences at the surface atoms. Right: Adsorption of ethene on the surface of the nickel crystal with formation of \( \text{C-Ni} \) bonds.](image)

It has been shown experimentally that ethene combines exothermically \( \Delta H^0 = -60 \text{ kcal/mol} \) and reversibly with a metal surface. Although the precise structure of the ethene-nickel complex is unknown, the bonding to nickel must involve the electrons of the double bond because saturated hydrocarbons, such as ethane, combine only weakly with the nickel surface. A possible structure with carbon-nickel \( \sigma \) bonds is shown in Figure 11-1.

Hydrogen gas combines with nickel quite readily with dissociation of the \( \text{H-H} \) bonds and formation of \( \text{Ni-H} \) bonds (nickel hydride bonds). The overall hydrogenation process is viewed as a series of reversible and sequential steps, as summarized in Figure 11-2. First the reactants, hydrogen and ethene, are adsorbed on the surface of the metal catalyst. The energies of the metal-hydrogen and metal-carbon bonds are such that, in a second step, a hydrogen is transferred to carbon to give an ethyl attached to nickel. This is the halfway point. In the next step, the nickel-carbon bond is broken and the second carbon-hydrogen bond is formed. Hydrogenation is now complete and the product is desorbed from the catalyst surface.

![Figure 11-2: A possible cycle of reactions for catalytic hydrogenation of ethene. Ethane is held much less tightly than ethene on the catalyst surface, so as long as ethene is present no significant amount of ethane is bound.](image)

Ethane has a low affinity for the metal surface and, when desorbed, creates a vacant space for the adsorption of new ethene and hydrogen molecules. The cycle continues until one of the reagents is consumed or some material is adsorbed that "poisons" the surface and makes it incapable of further catalytic activity. Because the reaction occurs only on the surface, small amounts of a catalyst poison can completely stop the reaction.
As might be expected for the postulated mechanism, the spacings of the metal atoms in the crystal lattice are quite important in determining the hydrogenation rates. The mechanism also accounts for the observation that hydrogen usually adds to an alkene in the suprafacial manner. To illustrate, 1,2-dimethylcyclohexene is reduced to cis-1,2-dimethylcyclohexane:

\[
\text{Pt, } \text{H}_2 \rightarrow
\]

1,2-dimethylcyclohexene\hspace{1cm} cis-1,2-dimethylcyclohexane

11-2B Catalyst Activity and Selectivity

For maximum catalytic activity, the metal usually is prepared in a finely divided state. This is achieved for platinum and palladium by reducing the metal oxides with hydrogen prior to hydrogenation of the alkene. A specially active form of nickel ("Raney nickel") is prepared from a nickel-aluminum alloy. Sodium hydroxide is added to the alloy to dissolve the aluminum. The nickel remains as a black powder which is pyrophoric (burns in air) if not kept moist:

\[
\begin{align*}
2 \text{Ni-Al} + 2 \text{OH}^- + 2 \text{H}_2\text{O} & \rightarrow 2 \text{Ni} + 2 \text{AlO}_2^- + 3 \text{H}_2
\end{align*}
\]

Highly active platinum, palladium, and nickel catalysts also can be obtained by reduction of metal salts with sodium borohydride \(\text{NaBH}_4\).

As mentioned previously, multiple bonds are not hydrogenated with equal facility. This fact can be used to advantage in carrying out selective reactions. For instance, hydrogenation of a carbon-carbon double bond can be achieved without simultaneously reducing a carbonyl bond in the same molecule. For example, the carbon-carbon double bond of the following aldehyde can be reduced selectively:

\[
\text{O} \hspace{1cm} \text{H}_2, \text{Pd} \hspace{1cm} \text{C} \hspace{1cm} \text{H}
\]

Alkynes are hydrogenated more easily than alkenes mainly because alkynes are adsorbed more readily on the catalyst surface. Hydrogenation proceeds in stages, first to the cis-alkene and then to the alkane. For example,

\[
\begin{align*}
\text{CH}_3\text{C}==\text{CCH}_3 \text{H}_2, \text{Pt} & \rightarrow \text{CH}_3\text{C}==\text{CCH}_3 \hspace{1cm} \text{H}_2, \text{Pt} & \rightarrow \text{CH}_3\text{CH}_3
\end{align*}
\]

2-butyne \hspace{1cm} \text{cis-2-butene} \hspace{1cm} \text{butane}

Normally, it is not possible to stop the hydrogenation of an alkyne at the alkene stage, but if the catalyst is suitably deactivated, addition to the triple bond can be achieved without further addition occurring to the resulting double bond. The preferred catalyst for selective hydrogenation of alkynes is palladium partially "poisoned" with a lead salt (Lindlar
catalyst). This catalyst shows little affinity for adsorbing alkenes and hence is ineffective in bringing about hydrogenation to the alkane stage:

\[
\text{CH}_3\text{C}≡\text{CCH}_3 \xrightarrow{\text{H}_2, \text{Lindlar catalyst (Pd-Pb)}} \text{CH}_3\text{C}≡\text{CCH}_3
\]

Aromatic hydrocarbons are hydrogenated with considerable difficulty, requiring higher temperatures, higher pressures, and longer reaction times than for alkenes or alkynes:

\[
\text{H}_2, \text{Ni} \quad 40 \text{ atm, } 170-230^\circ
\]

**Contributors**