

## Introduction to Catalysis

Ask the average person in the street what a catalyst is, and he or she will probably tell you that a catalyst is what one has under the car to clean up the exhaust. Indeed, the automotive exhaust converter represents a very successful application of catalysis; it does a great job in removing most of the pollutants from the exhaust leaving the engines of cars. However, catalysis has a much wider scope of application than abating pollution.

### Catalysis in Industry

Catalysts are the workhorses of chemical transformations in the industry. Approximately 85–90 % of the products of chemical industry are made in catalytic processes. Catalysts are indispensable in

- Production of transportation fuels in one of the approximately 440 oil refineries all over the world.
- Production of bulk and fine chemicals in all branches of chemical industry.
- Prevention of pollution by avoiding formation of waste (unwanted byproducts).
- Abatement of pollution in end-of-pipe solutions (automotive and industrial exhaust).

A catalyst offers an alternative, energetically favorable mechanism to the non-catalytic reaction, thus enabling processes to be carried out under industrially feasible conditions of pressure and temperature.

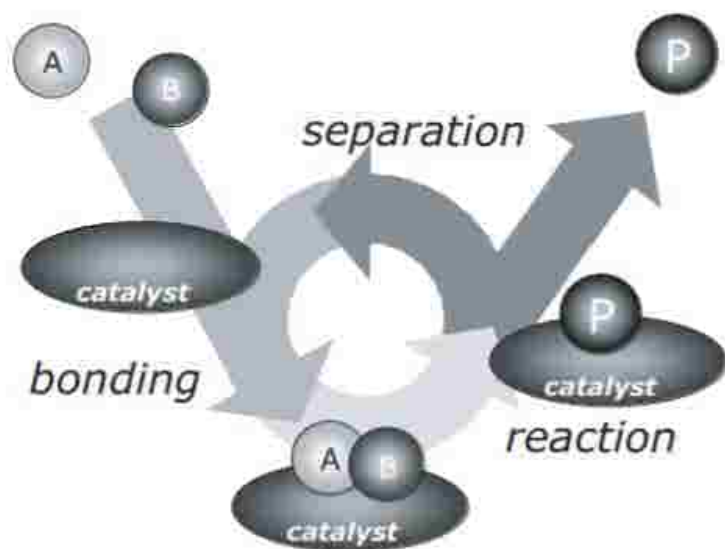
For example, living matter relies on enzymes, which are the most specific catalysts one can think of. Also, the chemical industry cannot exist without catalysis, which is an indispensable tool in the production of bulk chemicals, fine chemicals and fuels.

For scientists and engineers catalysis is a tremendously challenging, highly multidisciplinary field. Let us first see what catalysis is, and then why it is so important for mankind.

## What is Catalysis?

A catalyst accelerates a chemical reaction. It does so by forming bonds with the reacting molecules, and by allowing these to react to a product, which detaches from the catalyst, and leaves it unaltered such that it is available for the next reaction. In fact, we can describe the catalytic reaction as a cyclic event in which the catalyst participates and is recovered in its original form at the end of the cycle.

Let us consider the catalytic reaction between two molecules A and B to give a product P, see Fig. 1.1. The cycle starts with the bonding of molecules A and B to the catalyst. A and B then react within this complex to give a product P, which is also bound to the catalyst. In the final step, P separates from the catalyst, thus leaving the reaction cycle in its original state.

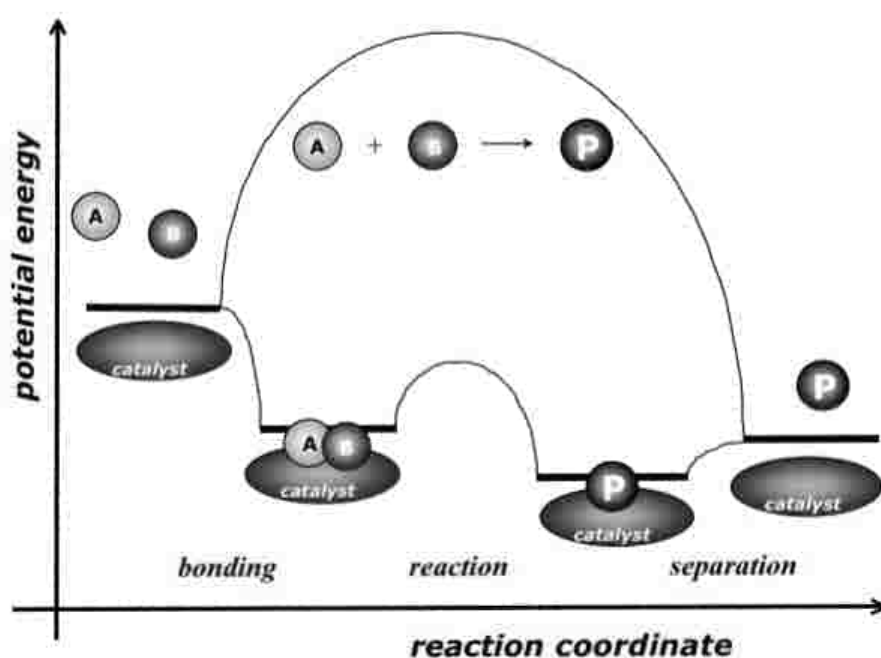


**Figure 1.1.** Every catalytic reaction is a sequence of elementary steps, in which reactant molecules bind to the catalyst, where they react, after which the product detaches from the catalyst, liberating the latter for the next cycle.

To see how the catalyst accelerates the reaction, we need to look at the potential energy diagram in Fig. 1.2, which compares the non-catalytic and the catalytic reaction. For the non-catalytic reaction, the figure is simply the familiar way to visualize the Arrhenius equation: the reaction proceeds when A and B collide with sufficient energy to overcome the activation barrier in Fig. 1.2. The change in Gibbs free energy between the reactants, A + B, and the product P is  $\Delta G$ .

The catalytic reaction starts by bonding of the reactants A and B to the catalyst, in a spontaneous reaction. Hence, the formation of this complex is exothermic, and the free energy is lowered. There then follows the reaction between A and B while they are bound to the catalyst. This step is associated with an activation energy; however, it is significantly lower than that for the uncatalyzed reaction. Finally, the product P separates from the catalyst in an endothermic step.





**Figure 1.2.** Potential energy diagram of a heterogeneous catalytic reaction, with gaseous reactants and products and a solid catalyst. Note that the uncatalyzed reaction has to overcome a substantial energy barrier, whereas the barriers in the catalytic route are much lower.

The energy diagram of Fig. 1.2 illustrates several important points:

- The catalyst offers an alternative path for the reaction, which is obviously more complex, but energetically much more favorable.
- The activation energy of the catalytic reaction is significantly smaller than that of the uncatalyzed reaction; hence, the rate of the catalytic reaction is much larger (we explain this in greater detail in Chapter 2).
- The overall change in free energy for the catalytic reaction equals that of the uncatalyzed reaction. Hence, the catalyst does not affect the equilibrium constant for the overall reaction of  $A + B$  to  $P$ . Thus, if a reaction is thermodynamically unfavorable, a catalyst cannot change this situation. A catalyst changes the kinetics but *not* the thermodynamics.
- The catalyst accelerates both the forward and the reverse reaction to the same extent. In other words, if a catalyst accelerates the formation of the product  $P$  from  $A$  and  $B$ , it will do the same for the decomposition of  $P$  into  $A$  and  $B$ .

Thus far it is immediately evident that there are also cases in which the combination of catalyst with reactants or products will not be successful:

- If the bonding between reactants and catalyst is too weak, there will be hardly any conversion of  $A$  and  $B$  into products.
- Conversely if the bond between the catalyst and one of the reactants, say  $A$ , is too strong, the catalyst will be mostly occupied with species  $A$ , and  $B$  is not available to form the product. If  $A$  and  $B$  both form strong bonds with the catalyst, the intermediate situation with  $A$  or  $B$  on the catalyst may be so stable that reaction becomes unlikely. In terms of Fig. 1.2, the second level lies so deep that the activa-