# Catalysis: Dr. Keshar Prasain

Berzelius in 1836 found that there are substances that increase the rate of a chemical reaction without themselves being consumed. He believed that the function of such substance was to weaken the bonds that hold the atoms in the reacting molecules together. Thus he coined the term catalyst for such substances. The word catalyst is derived from Greek word; **kata** = wholly and **lein** = to loosen.
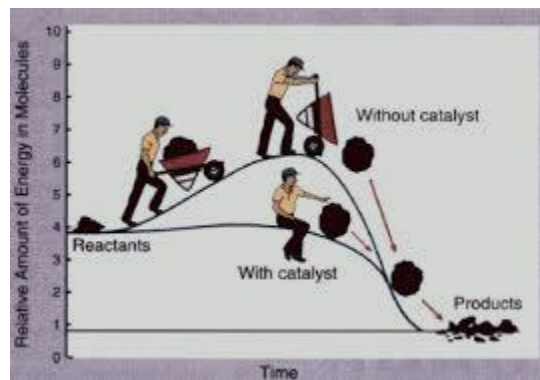
In most of the cases catalysts increase the rate of chemical reactions, but a number of cases are known in which catalysts are also found to decrease the rate of reactions. Thus *a catalyst is defined as a chemical substance that alters the rate of a chemical reaction without itself undergoing any change in mass and its chemical composition.*

When potassium chlorate is heated, it melts at about 340°C but no oxygen is evolved. It decomposes to evolve oxygen only around 600°C. However, on the addition of a little amount of manganese dioxide it decomposes even below its melting point producing oxygen. Furthermore, after the decomposition is over, no change is observed in the quantity and composition of manganese dioxide. In this reaction manganese dioxide is a catalyst. Similarly, hydrogen and oxygen at room temperature do not react for years but in the presence of small amount of platinum black, they react at room temperature to give water. In this case, platinum black is a catalyst.

The use of catalyst in industrial production of chemicals minimizes the production cost by lowering the consumption of energy and also by making the reaction fast. Annually, billions of dollars are saved globally by the use of catalyst. More than 95% of the chemical produced in the world use catalyst in one or more steps of the reactions.
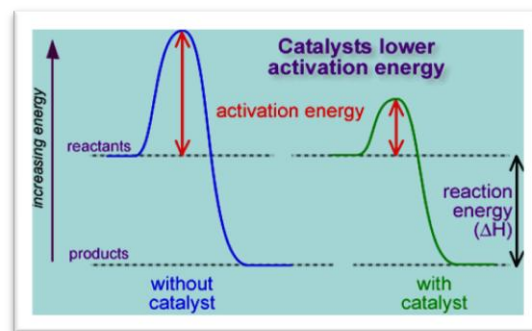

Catalysts increase the rate of reaction by providing alternative reaction pathway with lower activation energy so more reactant molecules can cross the activation energy barrier at any given concentration and temperature.

As evident from the definition, a catalyst may increase or decrease the rate of reaction. **A catalyst that increases the rate of reaction is known as positive catalyst and the process is positive catalysis.** Most of the used catalysts are positive catalysts. Few examples of positive catalysts are mentioned below:
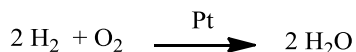
1. Manganese dioxide as a catalyst accelerates the decomposition of potassium chlorate to liberate oxygen.

$$2\ KClO_3 \xrightarrow{\ MnO_2\ } 2\ KCl\ +\ 3O_2$$
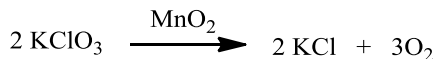
2. Platinum as a catalyst accelerates the decomposition of hydrogen peroxide.

$$2\ H_2O_2 \xrightarrow{\ Pt\ } 2\ H_2O\ +O_2$$
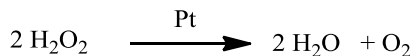
3. Platinum black as a catalyst accelerates the combination of hydrogen and oxygen to form water.

$$2\ H_2\ +O_2 \xrightarrow{\ Pt\ } 2\ H_2O$$

Similarly, **the catalyst that decreases the rate of reaction is known as negative catalyst or inhibitor and the process is known as negative catalysis or inhibition.** Negative catalysts are useful to slow down or stop any unwanted reactions. Few examples of negative catalysts are mentioned below:

1. The presence of 1-2% ethanol as catalyst, suppresses the oxidation of chloroform with oxygen to give a poisonous gas called phosgene.

$$4\ CHCl_3\ +\ 3O_2 \xrightarrow{\ 1\%\ ethanol\ } 4\ COCl_2\ +\ 2H_2O\ +\ 2\ Cl_2 \qquad \text{(slows down)}$$

2. The decomposition of hydrogen peroxide is suppressed by adding glycerol to the solution of hydrogen peroxide. Here glycerol acts as negative catalyst.

$$2\ H_2O_2 \xrightarrow{\ glycerol\ } 2\ H_2O\ +O_2 \qquad \text{(slows down)}$$
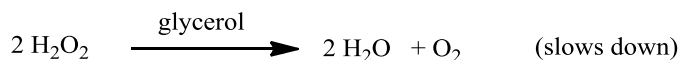
Criteria or characteristics of catalysts

   i.   The mass and chemical composition of catalyst should remain unchanged at the end of the reaction.

   ii.   A small amount of catalyst is enough to bring about an appreciable change in the rate of chemical reaction. For example, even 1 mg of fine platinum powder is enough to catalyze the combination of 2.5 liters of a mixture of hydrogen and oxygen to form water. However, there are some reactions that uses significant amount of catalyst.

   iii.   For solid catalyst, the use in powder form increases the activity of catalyst by increasing its surface area.

   iv.   For a reversible reaction, catalyst does not change the position of equilibrium but helps to attain the equilibrium faster.

   v.   Catalysts are specific in action (like a key can open a particular lock). For example, manganese dioxide can catalyze the decomposition of potassium chlorate but not potassium nitrate or other substances. A catalyst

effective in altering the rate of one reaction may not be necessarily effective in another reaction. The same reactants may give different product with different catalyst.

$$C_2H_5OH \xrightarrow{Al_2O_3} C_2H_4 + H_2O$$
$$\text{ethene}$$

$$C_2H_5OH \xrightarrow{Cu} CH_3CHO + H_2$$
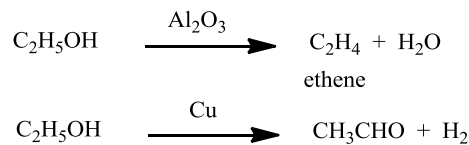
vi.   Catalyst by itself does not initiate a reaction. They only make the reaction fast.

vii.   A catalyst is most active at a particular temperature known as optimum temperature.

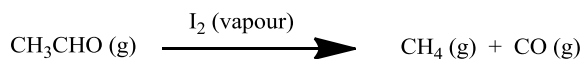## Homogenous and Heterogeneous Catalyst

Depending upon the state of reactant(s) and catalyst, the catalysts are divided into two major types:

Homogenous Catalyst: If the reactants and the catalyst are in the same phase, then the catalyst is homogenous catalyst and the process is homogenous catalysis. Examples:
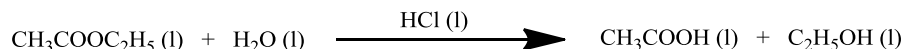
1. In lead chamber process for the manufacture of H_2SO_4, nitric oxide catalyses the oxidation of sulphur dioxide.

$$2\ SO_2\ (g)\ +\ O_2\ (g) \xrightarrow{NO\ (g)} 2\ SO_3\ (g)$$
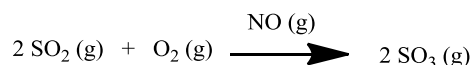
2. Decomposition of acetaldehyde is catalyzed by iodine vapours.

$$CH_3CHO\ (g) \xrightarrow{I_2\ (vapour)} CH_4\ (g)\ +\ CO\ (g)$$

3. Hydrolysis of ethyl acetate with acid.

$$CH_3COOC_2H_5\ (l)\ +\ H_2O\ (l) \xrightarrow{HCl\ (l)} CH_3COOH\ (l)\ +\ C_2H_5OH\ (l)$$

*Heterogeneous Catalyst:* If the reactants and the catalyst are in different phase, then the catalyst is heterogeneous catalyst and the process is heterogeneous catalysis. Examples:

1. In contact process for the manufacture of sulphuric acid, sulphur dioxide is directly oxidized to sulphur trioxide by atmospheric oxygen in the presence of platinum or vanadium pentaoxide as catalyst.

$$2\ SO_2\ (g)\ +\ O_2\ (g) \xrightarrow{Pt\ (s)\ or\ V_2O_5\ (s)} 2\ SO_3\ (g)$$
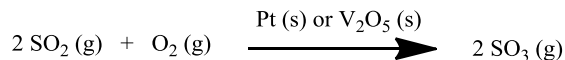
2. In Haber's process for the manufacture of ammonia, nitrogen and hydrogen in the volume ration of 1:3 are passed over heated iron catalyst, which contain molybdenum as promoter.

$$N_2\ (g)\ +\ 3\ H_2\ (g) \xrightarrow[Mo]{Fe\ (s)} 2\ NH_3\ (g)$$
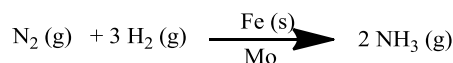
3. Hydrogenation of unsaturated hydrocarbons in presence of nickel as a catalyst.

$$CH_2=CH_2 \text{ (g)} + H_2\text{(g)} \xrightarrow{\text{Ni (s)}} CH_3\text{-}CH_3 \text{ (g)}$$
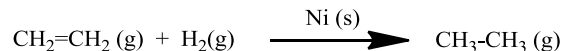
Activation Energy and Catalysis

According to the collision theory of reaction rates, a chemical reaction occurs by the collisions between the reactant molecules. However, all the collisions are not effective and only a fraction of the collisions brings about a reaction. A collision will be fruitful only when colliding molecules collide with sufficient kinetic energy and with proper orientation.
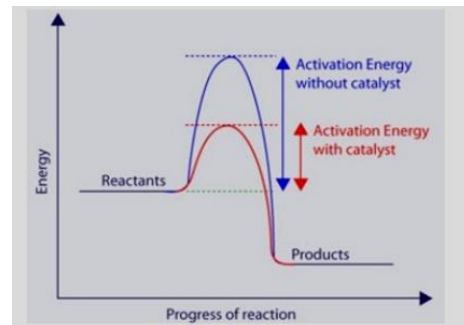

At ordinary temperature, the molecules do not possess enough energy and hence the collisions are not effective. The molecules do not react unless they attain a minimum amount of energy known as the activation energy. **Activation energy is the minimum energy the reacting molecule must possess to cause a chemical reaction.** But when the temperature of the system is raised, the kinetic energy of molecules increases. By doing so, the molecules possess the activation energy and then collide to form an activated complex or transition state. The activated complex then decomposes to from product(s).

A catalyst lowers the activation energy of the reaction by providing a new pathway. As a result, presence of the catalyst makes the reaction go faster.
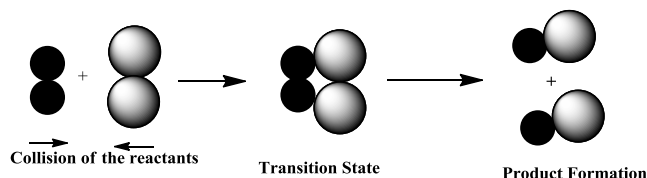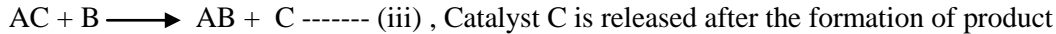

Theories of Catalysis

A. Intermediate Compound Formation Theory

In 1806 Clement and Desormes introduced this theory for homogenous catalysis. In the chemical reaction catalyst lowers the activation energy by providing a new pathway. According to this theory, the catalyst initially combines with one of the reactants forming an intermediate compound which is highly reactive (unstable). The intermediate compound then reacts with the other reactant to form product and release the catalyst.

Let us consider a reaction;

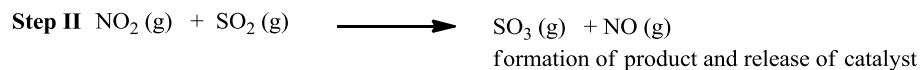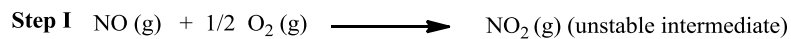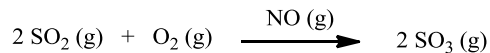$$A + B \xrightarrow{\text{C}} AB \text{------- (i)}$$
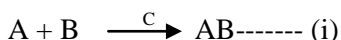
According to this theory, the reactant A first combines with catalyst C to form highly reactive intermediate compound AC. Then the intermediate compound reacts with reactant B to give product AB and release catalyst C as following:
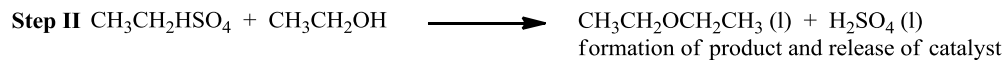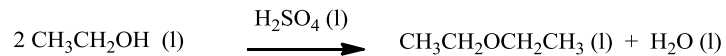
$A + C \longrightarrow AC$ ------- (ii), AC is highly unstable intermediate

$AC + B \longrightarrow AB + C$ ------- (iii) , Catalyst C is released after the formation of product

The activation energy for reaction (ii) and (iii) should be lesser than that of reaction (i).

Examples:

1. Catalytic oxidation of SO_2 in the presence of NO as catalyst.

$$2\ SO_2\ (g)\ +\ O_2\ (g) \xrightarrow{\quad NO\ (g)\quad} 2\ SO_3\ (g)$$

Step I $\quad NO\ (g)\ +\ 1/2\ O_2\ (g) \longrightarrow NO_2\ (g)$ (unstable intermediate)

Step II $NO_2\ (g)\ +\ SO_2\ (g) \longrightarrow SO_3\ (g)\ + NO\ (g)$
formation of product and release of catalyst

2. Preparation of diethyl ether from ethanol using concentrated sulphuric acid.

$$2\ CH_3CH_2OH\ (l) \xrightarrow{\quad H_2SO_4\ (l)\quad} CH_3CH_2OCH_2CH_3\ (l)\ +\ H_2O\ (l)$$

Step I $\quad CH_3CH_2OH\ +\ H_2SO_4 \longrightarrow CH_3CH_2HSO_4\ +\ H_2O$

Step II $CH_3CH_2HSO_4\ +\ CH_3CH_2OH \longrightarrow CH_3CH_2OCH_2CH_3\ (l)\ +\ H_2SO_4\ (l)$
formation of product and release of catalyst

B. Adsorption Theory

This theory has been developed to explain the mechanism of a reaction between two gases catalyzed by a solid catalyst, i.e., heterogeneous catalysis. In this process, the reaction is initiated by the adsorption of reactant molecules on the surface of the catalysts. The adsorption process results from the residual forces on the catalyst surface.

Let us consider a reaction;

$A\ (g) +\ B\ (g) \longrightarrow C\ (g)\ +\ D\ (g)$
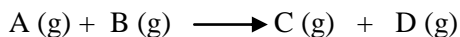
It involves the following steps:

Step I: Adsorption of reactant molecules

The reactant molecules A and B strike on the catalyst surface. The reactants molecules adsorb on the surface by weak Vander Waals forces or by partial chemical bond.

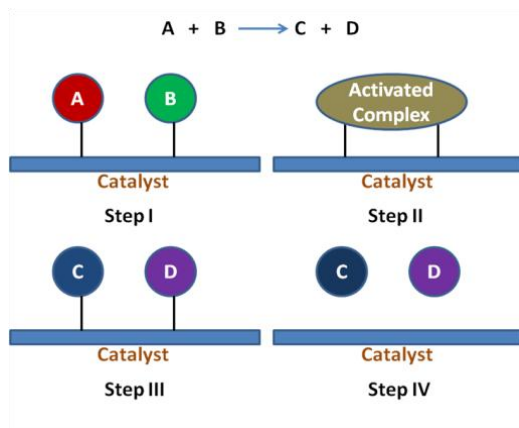**Step II: Formation of activated complex**

The adsorbed reactants combine together to give intermediate activated complex which is unstable.

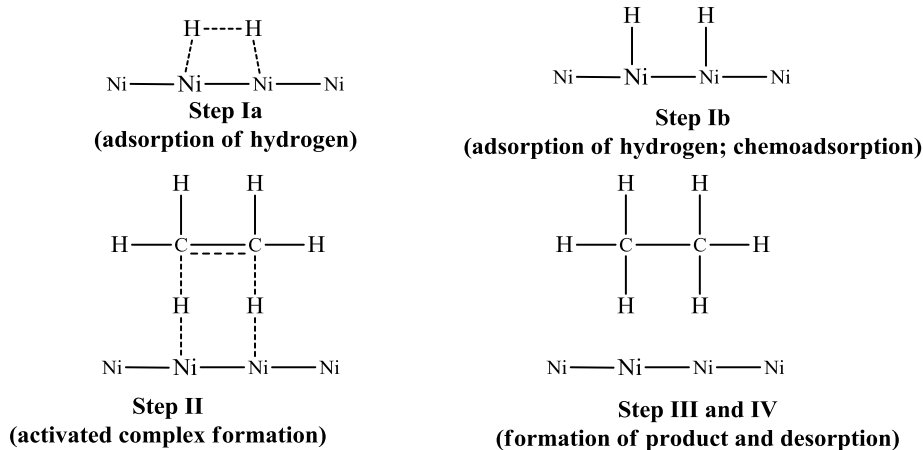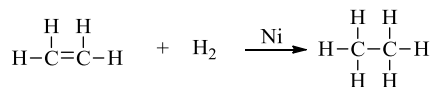**Step III: Decomposition of activated complex or formation of product**

The unstable activated complex decomposes to form product, which are held to the catalyst surface by weak force or chemical bond.

Step IV: Desorption of products

The products are desorbed or released from the surface of the catalyst. The products are stable and can exist independently.

Example: Hydrogenation of alkene in the presence of Nickel catalyst

Step Ia
(adsorption of hydrogen)

Step Ib
(adsorption of hydrogen; chemoadsorption)

Step II
(activated complex formation)

**Step III and IV**
(formation of product and desorption)

Promoters

A substance which itself is not a catalyst but promotes the activity of a catalyst is known as catalytic promoter or activator. For example; in the manufacture of ammonia by Haber's process, finely divided iron acts as a catalyst and molybdenum acts as a promoter.

$$N_2 \text{ (g)} + 3 H_2 \text{ (g)} \xrightarrow[\text{Mo}]{\text{Fe (s)}} 2 NH_3 \text{ (g)}$$
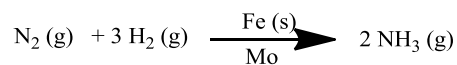
Lattice spacing

Explanation: With the addition of promoter in the catalyst, the lattice space of the catalyst is changed and increases the space between the catalyst particles. This result in the weakening and cleavage of the bonds of the reactant molecules making the reaction go faster. The presence of promoter also increases the peaks, cracks and corners on the catalyst surface increasing its surface area.
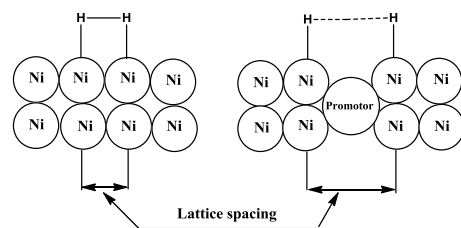
Catalytic Poisons

The substance that destroys the activity of catalyst even in the presence of trace amount is known as catalytic poison.

Explanation: The catalytic poison is adsorbed on the catalytic surface with more preference than the reactants. Therefore, the reactants are not allowed to get adsorbed on the catalyst. For example CO is preferentially bonded to the platinum surface not allowing hydrogen and oxygen to get adsorbed on the surface and prevent the reaction.

$$2 H_2 + O_2 \xrightarrow[\substack{\text{Poisoned} \\ \text{by CO}}]{\text{Pt}} 2 H_2O$$
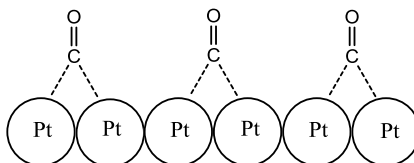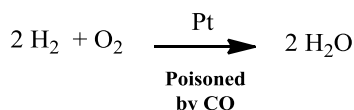
The poison may chemically react with the catalyst resulting in the loss of catalyst activity. For example, in Haber's process, the presence of H_2S poisons the activity of Fe by reacting with it to form FeS. The formed FeS is not capable in catalyzing the reaction.

$$Fe + H_2S \longrightarrow FeS + H_2$$
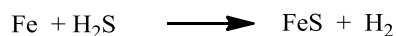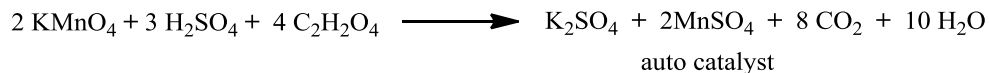
Auto-catalyst

If one of the products formed in the reaction is capable of catalyzing the reaction in which it is produced, this is called auto-catalyst and the phenomenon is known as auto catalysis. Reactions involving auto catalysts are slower in the beginning and gets faster later.

Examples:

1. In the hydrolysis of ethyl acetate, acetic acid (one of the product) acts as a catalyst.

$$CH_3COOC_2H_5 \ + \ H_2O \longrightarrow CH_3COOH \ + \ C_2H_5OH$$
<div align="center">auto catalyst</div>

2. In the decomposition of oxalic acid by $KMnO_4$, the Mn^{++} ions formed in the product (from $MnSO_4$) acts as a catalyst.

$$2 \ KMnO_4 + 3 \ H_2SO_4 + \ 4 \ C_2H_2O_4 \longrightarrow K_2SO_4 \ + \ 2MnSO_4 \ + \ 8 \ CO_2 \ + \ 10 \ H_2O$$
<div align="center">auto catalyst</div>

Criteria for choosing a catalyst for industrial application

  i.   It should be cheap and easily available.

 ii.   It should be stable under the reaction conditions.

iii.   It should be selective so that the desired product is the major product.

 iv.   It should possess maximum possible activity for the reaction under consideration in terms of the yield of the desired product.

Use of catalyst in industrial process

Process	Catalyst
1. Haber's process for the manufacture of ammonia.	Finely divided iron. Molybdenum as promoter.
2. Ostwald's process for the manufacture of nitric acid.	Platinished asbestos
3. Lead chamber process for the manufacture of sulphuric acid.	Nitric oxide.
4. Contact process for the manufacture of sulphuric acid.	Platinised asbestos or vanadium pentoxide (V_2O_5).
5. Deacon's process for the manufacture of chlorine.	Cupric chloride $(CuCl_2)$
6. Bosch's process for the manufacture of hydrogen.	Ferric oxide (Fe_2O_3). Chromic oxide as a promoter.
7. Hydrogenation of vegetable oils $Oil + H_2 \rightarrow$ Vanaspati ghee	Nickel (finely divided).
8. Bergius process for the synthesis of petrol from coal.	Ferric oxide (Fe_2O_3)