Types of catalysis.

Catalytic reactions can be broadly divided into the following types,

(1) **Homogeneous catalysis:** When the reactants and the catalyst are in the same phase (i.e. solid, liquid or gas). The catalysis is said to be **homogeneous**. The following are some of the examples of homogeneous catalysis.

(i) Oxidation of sulphur dioxide into sulphur trioxide with oxygen in the presence of oxides of nitrogen as the catalyst in the lead chamber process. $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$

The reactants, products and catalyst all are in gaseous state i.e. same phase.

(ii) Hydrolysis of methyl acetate is catalyzed by H^+ ions furnished by hydrochloric acid.

$$CH_3COOCH_3(l) + H_2O(l) \xrightarrow{HCl(l)} CH_3COOH(l) + CH_3OH(l)$$

(iii) Hydrolysis of sugar is catalyzed by H^+ ions furnished by sulphuric acid.

$$\underset{\text{(Sucrose solution)}}{C_{12}H_{22}O_{11}(l)} + H_2O(l) \xrightarrow{H_2SO_4(l)} \underset{\text{(Glucose solution)}}{C_6H_{12}O_6(l)} + \underset{\text{(Fructose solution)}}{C_6H_{12}O_6(l)}$$

(2) **Heterogeneous catalysis:** The catalytic process in which the reactants and the catalyst are in different phases is known as **heterogeneous catalysis.** Some of the examples of heterogeneous catalysis are given below.

(i) Oxidation of sulphur dioxide into sulphur trioxide in the presence of platinum metal or vanadium pentaoxide as catalyst in the contact process for the manufacture of sulphuric acid. The reactants are in gaseous state while the catalyst is in solid state.

$$2SO_2(g) + O_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$$

(ii) Combination between nitrogen and hydrogen to form ammonia in the presence of finely divided iron in **Haber's process.**

$$N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

(iii) Oxidation of ammonia into nitric oxide in the presence of platinum gauze as a catalyst in **Ostwald's process.**

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt(s)} 4NO(g) + 6H_2O(g)$$

(iv) Hydrogenation of vegetable oils in the presence of finely divided nickel as catalyst.

$$\text{Vagetable oils}(l) + H_2(g) \xrightarrow{Ni(s)} \text{Vegetable Ghee}(g)$$

(3) **Positive catalysis:** When the rate of the reaction is accelerated by the foreign substance, it is said to be a **positive catalyst** and phenomenon as **positive catalysis.** Some examples of positive catalysis are given below.

(i) Decomposition of H_2O_2 in presence of colloidal platinum.

$$2H_2O_2(l) \xrightarrow{Pt} 2H_2O(l) + O_2(g)$$

(ii) Decomposition of $KClO_3$ in presence of manganese dioxide.

$$2KClO_3(s) \xrightarrow[270^oC]{MnO_2(s)} 2KCl(s) + 3O_2(g)$$

(iii) Oxidation of ammonia in presence of platinum gauze.

$$4NH_3(g) + 5O_2(g) \xrightarrow[300^oC]{Pt(s)} 4NO(g) + 6H_2O(g)$$

(iv) Oxidation of sulphur dioxide in presence of nitric oxide.

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

(v) Oxidation of sulphur dioxide in presence of platinized asbestos or vanadium pentaoxide.

$$2SO_2(g) + O_2(g) \xrightarrow[or\ Pt(s)]{V_2O_5(s)} 2SO_3(g)$$

(vi) Oxidation of hydrochloric acid into chlorine by **Deacon's process** in presence of $CuCl_2$.

$$4HCl(g) + O_2(g) \xrightarrow[450^oC]{CuCl_2(s)} 2Cl_2(g) + 2H_2O(g)$$

(vii) Formation of methane in presence of nickel. $CO(g) + 3H_2(g) \xrightarrow{Ni(s)} CH_4(g) + H_2O(g)$

(viii) Synthesis of ammonia by **Haber's process** in presence of a mixture of iron and molybdenum.

$$N_2(g) + 3H_2(g) \xrightarrow[450-500^oC]{Fe(s)\&\ Mo(s)} 2NH_3(g)$$

(ix) Hydrogenation of vegetable oil in presence of nickel.

$$\text{Vegetable oil}\ (l) + H_2(g) \xrightarrow{Ni(S)} \text{Ghee}\ (s)$$

(x) Manufacture of methyl alcohol in presence of ZnO / Cr_2O_3.

$$CO(g) + 2H_2(g) \xrightarrow[Cr_2O_3(s)]{ZnO(g)\,250^0C} CH_3OH(g)$$

Note:Positive catalyst increases the rate by lowering activation energy of reaction. Catalyst changes the mechanism by changing the intermediate i.e. intermediate of low energy is formed. It increases the rate by converting some inactive molecule into active one.

(4) **Negative catalysis:** There are certain, substance which, when added to the reaction mixture, retard the reaction rate instead of increasing it. These are called **negative catalyst** or **inhibitors** and the phenomenon is known as **negative catalysis**. Some examples are as follows.

(i) The oxidation of sodium sulphate by air is retarded by alcohol. Alcohol acts as a negative catalyst

$$2Na_2SO_3(s)O_2(g) \xrightarrow{Alcohol\,(l)} 2Na_2SO_4(s)$$

(ii) The oxidation of chloroform by air is retarded it some alcohol is added to it.

$$2CHCl_3(l) + O_2(g) \xrightarrow{Alcohol\,(l)} 2COCl_2(g) + 2HCl(g)$$

(iii) The oxidation of benzaldehyde is retarded if some diphenyl amine is added. It acts as a negative catalyst.

$$2C_6H_5CHO(l) + O_2(g) \xrightarrow[amine\,(l)]{Diphenyl} 2C_6H_5COOH(l)$$

(iv) Addition of small amount of acetanilide or glycerin slow down the decomposition of hydrogen peroxide.

(v) Tetra ethyl lead (TEL) is added to petrol to retard the ignition of petrol vapors on compression in an internal combustion engine and thus minimize the **knocking effect.**

(5) **Auto-catalysis:** In certain reactions, one of the product acts as a catalyst. In the initial stages the reaction is slow but as soon as the products come into existences the reaction rate increases. This type of phenomenon is known as **auto-catalysis.** Some examples are as follows,

(i) The rate of oxidation of oxalic acid by acidified potassium permanganate increases as the reaction progresses. This acceleration is due to the presence of Mn^{2+} ions which are formed during reaction. Thus Mn^{2+} ions act as auto-catalyst.

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$

(i) When nitric acid is poured on copper, the reaction is very slow in the beginning, gradually the reaction becomes faster due to the formation of nitrous acid during the reaction which acts as an auto-catalyst.

(iii) In hydrolysis of ethyl acetate, acetic acid and ethyl alcohol are formed. The reaction is initially very slow but gradually its rate increases. This is due to formation of acetic acid which acts as an auto-catalyst in this reaction.

(6) **Induced catalysis:** When one reaction influences the rate of other reaction, which does not occur under ordinary conditions, the phenomenon is known as **induced catalysis.** Some examples are as follows,

(i) Sodium arsenite solution is not oxidized by air. If, however, air is passed through a mixture of the solution of sodium arsenite and sodium sulphate, both of them undergo simultaneous oxidation. The oxidation of sodium sulphate, thus, induces the oxidation of sodium arsenite.

(ii) The reduction of mercuric chloride $(HgCl_2)$ with oxalic acid is very slow, but potassium permanganate is reduced readily with oxalic acid. If, however, oxalic acid is added to a mixture of potassium permanganate and $HgCl_2$ both are reduced simultaneously. The reduction of potassium permanganate, thus, induces the reduction of mercuric chloride.

(7) **Acid-base catalysis:** According to the **Arrhenius** and **Ostwald** H^+ or H^- ion act as a catalyst.

(i) For example, Hydrolysis of an ester,

$$CH_3COOC_2H_5(l) + H_2O(l) \xrightarrow[OH^-]{H^+ or} CH_3COOH(l) + C_2H_5OH(l)$$

(ii) Inversion of cane sugar, $\underset{\text{Sugar}}{C_{12}H_{22}O_{11}(l)} + H_2O \xrightarrow{H^+} \underset{\text{Fructose}}{C_6H_{12}O_6(l)} + \underset{\text{Glucose}}{C_6H_{12}O_6(l)}$

(iii) Conversion of acetone into diacetone alcohol,

$$CH_3COCH_3(l) + CH_3COCH_3(l) \xrightarrow{OH^-} CH_3COCH_2.C(CH_3)_2OH(l)$$

(iv) Decomposition of nitramide, $NH_2NO_2(l) \xrightarrow{OH^-} N_2O(g) + H_2O(l)$

Note:All **Bronsted** acids and bases act as acid base catalysts.

Catalytic converter for an automobile: The catalytic converter in the exhaust systems of cars, which converts polluting exhaust gases into non-toxic gases contains a **heterogeneous catalyst.** Mixtures of transition metals and their oxides embedded in inert supports act as catalyst. When the gases are passed through the catalyst bed, carbon monoxide (CO) and unburnt petrol are oxidized to carbon dioxide and water while nitric oxide (NO)is reduced to N_2 as,

$2CO + O_2 \xrightarrow{\text{Catalyst}} 2CO_2$; Hydrocarbo ns $\xrightarrow[O_2]{\text{Catalyst}} CO_2 + H_2O$;
(Unburnt petrol)

$2NO \xrightarrow{Catalyst} N_2 + O_2$