CATALYSIS

A catalysis is defined as a substance which increases the rate of the reaction without undergoing any charge and can be recovered at the competition of reaction.
The phenomenon of increase in the rate of a reaction with the help of a catalyst is known as catalyst .

1) Positive catalyst: - when a catalyst accelerates the speed of reaction it is called as positive catalyst.
   Eg: MnO_2 in the decomposition of $KClO_3$ and kcl and O_2

2) Negative catalyst: - if the catalytic substance retards the chemical reaction is called negative catalyst.
   Eg: alcohol retards the oxidation of chloroform.

3) Auto catalyst: - when a product formed in the course of reaction .The phenomenon is called as auto catalyst.
   Eg: hydrolysis of an ester by water is an auto catalytic process.

Characteristic of catalyst

- A catalyst remains unchanged in mass and chemical composition at the end of the reaction.
- A small amount of catalyst is sufficient to bring about an appreciable change in the velocity of the reaction.
- A catalyst can only alter the speed of reaction but does not affect the final state of the equilibrium. Since it alters the rate of forward as well as backward reaction to the same extent, thereby the composition of the equilibrium mixture remains the same.
- A catalyst can exert a selective action like a key can open a particular lock.
- According to ostwards, a catalyst cannot be a reaction but it can only decrease or increase its rate.
- A catalyst is most active at a particular temperature called the optimum temperature.
- The addition of a small amount of foreignsubstance, which are not themselves catalytically active, sometimes increases the activity of catalyst.
- The activity of a catalyst is inhibited or completely destroyed by the presence of even minute traces of a certain substance called catalytic poison or anti catalyst.

TYPES OF CATALYST

Homogeneous catalyst: - In this the catalyst is present in the same phase as the reacting substance.

Eg:-GAS PHASE.

Nitric Oxide acts as a catalyst in the combination of carbon monoxide and oxygen.

NO (g)

$$2CO + O_2 \longrightarrow 2CO_2$$

LIQUID PHASE:

In acid - base catalysis

EX :) Inversion of cane sugar by hydrolysis of ester.

H_3O^+

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

Heterogeneous catalyst :- In such a reaction the catalyst is present in a different phase from the reacting substance .

Eg : in contact process for the manufacture of H_2SO_4 sulphur dioxide is directly oxidized to sulphur trioxide by atmospheric oxygen in the presence of platinum or vanadium pentoxide as catalyst .

$Pt\backslash V_2O_3$

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

In haber's process for the manufacture of NH3 , nitrogen and hydrogen in the volume ratio of 1:3 are passed over the heated iron catalyst , which contains a promoter [molybdenum]

Fe

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Mo

THEORIES OF CATALYST

To explain the mechanism of the catalyst the following two theories have been forwarded .

1} Unstable intermediate compound formation theory

According to this theory the catalyst forms a very reactive and unstable intermediate compound with reactants ,which immediately reacts with other reactants yielding the products of the reaction and liberating the catalyst in its original chemical composition .

Thus, the reaction of type $A + B \rightarrow AB$ which take place in the presence of catalyst , K may occurs as ,

$A + B = AK$ [intermediatecompound]

$AK + B = AB + K$

[product] [catalyst]

Eg : - Catalytic action of NO in the manufacture of H_2SO_4 by chamber process .

$2NO + O_2 = NO_2$

(catalyst) (reactant) (intermediate product)

$2SO_2 + 2NO_2 = 2SO_3 + [NO]$

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Other reactant

$[2NO] + 2SO_2 + O_2 = 2SO_3 + 2[NO]$

-ADSORPTION OR CONTACT THEORY

According to this theory

- The surface of the solid catalyst processes some isolated active spots [or centres] having residue affinity or free unsatisfied valancy forces .
- Due to these free unsatisfied valency forces on the catalyst surface the molecule of the gaseous reactants got absorbed in the unimolecular thickness layer .
- The adsorbed molecules react due to their close proximity ,forming products .
- The chemical action accelerated on account of increased concentration of the reacting substances .
- The forces which keep the molecule of reactants intact with catalysts also attract the reacting molecules .
  Example : Reaction between ethene and hydrogen in the presence of nickel catalyst ‘
  Ni

$$CH_2=CH_2 + H_2 \rightarrow CH_2CH_3$$

NOTE

1 Ethene molecules are absorbed on the surface of the nickel. The double bond between the carbon atoms breaks and the electrons are used to bond it to the nickel surface . fig(a)

2 Hydrogen molecules are also adsorbed on the surface of the nickel . When this happens the hydrogen molecules are broken into atoms .fig (b)

3 If a hydrogen atom diffuses close to one of the bonded carbons the bond between the carbon & nickel is replaced by one between carbon & hydrogen. [fig(1)]

4 The end of the original ethene now breaks free of the surface and eventually the same thing will happen at the other end. [fig(d)}

5 As before, one of the hydrogen atoms forms a bond with the carbon and that end also breaks free. [Fig(e)]

ETHENE MOLECULE ABSORBED TO THE SURFACE OF NICKEL:

INDUSTRIAL APPLICATION OF CATALYST:-

➔ Hydrogen industry (coal, hydrogenation)
➔ Natural gas processing.
➔ Petroleum refining.
➔ Petrochemical.

➔ Fine chemicals (pharma, agrochemical, fragrance, textile coating, laundry etc)
➔ Environmental catalyst (sub exhaust)

- Manufacture of H_2 from water gas and steam :

  $CO + H_2 + H_2O \rightarrow CO_2 + H_2O$

(water gas)

Catalyst: $Fe_2O_3 + Cr_2O_3$ (promoter) at 400- 450°C

- Manufacture of NH_3 of (Haber's process)

$N_2 + 3H_2 \rightarrow 2NH_3$

Fe catalyst: $Al2O_3 + K_2O$ = promoter at 400°C

- Hydrogenation of of vegetable oil

  $-CH_2=CH + H_2 \rightarrow -CH_2-CH_2-$

  (oil) (fat)

  Catalyst - Nickel at 150-300°C

- Synthesis of CH_3OH

  $CO + H_2 + H_2 \rightarrow CH_3OH$

  ZnO catalyst + Cr_2O_3 (Promoter) 400- 450°C

- Oxidation of NH_3 to NO (Ostward process for HNO_3)

$4\ NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

Catalyst - Platinum gauze at 500°C

- Deacon's Process of Cl2 manufacture

$4HCl + O_2 \rightarrow 2CH_3COOH$

Catalyst - Cu2Cl2 (500°C)

- Oxidation of acetaldehyde to acetic acid by air

  $2CH_2CHO + O_2 \rightarrow 2CH_3COOH$

  Catalyst - manganous acetate or V_2O_5

PHASE TRANSFER CATALYST:

In chemistry, a phase transfer catalyst or PTC is a catalyst that facilitates the migration of reactants from one phase to another phase when reaction occurs.

Quaternary ammonium salts under this, phosphonium compounds.

Deactivation of catalyst or regeneration of a catalyst:

The catalyst poison preferentially adsorbs on the active sites of the catalyst, thereby reducing a number of active sites available for the adsorption as the molecule of the reaction.

Eg: In contact process for manufacture of sulfuric acid, catalytic poison AS_2S_3 adsorb on the active site of Pt forming Platinum sulphide, on the surface of Pt, thereby reducing the catalytic activity of Pt.

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