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Catalysis :-

A catalyst is a substance that changes the rate of a reaction but is recovered chemically unchanged at the end of the reaction & This phenomenon is known as catalysis.

Types of catalysis :

1. Positive catalysis
2. Negative catalysis

If a catalyst increases the rate of a reaction, it is called a positive catalyst & the phenomenon is called positive catalysis.

e.g i) Decomposition of potassium chlorate in presence of MnO_2 as catalyst.

$$2KClO_3(s) \xrightarrow{MnO_2(s)} 2KCl(s) + 3O_2(g)$$

ii) Oxidation of SO_2 to SO_3 using NO as catalyst

$$SO_2(g) + \frac{1}{2}O_2(g) \xrightarrow{NO(g)} SO_3(g)$$

iii) Manufacture of ammonia by Haber's process using finely divided iron as catalyst

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

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Specificity & Selectivity –

A catalyst is specific in nature. A particular substance may act as a catalyst for one reaction but the same substance may not act as catalyst even for a similar reaction. or They have an ability to direct the reaction to yield a particular product.

Selectivity – The reaction with same reactants but different catalyst may yield different products. This is termed as selectivity of catalyst. Catalysts are highly selective in nature. They can accelerate a particular reaction while inhibit another reaction. Hence, we can say a particular catalyst can catalyse one particular reaction only. It may fail to catalyse another reaction of the same type.

e.g Rxn. of hydrogen & carbon monoxide yields methane when nicked is used as catalyst, methanol when a mixture of zinc oxide and chromium oxide is used as catalyst & methanal when only copper is used as catalyst.

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e.g. (i) $CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$

ii) $CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO-Cr_2O_3} CH_3OH(g)$

iii) $CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$

Mechanisms of catalysed reactions at solid surfaces :-

When in a reaction, the catalyst is present in a different phase than that of the reactants, it is called heterogenous catalysis. The catalysts are usually solids whereas the reactants are gaseous or liquid. The reactions occur at the surface of the catalyst. That is why this type of catalysis is also called <u>surface catalysis</u>.

∴ greater is the surface area of the catalyst, greater is the efficiency of the catalyst. For this reason, finely divided solids are usually used as catalysts. As heterogenous catalysts stay in position & can be readily recovered, they are much more widely used in industry than the homogenous catalysts.

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Examples of Heterogenic Catalytic Reactions:-

i) Manufacture of ammonia from nitrogen and hydrogen using finely divided iron as catalyst

$$N_2(g) + 3H_2(g) \xrightarrow[\text{divided Fe}]{\text{Finely}} 2NH_3(g)$$

ii) Formation of SO_3 from SO_2 and O_2 in contact process in the manufacture of H_2SO_4 using finely divided Pt or Vanadium pentoxide as catalyst

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

iii) Hydrogenation of oils using finely divided nickel as catalyst.

Mechanism of Heterogenous catalytic Rxns (Adsorption theory):-

Heterogenous catalytic reactions takes place through the following sequence of steps:-

i) Diffusion of the reactant molecules towards the surface of the catalyst

ii) Adsorption of the reactant molecules on the surface of the solid.

iii) Chemical reaction of the adsorbed

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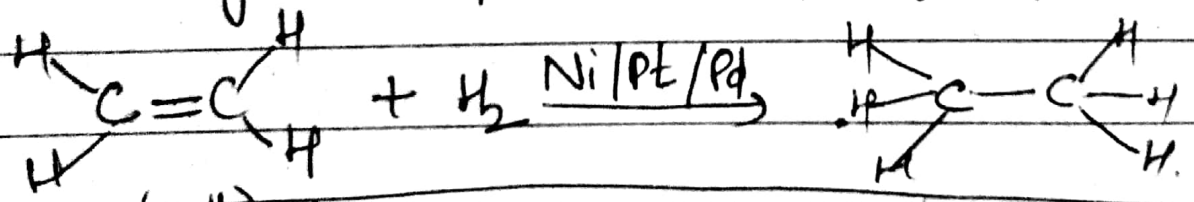
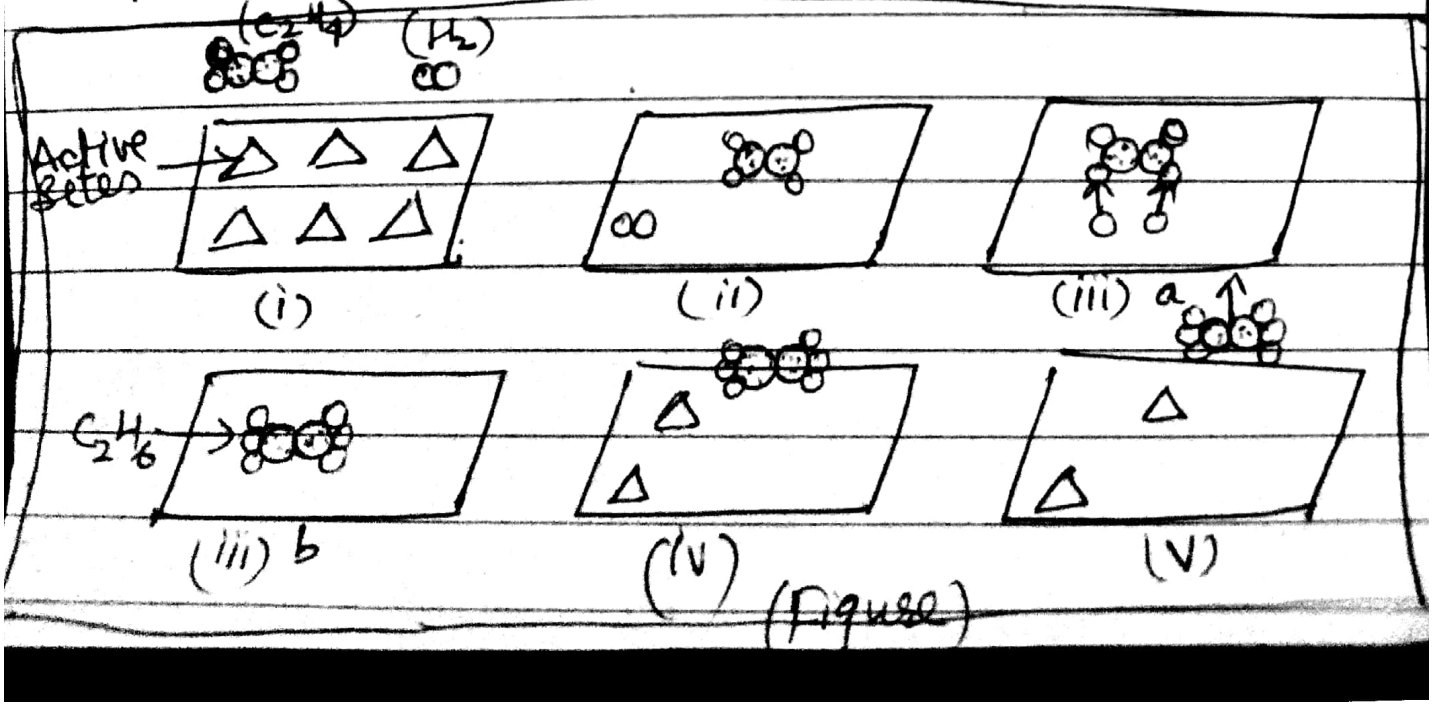
molecules with the surface of the catalyst resulting into stretching and weakening of bonds forming an activated complex with the catalyst which then decomposes or even breaking of bonds of reactant molecules.

Steps (ii) & (iii) are jointly called chemisorption.

iv) Desorption of the products from the surface.
v) Diffusion of the products away from the surface.

The various steps are illustrated with the following examples: Hydrogenation of ethylene in the presence of finely divided Ni, Pt or Pd





(Figure)

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Above figure represents mechanism for the reaction between ethylene and hydrogen on a catalytic surface.

i) Diffusion of C_2H_4 & H_2 towards surface.
ii) Adsorption of C_2H_4 + H_2 at the active sites
iii) a) Dissociation of H_2 into H atoms
b) Linking of the H-atom to C_2H_4 to form C_2H_6.
iv) Desorption of C_2H_6 from the surface.
v) Diffusion of C_2H_6 away from the surface.

b) Decomposition of HI in the presence of Platinum

$$2HI_{(g)} \xrightarrow{Pt} H_{2(g)} + I_{2(g)}$$

The mechanism of the reaction may be represented as follows:

$$H-I + \underset{\text{(A Pt atom on the surface of the solid)}}{-Pt-} \longrightarrow \underset{\text{(HI adsorbed on the surface of Pt atom)}}{\overset{H-I}{-Pt-}}$$

$$\longrightarrow \underset{\text{Transition state formed}}{\overset{H\cdots I}{-Pt-}} \longrightarrow -Pt- + \underset{\text{Transition state decomposes into products}}{\frac{1}{2}H_2 + \frac{1}{2}I_2}$$

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