Lecture 2

Adsorption on solid surfaces

Importance of adsorption in solid catalysis

As discussed in the previous section, heterogeneous solid catalysis is strongly associated with adsorption phenomenon. In solid catalysis, at least one of the reactant needs to be adsorbed on the surface of the catalyst. Adsorption of a component 'A' on surface of material 'B' is defined as preferential accumulation of the component 'A' on the surface of the material 'B'. The component 'A' is called adsorbate and surface 'B' is called adsorbent. The surfaces include both external surface and internal surface due to the pores. For highly porous material, the internal surface area due to the pores is much higher than the external surface area. The pores in a solid material can be of different dimensions. Pores with diameter less than 2nm (20 A^0) are called micropores, pores in the range of 2- 50 nm (20 – 500 A^0) are called mesopores, whereas pores greater than 50 nm are called macropores. The pore size distribution of a catalyst is affected by preparation condition and amount of loading of active component. Usually a wide pore size distribution exists in a catalyst. However, catalyst can also be designed to have a very narrow pore size distribution. Fig 1 shows the schematic representation of a typical porous solid catalyst particle having both the mesopores and micropores. The active sites are dispersed throughout the porous matrix. Under suitable conditions of temperature and pressure, a gas can gradually adsorb on the solid surface and finally lead to its complete coverage.
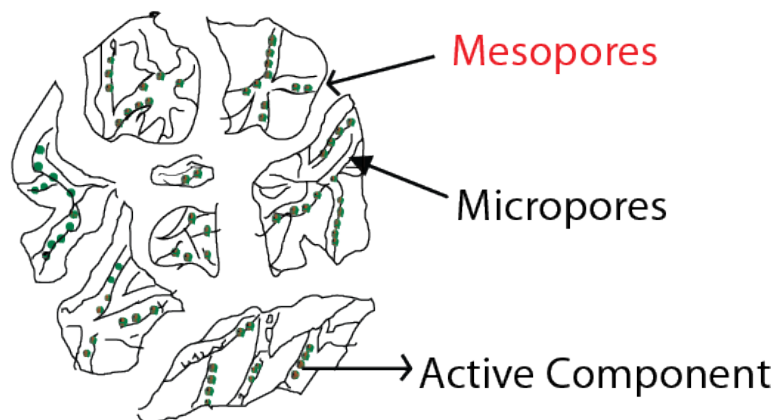

Fig. 1. Schematic representation of typical porous support impregnated with active component

Why adsorption takes place on solid surface

In the bulk of the adsorbent, the molecules are associated with their neighbours equally in all direction and the molecular forces are therefore balanced. However on the adsorbent surface, the molecules are bounded to the inner molecules at one side leaving unbalanced molecular forces on the other side. These unbalanced molecular forces on adsorbent surfaces create the attractive force for the adsorbate molecules approaching the surface. These molecular forces are weak in nature and called van der Waals attraction forces.

Types of adsorption

Depending on the nature of interaction, the adsorption can be of two types:

1. Physisorption
2. Chemisorption

The phenomenon of adsorbate molecules attaching themselves to adsorbent surface under the influence of van der Waals forces is called physisorption or physical adsorption. The van der Waals forces mainly consist of dipole –dipole interactions. This is an exothermic process with a low enthalpy change known as heat of adsorption. This process resembles liquefaction and heat of adsorption for physisorption is also known as heat of liquefaction.

At higher temperature, the adsorbed molecules can undergo electronic rearrangement with the surface molecules. This phenomenon is called chemisorption. The electronic rearrangement may include formation and breaking of chemical bonds. The electronic rearrangement occurs only when there is significant interaction between adsorbate and the adsorbent molecules. Hence all adsorbate will not be chemisorbed on all adsorbent surfaces. Chemisorption process is selective and an adsorbate molecule will chemisorbed only on selected adsorbent. The adsorption processes are shown in Fig 2. The Fig. 2(a) depicts the situation when the adsorbate molecule approach any adsorbent surface under the influence of attractive forces created by the unbalanced molecular forces on adsorbent surfaces. The Fig. 2(b) represents the phenomenon, when any molecule is physisorbed on surface by van der Waals forces. No bond formation occurs in this situation. A chemisorption situation is represented in Fig. 2(c) when there is a weak bond formation between adsorbate and adsorbent molecule. As discussed above, the adsorbate molecule will be chemisorbed only on selected adsorbent surface with which it can interact significantly.
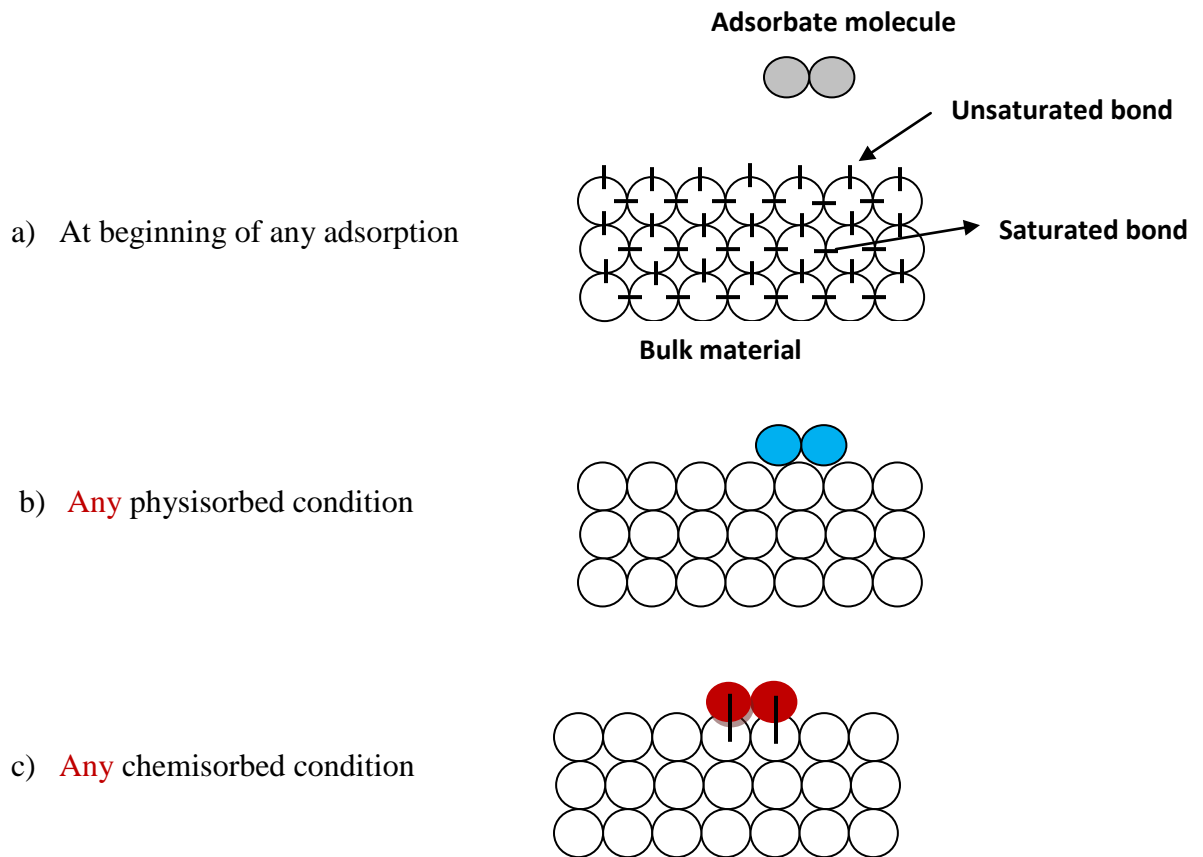
Adsorbate molecule

Unsaturated bond

a) At beginning of any adsorption

Saturated bond

Bulk material

b) Any physisorbed condition

c) Any chemisorbed condition

Fig. 2. Schematic representation of different adsorption processes

Physisorption versus Chemisorption

1. Since physisorption involves only weak molecular interaction, the associated enthalpy changes are small (in the range of 10 to 40 kJ /mol) . On the other hand, in case of chemisorption, enthalpy change is quite large and can range from 80-400 kJ /mol.

2. The Fig. 3 compares the volume of gas adsorbed as a function of temperature under physisorbed and chemisorbed conditions. In physisorption, the molecules are adsorbed on surface by weak interaction. With increase in temperature, adsorbed molecules gain excess energy and their tendency to escape from the surface increases. Hence volume of gas adsorbed on the surface decreases with temperature as shown in Fig. 3. However, the chemisorption involves higher interaction energy between adsorbate and adsorbent molecules and hence is favored by temperature rise. Hence at low temperature range volume of adsorbed gas increases with temperature. However, at higher temperature range as the adsorbed molecules gains excess energy, rate of desorption becomes higher resulting in decrease in adsorbed gas volume as shown in Fig. 3.
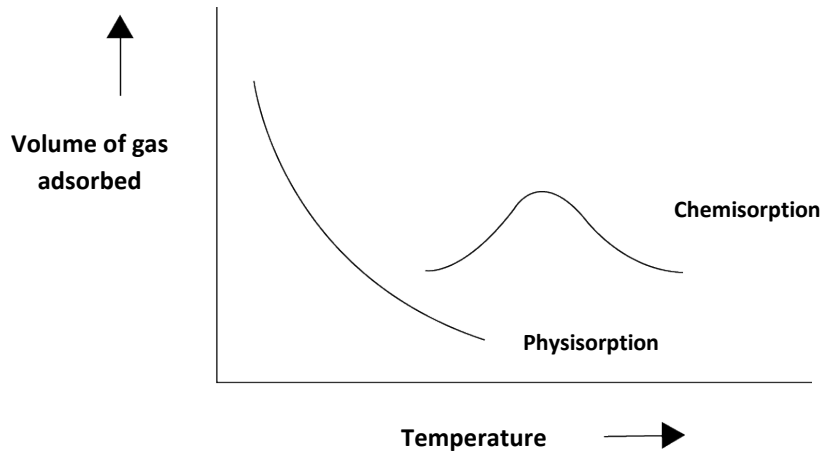
Fig. 3. Volume of gas adsorbed as a function of temperature for physisorption and chemisorption processes

3. In case of chemisorption, since there is electronic interaction between adsorbate and adsorbent molecules, only a monolayer of adsorbate can be formed on the adsorbent surface. In case of physisorption, the first monolayer formed on the surface of the adsorbent can act as adsorbing surface for formation of next layer of adsorbate and so on. This phenomenon is called multilayer adsorption. The formation of monolayer and multilayers of the adsorbed molecules on a surface is shown in Fig. 4. For the physisorption, volume of gas adsorbed increases with pressure due to increase in concentration of adsorbate and formation of multilayers. However for chemisorption process which corresponds to monolayer formation, the effect of pressure is not significant.
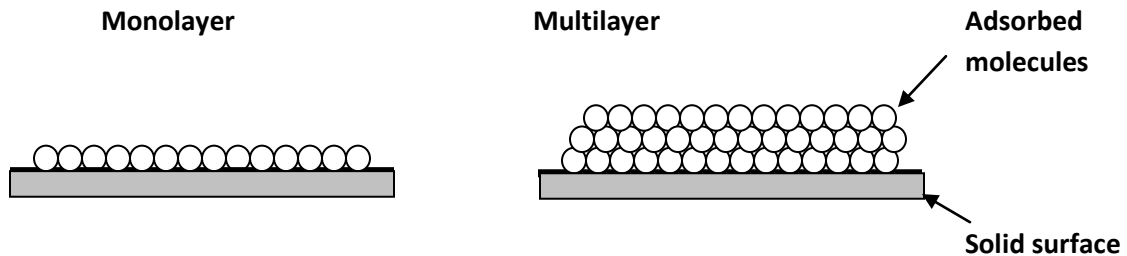

Fig. 4 . Monolayer and multilayer formation of the adsorbed molecules on a surface

4. Chemisorption is specific for adsorbate and adsorbent pair. Specific solid adsorbent can undergo electronic interaction only with specific adsorbate gas molecule.
5. Physisorption is highly reversible while chemisorption can be irreversible.
6. Physisorption is important for estimating the total surface area. It also provides a basis for estimating the pore volume and pore size distributions. On the other hand, chemisorption is important in estimation of area of catalytic active sites as well as its dispersion.

Examples :

Physisorption : Adsorption of nitrogen on carbon or alumina.

Chemisorption : Adsorption of hydrogen on active platinum sites on any support.

Potential energy diagram of approaching molecule towards a solid surface

The potential energy variation of a molecular system as it approaches a solid surface can be depicted by the potential energy diagram, where the potential energy is plotted as a function of distance of the approaching molecule from adsorbent surface. When the molecule approaches the surface, at first it becomes attracted by a weak attractive force resulting in relatively flat potential minimum corresponding to non – dissociative physical adsorption. Then depending on extent of interaction it can be carried to non-dissociative chemisorbed state and finally to stable dissociated state. When the extent of interaction is less, the adsorbate molecules are only physically adsorb on the adsorbent surface or may occur in non-dissociative chemisorbed state. If the interaction is only van der Waals type then the adsorbates will be in physisorbed state. In case of stronger electronic interaction the process may be directly carried on to dissociative chemisorption. If the crossing points are below the line of zero potential energy as shown in Fig. 5, then the overall process is non-activated. If they are above, the overall process requires activation.
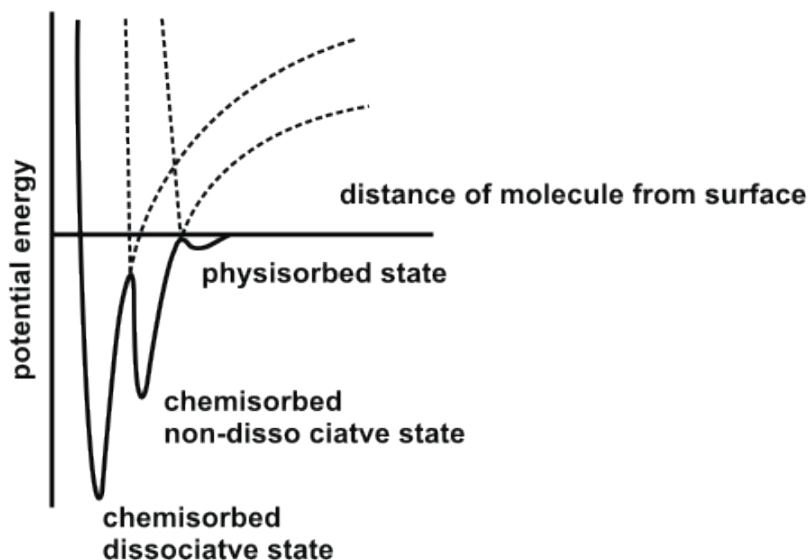

Fig. 5. Potential energy diagram for non activated dissociative chemisorption