Catalysis

Introduction to catalysis

The science and technology of catalysis is of great significance as it affects our daily life. Four major sectors of the world economy; petroleum and energy production, chemicals and polymer production, food industry and pollution control, involve catalytic processes.

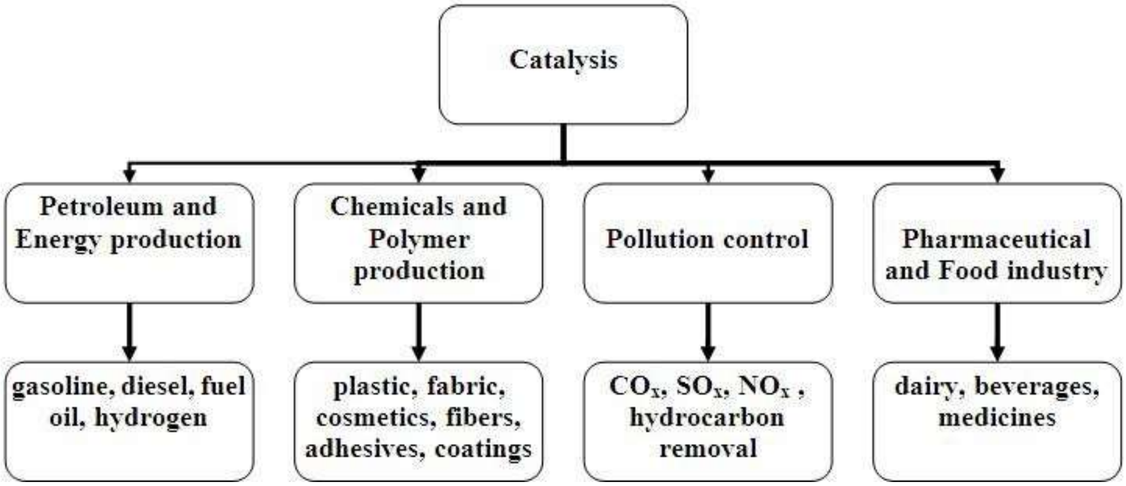


Fig. 1. Four major sectors of world economy that involve catalytic processes

Catalysts are used to produce fuels such as gasoline, diesel, heating oil, fuel oil etc. Production of plastics, synthetic rubbers, fabrics, cosmetics etc. involve catalytic processes. The production of clean energy from renewable energy sources, such as hydrogen for fuel cells and transportation fuels from non-edible biomass are also catalyst dependent processes. Automobile emission catalysts are used to reduce emissions of CO, NO_x and hydrocarbons from mobile vehicles. Catalysts are also used in the production of the polymers including adhesives, coatings, foams, textile and industrial fibers. The pharmaceutical industry uses catalysts for production of drugs that are used to save lives and improve the health of people. Catalysts are also widely used in food processing. More than 90 % of industrial processes actually use catalysts in one form or the other. Owing to expanding need of mankind, production in all sectors is increasing at a fast rate and catalysis science and technology has a major contribution in this. Thrusts are being given in the areas of catalyst upgrading to new and more efficient catalysts. Increasing catalyst life is another area of importance to maximize catalyst efficiency.

History : Catalyst technology has been used for many centuries. It ranged from inorganic catalyst to make soaps to enzyme catalysts for producing wines, cheese and other food and beverages. The industrial catalyst technology started with the large-scale production of sulfuric acid on platinum catalyst in 1875. In subsequent years, various major catalytic processes were invented. In 1903, ammonia oxidation on Pt gauge was developed by Ostwald for nitric acid production. Another major breakthrough was ammonia synthesis with promoted iron in 1908-1914 by Mittasch, Bosch and Haber.

Conversion of synthesis gas to liquid hydrocarbons by hydrogenation of CO, which was developed in 1920-1940, was a major development in the energy sector. In petroleum industry, the development of catalytic cracking process during 1935- 1940 changed the energy scenario. This process used a solid catalyst in the petroleum industry for the first time. Subsequent decades saw the development of various catalytic hydrocarbon processes such as catalytic naphtha reforming (1950) and hydrotreating for removal of sulphur, nitrogen, metals from petroleum feed stock (1960). With the discovery of Ziegler-Natta catalyst in 1955, the polymer industry grew significantly. The first large scale industrial homogeneous catalytic process came up in 1960 in the form of Walker process for making acetaldehyde from ethylene. The development of shape selective catalysts such as molecular sieves or zeolites for cracking (1964) resulted in the production of exclusively shape selective products. The other major development in catalysis was in 1970-1980 for environmental pollution control. Noble metal catalysts were developed for emission control of CO, NO_x and hydrocarbons from automobiles. Vanadia-titania and zeolite catalysts were developed for selective reduction of NO_x. Catalysis is a continuously growing area and discovery of new catalysts and their applications has led to major development in the chemical industry.

Catalysis involves understanding of the thermodynamics, kinetics, electronic interaction, crystal structure, reactor design and process development for a catalytic process. It is an interdisciplinary area involving contribution from chemical engineers, chemists and material scientists for successful implementation of the entire process starting from preparation of catalysts to final utilization in a chemical reactor.

Catalytic reactions

In a thermodynamically feasible chemical reaction, when addition of a small amount a chemical substance increases the rate of attainment of chemical equilibrium but the substance itself does not undergo any chemical change, then the reaction is called a catalytic reaction. The substance that enhances the reaction rate is called a catalyst. Catalysts work by providing alternative mechanism involving a different transition state of lower energy. Thereby, the activation energy of the catalytic reaction is lowered compared to the uncatalyzed reaction as shown in Fig 2.

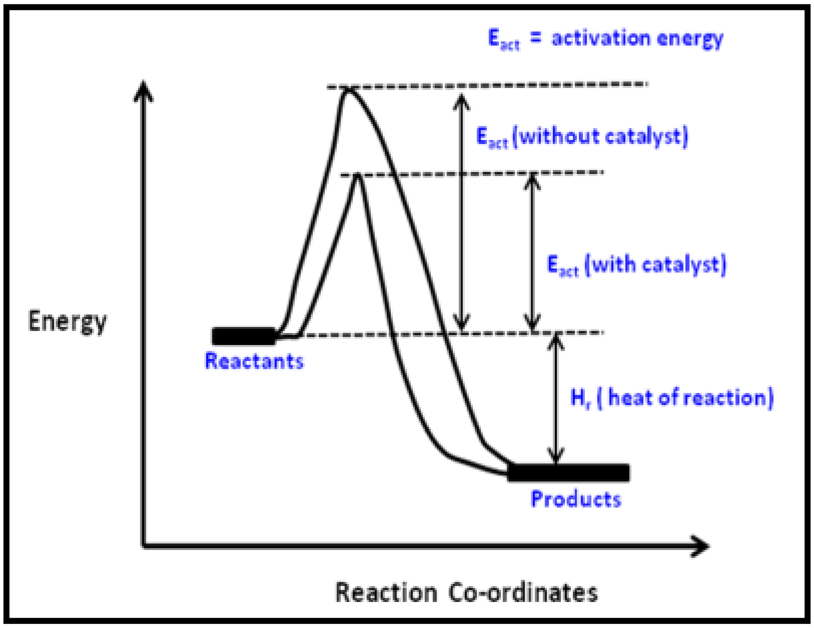


Fig. 2 . Comparison of activation energies of exothermic catalytic and non-catalytic reactions

A catalyst accelerates both the rates of the forward and reverse reaction. Equilibrium of a reversible reaction is not altered by the presence of the catalyst. For example, when oxidation of SO_2 is carried out in the presence of three different catalysts, namely Pt, Fe_2O_3 and V_2O_5 , the equilibrium composition is the same in all three cases. Another important characteristic of catalyst is its effect on selectivity. The presence of different catalysts can result in different product distribution from the same starting material. For example, decomposition of ethanol in the presence of different catalysts results in different products as shown below.

$$\text{ethanol} \xrightarrow{\text{boron phosphate}} \text{ethylene+diethyl ether}$$

$$\text{ethanol} \xrightarrow{Mo_2C\text{/carbon}} \text{hydrogen + acetaldehyde}$$

Types of catalytic reactions

Catalytic reactions can be divided into two main types –

1. Heterogeneous
2. Homogeneous

Heterogeneous catalysis

In heterogeneous catalytic reaction, the catalyst and the reactants are in different phases. Reactions of liquid or gases in the presence of solid catalysts are the typical examples.

An example is the Contact Process for manufacturing sulphuric acid, in which the sulphur dioxide and oxygen are passed over a solid vanadium oxide catalyst producing sulphur trioxide. Several hydrocarbon transformation reactions such as cracking, reforming, dehydrogenation, isomerization also fall in this category.

Homogeneous catalysis

In a homogeneous catalytic reaction, the catalyst is in the same phase as the reactants. Typically, all the reactants and catalysts are either in one single liquid phase or gas phase. Most industrial homogeneous catalytic processes are carried out in liquid phase. Ester hydrolysis involving general acid-base catalysts, polyethylene production with organometallic catalysts and enzyme catalyzed processes are some of the important examples of industrial homogeneous catalytic processes.

Relative significance

Catalytic processes have great significance and about 90 % of all chemical industry involves catalytic processes. Of all the industrial catalytic processes, approximately 80 % involve the use of solid catalysts, 17 % homogeneous catalysts and rest 3 % biocatalysts. Thus, heterogeneous catalysts, particularly solid catalysts, dominate the industrial catalytic processes. Though the contributions of homogeneous catalytic processes in chemical industry are significantly smaller than that of heterogeneous catalytic processes, but because of high selectivities, homogeneous process are finding increasing importance for production of many important value added products such as manufacturing of tailor made plastics, fine chemicals, pharmaceutical intermediates etc.

Heterogeneous catalytic theory

In general, it is believed that the entire surface of the solid catalyst is not responsible for catalyzing any reaction. Only certain sites on the catalyst surface actually participate in the reaction and these sites are called active sites on the catalysts. These sites may be the unsaturated atoms resulting from surface irregularities or atoms with chemical properties that enable the interaction with the adsorbed reactant atoms or molecules. Activity of the catalyst is directly proportional to the number of these active sites available on the surface and is often expressed in terms of turnover frequency. Turnover frequency is defined as the number of molecules reacting per active site per second at the condition of experiments.

A solid catalytic reaction $A \rightarrow B$ goes through the following steps. The steps are illustrated in Fig 3.

1. Transportation of reactant (A) from bulk fluid to pore mouth on the external surface of catalysts pellets
2. Diffusion of the reactant (A) from the pore mouth through the catalyst pores to the immediate vicinity of internal catalytic surface
3. Adsorption of reactant (A) onto the catalyst surface
4. Reaction of (A) on the catalyst surface producing product (B)
5. Desorption of the product (B) from the surface

6. Diffusion of the product (B) from interior part of the pores to the pore mouth on the external surface
7. Transfer of the product (B) from pore mouth on the external surface to the bulk fluid

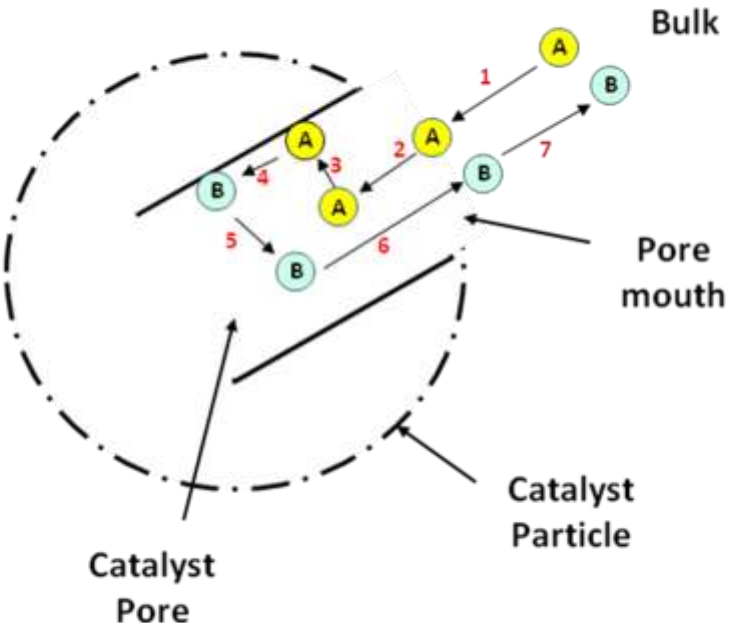


Fig. 3. Steps in solid catalytic reactions.

The overall rate of reaction is equal to the rate of slowest step in the mechanism. When the mass transfer and diffusion steps [1,2,6,7] are very fast compared to adsorption and reaction steps [3,4,5], concentration in the immediate vicinity of the active sites is the same or indistinguishable from that in the bulk fluid. Consequently, the transport or diffusion steps do not affect the overall rate of the reaction. Alternatively, if reaction and diffusion steps are fast compared to the mass transfer steps, then mass transfer does affect the rate of reaction. When mass transfer from the bulk phase to the pore mouth is slow and affects the reaction rate, then changing the flow conditions past the catalyst should change the overall reaction rate. In case of porous catalysts, diffusion within the catalyst pores may limit the reaction rate. Under this condition external flow does not affect the reaction rate but internal diffusion does affect.

Book References

- R. J. Farrauto & C. H. Bartholomew, Fundamentals of Industrial catalytic Processes, Blackie Academic & Professional, 1997
- H. S. Fogler, Elements of Chemical reaction engineering, Prentice – Hall of India, 2002, Third edition.
- J.J. Carberry , Chemical and catalytic reaction Engineering, Dover Publications, 2001
- J. M. Thomas & W. J. Thomas, Principles and Practice of Heterogeneous Catalysis, VCH, 1997
- J. M. Smith , Chemical Engineering Kinetics, McGraw-Hill Book Company, 1981

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.

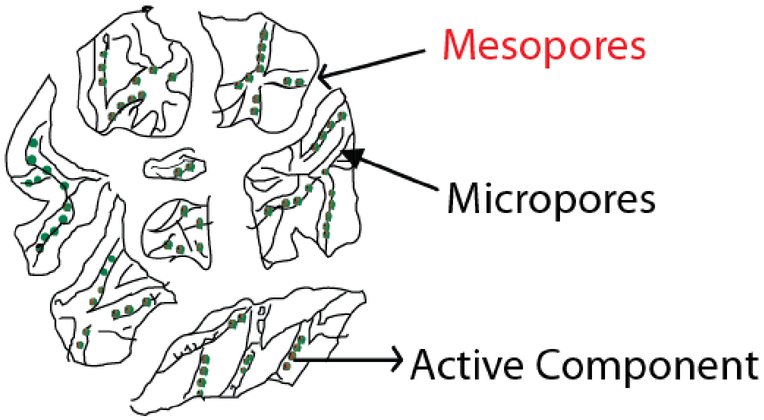


Fig. 1. Schematic representation of typical porous support impregnated with active component

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.

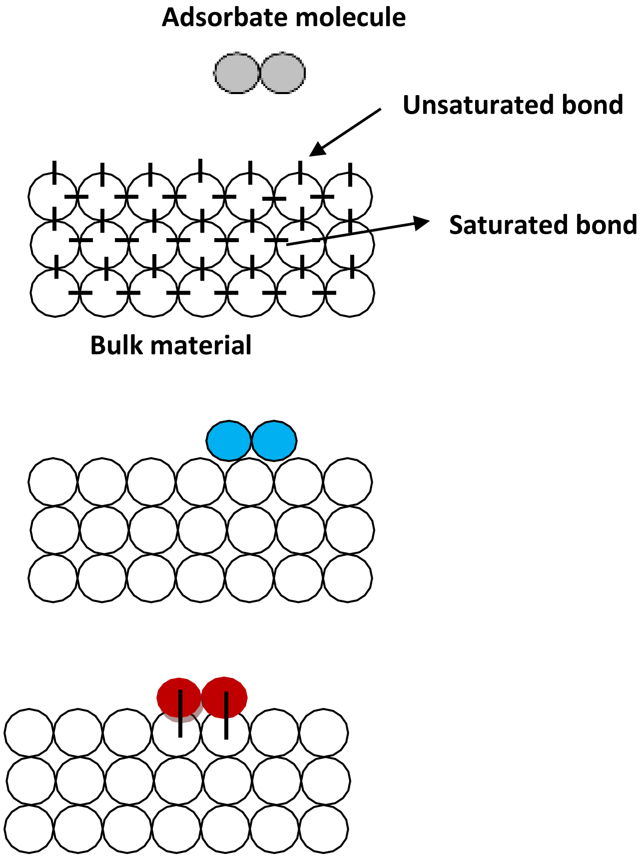
Types of adsorption

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.



a) At beginning of any adsorption

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.

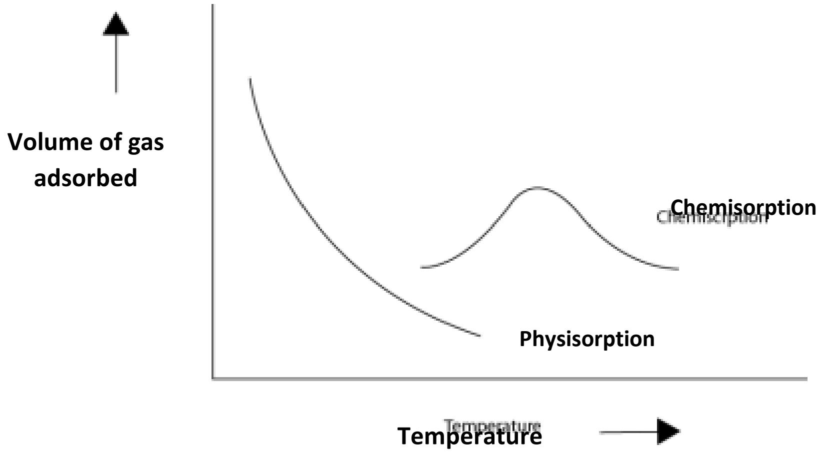


Fig. 3. Volume of gas adsorbed as a function of temperature for physisorption and chemisorption processes

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.

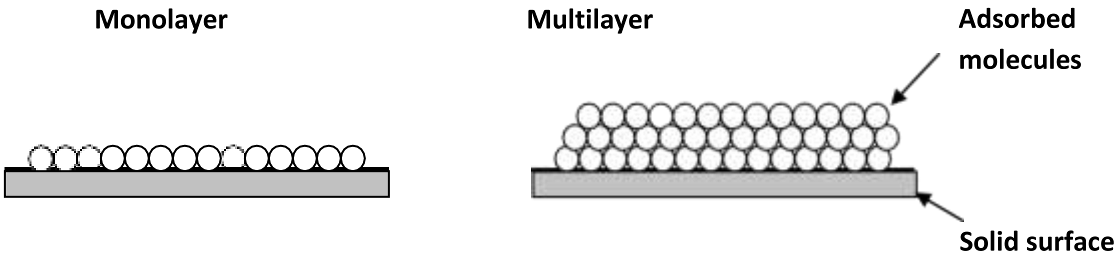


Fig. 4 . Monolayer and multilayer formation of the adsorbed molecules on a surface

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.

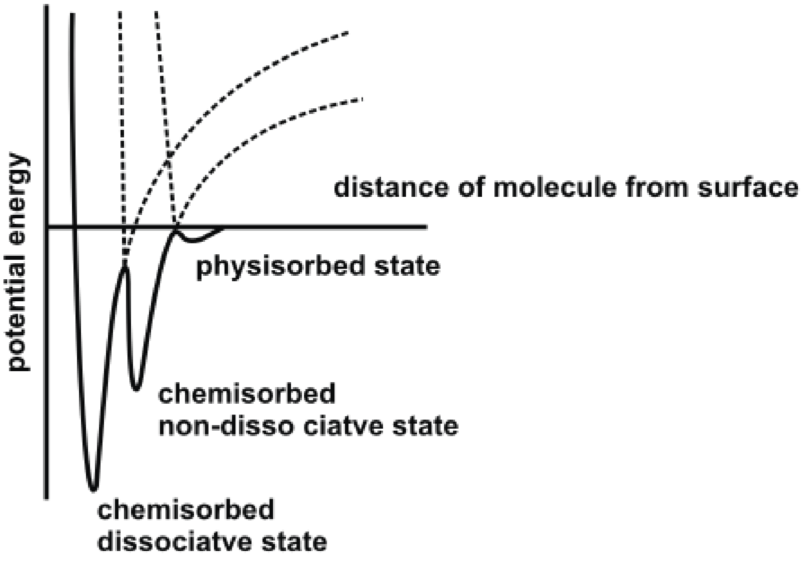


Fig. 5. Potential energy diagram for non activated dissociative chemisorption

Book References :

- J.J. Carberry , Chemical and catalytic reaction Engineering, Dover Publications, 2001
- J. M. Thomas & W. J. Thomas, Principles and Practice of Heterogeneous Catalysis, VCH, 1997
- J. M. Smith , Chemical Engineering Kinetics, McGraw-Hill Book Company, 1981
- R. J. Farrauto & C. H. Bartholomew, Fundamentals of Industrial catalytic Processes, Blackie Academic & Professional, 1997
- D.M. Ruthven, Principle of adsorption & adsorption processes, John Wiley & sons, 1984.