

Synthesis and Application of Catalysts

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1.0 Introduction to catalysis

Since Berzelius coined the term "catalysis" in 1836, catalysis has grown in relevance to the global economy. Catalysts are used in about 80% of all chemical processes in the chemical, food, pharmaceutical, vehicle, and petrochemical sectors, according to estimates [1]. Catalysis, according to Berzelius, is the decomposition of bodies by the catalytic force. This was the first time catalysis was recognized as widespread natural phenomena! Ostwald (1895) gave another definition, which is still valid today: "a catalyst is a material that accelerates a chemical reaction

without changing the equilibrium or thermodynamics of the reaction.” Ostwald recommended that catalysis be viewed as a universal dynamic process that could be explained using physical chemistry equations. In 1909, he was awarded the Nobel Prize in Chemistry for his groundbreaking discoveries [2].

1.1 What is Catalysis?

Catalysis is the gateway to chemical transformation. It's a phenomenon in which a small amount of foreign material called as a catalyst accelerates chemical reactions. By creating bonds with the adsorbents (A and B) and allowing them to react with one other to produce products (P), a catalyst speeds up the rate of a chemical process. The products can then desorb from the catalyst, which is then returned to its original state at the end of the reaction cycle [2].

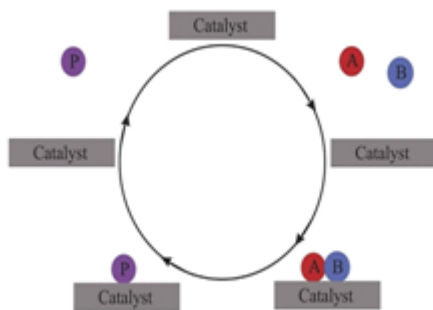


Figure 1. The reactants (A and B) adsorb and react with the catalyst, create the product (P), and finally detach from the catalyst in a catalytic process. The catalyst is thus free to

begin a new catalytic cycle (ref.2)

There is no unlimited life for catalysts. In a chemical reaction, production of side reactions or structural changes of the catalyst leads to deactivation of the catalyst. Therefore, for the next reaction, the catalyst must be reactivated or a new catalyst must be installed. The catalyst speeds up both the forward and backward reactions: if a catalyst speeds up the formation of products from reactants, it will also speed up the decomposition of products into reactants when they pass through transition states [3]. The use of a catalyst in a chemical reaction may be unnecessary depending on the bond strength between the reactants and the catalyst. As a result, an effective combination of catalyst and reaction is one in which the interaction between the reactants and the catalyst is neither too weak nor too strong [2].

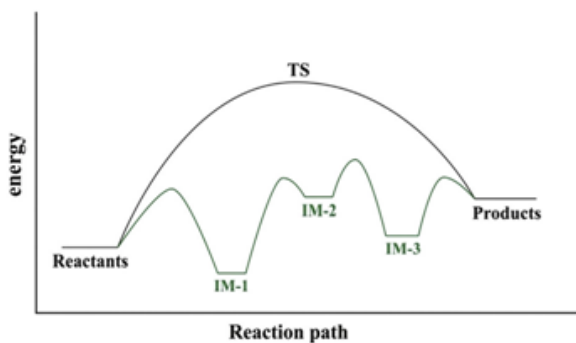


Figure 2. The energy profiles of an uncatalyzed and a

catalyzed reaction. IM, intermediate; TS, transition state (ref.2)

Catalysts ensure that the desired products are converted in a practical and high-yielding manner, with no unwanted by-products. Single atom catalysts (SACs) have recently emerged as the best alternative for both homogeneous and heterogeneous catalysts used in a variety of catalytic applications. Carbon-based SACs are widely investigated catalysts due to their extraordinary features such as tunable morphologies, ordered porosity, and easy immobilization through various metals, which make them highly efficient single atom catalysts for a wide range of important catalytic applications [4-5].

2.0 Theories of Catalysis

The two main theories of catalysis are –

- A. Intermediate compound formation theory
- B. Adsorption theory

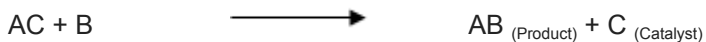
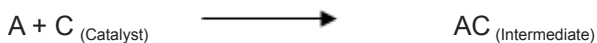
Intermediate compound formation theory-

The catalyst, according to this theory, produces an intermediate compound with one of the reactants first. The compound is produced with less energy than is required for the reaction to take place. The catalyst is renewed when the unstable intermediate compound reacts with additional reactants to create the desired product.

For example, the reaction $A + B \longrightarrow AB$

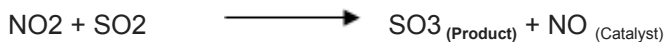
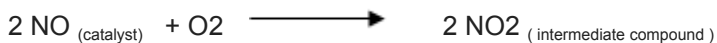
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Which occurs in the presence of a catalyst (C), will follow the following steps:-



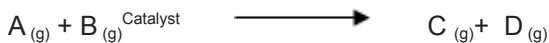
Based on this theory, many catalytic reactions can be explained

In the lead chamber process, catalytic oxidation of SO₂ to SO₃ takes place as-



This theory describes the heterogeneous catalytic mechanism. The catalyst works here via adsorption on the surface of the reacting molecules.

The heterogeneous catalysis involves four stages-



Step 1. Adsorption of reactant molecules

The reactant molecules A and B hit the catalytic

surface. At the surface, they are kept together by weak van der Waal's forces or partial chemical bonds.

Step 2. Formation of Activated complex

The adjacent particles of the reactants combine to create an intermediate complex (A-B). The activated complex is in a state of instability.

Step 3. Decomposition of Activated complex

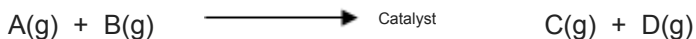
The activated complex breaks down into products C and D. By partial chemical bonding, the separated product particles adhere to the catalyst surface.

Step 4. Desorption of Products

The product particles are either desorbed or released from the surface [6].

Adsorption theory

The mechanism of heterogeneous catalysis is explained by this theory. In this case, the catalyst works by adsorbing the reactive molecules onto its surface.



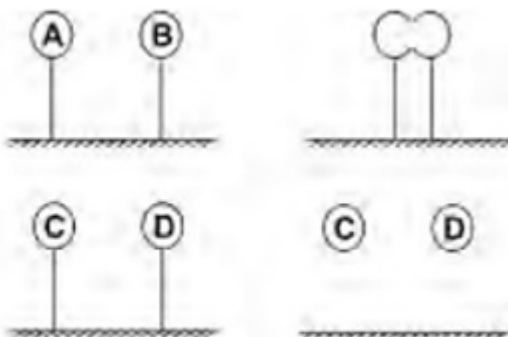


Figure 3. Adsorption of reactants (adapted from ref.6)

Step 1. Adsorption of reactant molecules

The reactant molecules A and B collide with the catalyst's surface. At the surface, they are bound together by weak van der Waal's forces or partial chemical bonds.

Step 2. Formation of Activated Complex

The adjacent particles of the reactants combine to produce an intermediate complex (A-B). An unstable activated complex is formed.

Step 3. Decomposition of Activated Complex

The activated complex disintegrates into products C and D. Partial chemical bonds hold the separated product particles to the catalyst surface.

Step 4. Desorption of Products

The product particles are desorbed and released from the surface [6].

Catalyst support material

The majority of the catalysts currently in use are Pt-based and are typically supported on porous conductive materials with a high specific surface area. The support materials are needed to attain high dispersion and narrow distribution of Pt and Pt-alloy nanoparticles, which is required to achieve the high catalytic performance of catalysts. Support materials can also interact with catalytic metals, affecting catalytic activity. The catalyst's durability is also highly reliant on its support. The following are the requirements for catalyst support materials: 1) high specific surface area, which is necessary for improving catalytic metal dispersion, 2) low combustive reactivity in both dry and humid air at low temperatures (150 C or less), 3) high electrochemical stability under fuel cell operating conditions, 4) high conductivity, and 5) easy-to-recover Pt in the used catalyst. To improve catalytic activity and durability, the interaction between catalytic metals and support materials should be considered. Vulcan XC-72 carbon black is the most popular support material. As an alternative to conventional internal combustion engines, secondary batteries, and other conventional power sources, polymer electrolyte membrane (PEM) fuel cells are being explored as electrical power sources for automobiles, stationary and portable applications. The cost, performance, and durability of polymer electrolyte membrane (PEM) fuel cells are all influenced by catalyst support materials. Apart

from the recent focus on electrocatalytic metals, significant effort has gone into inventing novel catalyst supports, such as innovative nanostructured carbons (such as carbon nanotubes [CNTs], carbon nanofibres [CNFs], and mesoporous carbon), oxides, carbides, nitrides, and so on. Other atoms or compounds can be doped into nanostructured carbon to improve the catalytic activity and durability of the resulting catalysts. These supporting items can be divided into two categories: 1) primary supports, such as new nanostructured carbons and conductive diamonds; and 2) secondary supports, such as oxides, which are primarily utilized to modify and promote primary supports but can also be used as independent supports [7].

Many industrial catalysts are made consisting of metals or metal compounds supported on a suitable support, whose primary function is to keep the catalytically active phase in a highly dispersed state. Spreading the active phase on support provides the advantage of dispersing it throughout the pore system, resulting in a large active surface per unit weight used. A supported catalyst improves the dissipation of reaction heat, delays the sintering of the active phase, and increases poison resistance by facilitating the passage of gases through the reactor and the diffusion of reactants via the pores to the active phase. Alumina, silica, and carbon (mainly activated carbon) are mostly used for industrial-supported catalysts. Activated carbon will be given

as an example of carbon materials utilized as support in heterogeneous catalysis because of its physical and chemical properties. All activated carbons are porous, with a small number of chemically bound heteroatoms (mainly oxygen and hydrogen). Furthermore, activated carbon may contain up to 15% mineral matter (the nature and amount of which is dependent on the precursor), which is typically expressed as ash content. The average structure is now thought to be made up of aromatic sheets and strips, often bent and resembling a combination of wood shavings and crumpled paper, with varied molecular spaces between them, which are the micropores. The precursor and treatment have an impact on the material's extremely disorganized structure. Slit-shaped micropores could be considered. The degree of activation will influence the number of aromatic sheets in the original char, leaving single and, in general, nonplanar layers in some cases [8].

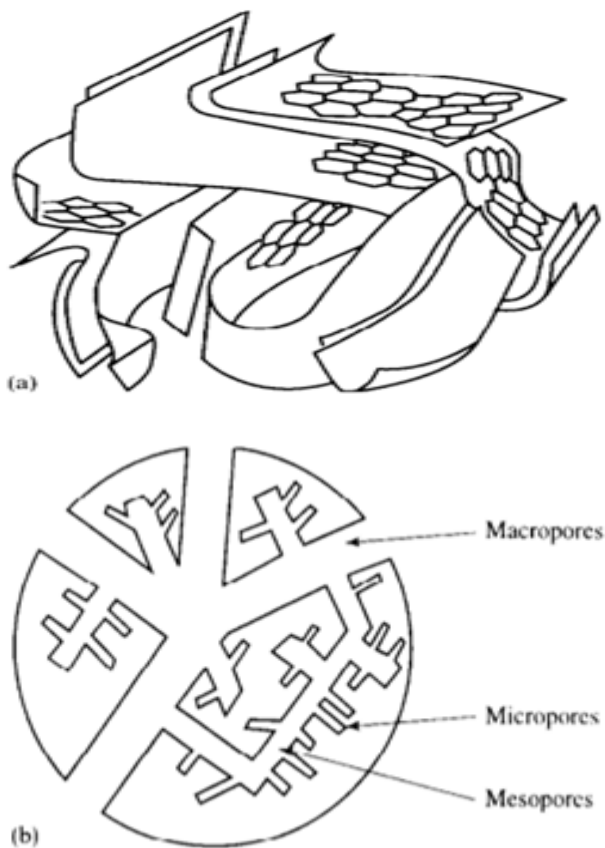


Figure 3. (a) Schematic representation of the structure of activated carbon (b) schematic representation of activated carbon (adapted from ref. 8)

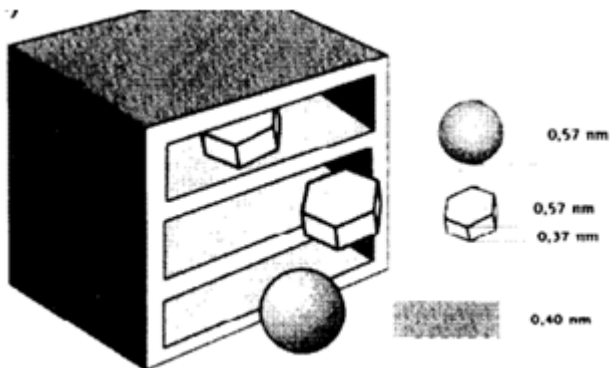


Figure 4. Schematic representation of microporosity in a porous carbon (adapted from ref. 8)

Although most adsorption occurs in the micropores of activated carbon, meso- and macropores play a critical role in any adsorption process because they serve as a pathway for the adsorbate to reach the micropores, which are sparsely distributed on the carbon particle's outer surface. It becomes clear why proper control of the activation process is critical for obtaining activated carbons for certain applications like catalyst supports because such control allows for porosity tailoring within certain limits.

Activated carbon's adsorptive characteristics are influenced not only by its porous structure but also by its chemical composition. The dispersion component of the vander Waals forces is primarily responsible for adsorption in graphite, which has a highly oriented structure. However, the

random ordering of imperfect aromatic sheets in activated carbon results in incompletely saturated valences and unpaired electrons, which will influence adsorption behavior, particularly for polar or polarizable molecules. Furthermore, activated carbon is often associated with significant amounts of heteroatoms like oxygen and hydrogen (derived either from the starting material or chemically bound to the structure during manufacture) as well as inorganic ash components. Carbon oxygen surface groups can be formed from reaction with many oxidizing gases (ozone, nitrous oxide, nitric oxide, carbon dioxide, etc.), and with oxidizing solutions (nitric acid, sodium hypochlorite, hydrogen peroxide, etc.). Surface area, particle size, and ash content, as well as temperature and degree of carbonization, influence the nature and number of oxygen surface complexes formed by a given carbon [8].

4.0 Catalyst Synthesis

Some typical ways for preparing bulk catalysts include: (i) Precipitation or coprecipitation, in which precursor solutions are often precipitated by controlled pH change (ii) the sol-gel method, during which Organic (alkoxides) or inorganic substances are hydrolyzed to a gel by the production of a colloidal suspension (a "sol") (iii) hydrothermal (or solvothermal) synthesis, during which a precursor solution (nitrates, acetates, etc.) is processed by heating it to a high temperature while maintaining an autogenous pressure

increase (For example this method is used to synthesize zeolites and MOFs) and (iv) Flame hydrolysis. The final catalyst is normally obtained after a few steps, which include washing and purification, as well as drying and calcination, with an optional activation procedure (usually involving a controlled atmosphere pretreatment). In the case of supported catalysts, the support (or its precursor) is usually synthesized first (and optionally shaped), and then the active phase is deposited using a variety of methods:

1. *Impregnation* is a widely used approach based on the interaction of a precursor(s) solution with solid support. For incipient wetness impregnation, the solid to be impregnated's water pore volume (or pore volume accessible to any other solvent) is first measured, and then the desired amount of active-phase precursor is dissolved in the exact amount of solvent required to fill the solid's pores. In this method, the amount of active phase that can be deposited in a single operation is restricted by the precursor's solubility (s). This solubility limit is overcome in excess solvent impregnation, where the support is immersed in a solution containing the precursors in substantial quantities. In this second method, an equilibrium is achieved between the species in solution and those chemically bonded to the support.
2. *Chemical vapor deposition (CVD)* is a method of sublimating a bulk catalytic phase. After that, the gaseous

precursor is brought into contact with the support, where it solidifies into thin layers.

3. Other approaches include/involve solid-liquid interface chemistry (oxide surfaces, surface acidity, and charge), ion exchange and equilibrium adsorption, grafting, metal particle and cluster immobilization, deposition precipitation, spreading and wetting, and heterogenization of homogeneous catalysts (anchoring) [9].

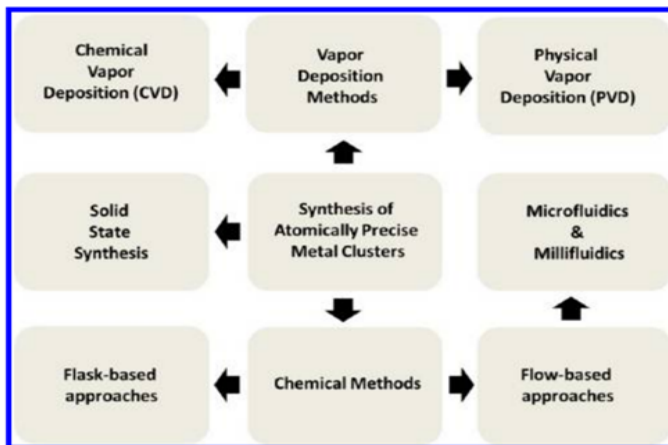


Figure 5. Different approaches overview for the synthesis of atomically precise clusters (Adapted from reference 10).

5.0 Catalyst Characterization

To have a comprehensive understanding of the structural aspects of catalysts employed in practical processes, shaped catalysts must be characterized. To get multi-scale structural information on shaped catalysts, new

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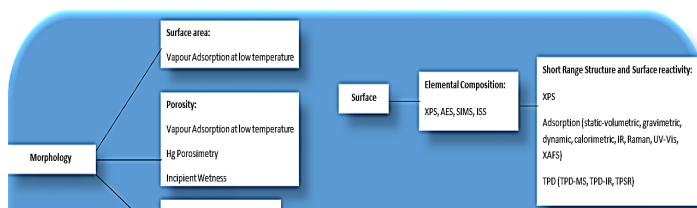
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strategies are needed to employ current characterization techniques[11].The olivine ((Mg_{1.78}, Fe_{0.13}) SiO₄) catalyst is a naturally occurring silicate mineral containing magnesium, silicon, and iron.

Catalyst Characterization techniques-

XPS is based on the photoelectric effect, in which the kinetic energy of the emitted photoelectron is used to compute the photoelectron's binding energy, which is distinctive of an element. In a VGEScalab 200 spectrometer, XPS measurements are performed with an aluminum anode (Al K α = 1486.3 eV) running at 510 W and a background pressure of 2×10^{-9} mbar. Al K α X-rays are used to excite the sample's surface, and photoelectrons from the first 3 to 10 nm of The FEI XL 30 ESEM-FEG performs scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. SEM is a technique that can give information about a particle's composition and internal structure.

Two techniques can be employed to evaluate the attrition resistance of the catalyst: To get the strength of the catalyst, repeated impact testing is employed, and to incorporate inter-particle interaction, fluidized bed testing is done. The impact testing is used to generate controlled and well-defined collision particles with a target, which helps to study the mechanical behavior of particles after many controlled impacts[12].



Techniques like SEM-TEM, XRD, XPS, Chemisorption are important for the physical characterization. The average size is determined by physical characterization, whereas the number of exposed atoms is determined directly by chemisorption of probe molecules [13].

6.0 Applications of catalysts

As a process of organic synthesis, catalysis is recognized and used. It's mostly utilized to transform a functional group of a given molecule into a new one selectively in order to create the starting material for the next synthetic step.

Catalysts are used for the following processes

(i) Hydrogenation of C=C bonds

Hydrogenation is a chemical process that is applied to a variety of commercial applications, ranging from food to petrochemicals and pharmaceuticals. Heavy metals, such as palladium or platinum, are typically used to catalyze the chemical reaction in this process. The hydrogenation of carbon-carbon double bonds is the most common hydrogenation reaction used in industry [14].

(ii) Semi-Hydrogenation of C — C ~~triple~~ bonds (Lindlar type)

One of the most valuable hydrogenations for the production of vitamins is the semi-hydrogenation of carbon-carbon triple bonds to alkenes; however, excellent selectivity requires careful selection of catalyst and reaction

conditions. The completely saturated alkane product is formed when acetylenes are hydrogenated with a metal catalyst, but the second hydrogenation (alkene to alkane) is often faster than the first (alkyne to alkene). The selectivity of the metal catalyst can be increased by using catalyst poisons that change the activity of the metal catalyst. The catalyst created by Lindlar is one of the most commonly used and selective catalysts. During the manufacturing process, the palladium supported on calcium carbonate is doped with a lead acetate solution. This catalyst can then be employed directly in hydrogenation or further modified with an organic component like an amine.

Catalysts in Pharmaceuticals

Catalytic organic synthesis is used in the production of active pharmaceutical ingredients (APIs), resulting in cleaner procedures and greener chemistries. Transition metal catalysts, which have various advantages over classical reaction chemistries, are often used in these processes. For example, coupling reactions which include transition metal catalyst are Heck, Fukuyama and Suzuki reactions. The platinum group metals (PGM) are widely employed in pharmaceutical syntheses among the transitional metals. Ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt) are examples of PGMs [14].

Energy Processing

Alkylation, catalytic cracking (breaking long-chain hydrocarbons into smaller pieces), naphtha reforming, and steam reforming are all common uses of catalysis in petroleum refining (conversion of hydrocarbons into synthesis gas). The Fischer-Tropsch synthesis of hydrocarbons from synthesis gas, which is conducted by water-gas shift processes catalysed by iron, is an old but still significant technique in synthetic fuels. Inorganic and biocatalysts are used to convert biodiesel and similar biofuels. Catalysts are used in both anodic and cathodic processes in fuel cells. From a supply of combustible fuel, catalytic heaters produce flameless heat.

Bulk Chemicals

Some of the largest-scale chemicals produced via catalytic oxidation, often using oxygen, include nitric acid (from ammonia), sulfuric acid (from sulphur dioxide to sulphur trioxide by the contact process), terephthalic acid from p-xylene, acrylic acid from propylene or propane, and acrylonitrile from propane and ammonia [15].

Ammonia production is one of the most large-scale and energy-intensive processes. Over an iron oxide catalyst, nitrogen is mixed with hydrogen in the Haber process. Copper-zinc catalysts are used to make methanol from carbon monoxide or carbon dioxide [16].

Fine Chemicals

Catalysis is used to make a variety of fine compounds; methods include heavy-industry operations as well as more specialized processes that would be prohibitively expensive on a large scale. The Heck reaction and the Friedal–Crafts reaction are two examples. Because most bioactive compounds are chiral, enantioselective catalysis is used to make many pharmaceuticals[17].

Environment

Catalysis has an indirect impact on the environment by boosting the efficiency of industrial processes, but it also has a direct impact. The catalytic action of chlorine free radicals in the decomposition of ozone is a good example. The action of UV radiation on chlorofluorocarbons produces these radicals (CFCs).

Food Processing

The hydrogenation (reaction with hydrogen gas) of fats using nickel catalyst to produce margarine is one of the most visible applications of catalysis. Biocatalysis is also used to make a variety of other foods [18].

7.0 Catalyst Deactivation

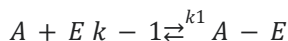
Poisoning, coking or fouling, and ageing are the main causes of deactivation. Poisoning can be reversible or irreversible, and it can be accompanied by a geometric or electrical effect. Depending on the interaction between the catalyst sites and the poison affinity, as well as the kinetics of

these processes, it can be selective, nonselective, or nonselective. Coke's catalytic effect, which is most essential in refineries, is regulated through direct active-site covering or pore clogging. It is determined by the reaction conditions, pore type, and, in some cases, the acidity of the catalyst surface. The mechanism of the coking reaction and its diffusion restrictions affect the kinetics of such coking. In many cases, sintering is the primary cause of catalyst ageing. Depending on the prevailing reaction parameters, such as temperature and/or reactant concentration, it may be thermal or chemical in nature. Deactivation can be handled with two ways: avoiding it if feasible, as in feed purification, or accepting it while attempting to limit its effects. Deactivation of a catalyst is the temporary or permanent loss of active sites due to chemical or physical factors. Deactivation occurs by-

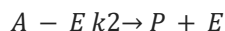
1. Chemisorption, or reactivity, of certain substrates causes chemical poisoning of the surface. For example- H₂S on Pt in hydrogenation reactions;
2. Coking , occur when hydrocarbons decompose into hydrogen-poor molecules, resulting in the formation of coke;
3. Fouling caused by solid deposition from dusty materials within the feed;
4. Crystallization or segregation and sintering of the catalytic material due to thermal effects [19].

8.0 Study of Chemical Kinetics of Catalytic Reactions

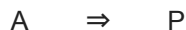
Kinetics of Catalytic Reactions can be explained by taking an example of Enzyme Catalyzed reaction. A simple series of elementary steps which frequently explains an enzyme-catalyzed biological process converting reactant A into product P is given below:



(i)



(ii)



(iii)

The rate of the overall reaction given by equation (iii)

is:

$$r = -d[A]/dt = d[P]/dt = k_2 [A - E]$$

(i)

The above steps cannot be assumed to be quasi-equilibrated if the rate of step (ii) is high enough compared to the forward and reverse rates of step (i). Thus to eliminate the unknown concentration of the active complex [A-E], SSA must be employed; i.e.,

$$D[A - E]/dt = k_1[A][E] - k_{-1} [A - E] - k_2 [A - E] = 0$$

(ii)

Thus

$$[A - E] = k_1 [A][E] / (k_{-1} + k_2).$$

(iii)

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The active site balance in the enzyme, where L_e is the total enzyme concentration is given by :

$$L_e = [E] + [A - E]$$

(iv)

Solving equations (iii) and (iv) simultaneously gives:

$$[A - E] = \frac{Lek_1[A]}{k_1+k_2+k_1[A]}$$

(v)

Substituting the above value in equation (i) gives the final rate law equation:

$$r = \frac{Lek_1k_2[A]}{k_1+k_2+k_1[A]} = \frac{Lek_2[A]}{\frac{k_1+k_2}{k_1} + [A]}$$

(vi)

This equation is Known as Michaelis-Menten equation which is represented as:

$$r = \frac{r_{max}[A]}{K_m + [A]}$$

(vii)

Here r_{max} represents the maximum or limiting rate and K_m being called the Michaelis constant.

Equation (vii) is expressed as:

$$v = \frac{VA}{K+A} = \frac{vmaxS}{Km+S}$$

(viii)

where A and S represents the concentration of reactant and S respectively.

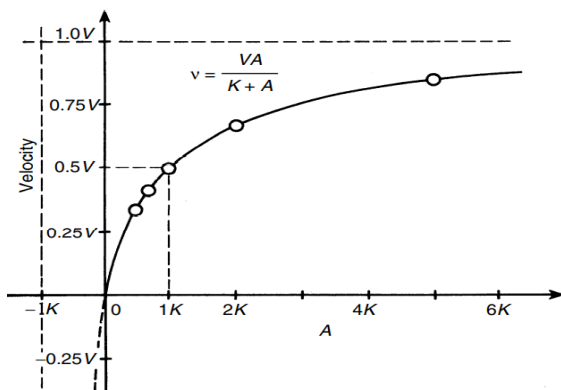


Figure 6. Michaelis-Menten Kinetics (adapted from reference 20)

The above equation can be readily linearized to give:

$$\frac{1}{v} = \left(\frac{K}{V}\right)\left(\frac{1}{A}\right) + \frac{1}{V},$$

This is commonly known as Lineweaver-Burke plot.

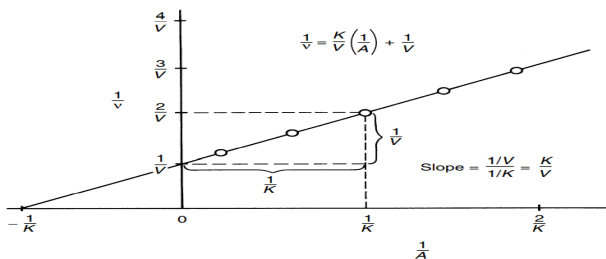


Figure 7. Lineweaver- Burke plot (adapted from reference 20)

From equation (vii), some conclusions can be made:

When $[A] \gg K_m$, $r_{\max} = L_e k_2$

When $[A] = K_m$, rate is one half of its maximum value [20].

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