

Chemical Reaction Engineering -II (2170501)

Chapter-05: Catalysis



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Introduction

In many reactions, the rates are affected by materials which are neither reactants nor products. Such materials called catalysts **can speed a reaction by a factor of a million or much more, or they may slow a reaction** (negative catalyst).

There are two broad classes of catalysts:

1. those that operate at **close to ambient temperature with biochemical systems, and**
2. **the man-made catalysts that operate at high temperature.**

*The **biochemical catalysts, called enzymes,** are found everywhere in the biochemical world and in living creatures,*

*In addition, in our bodies hundreds of **different enzymes and other catalysts** are busily at work all the time, keeping us alive.*

Catalyst Definition

A catalyst is a substance that affects the rate of a reaction but emerges from the process unchanged.

A catalyst usually changes a reaction rate by promoting a different molecular path (mechanism) for the reaction

For example gaseous hydrogen and oxygen are virtually inert at room temperature, but react rapidly when exposed to platinum

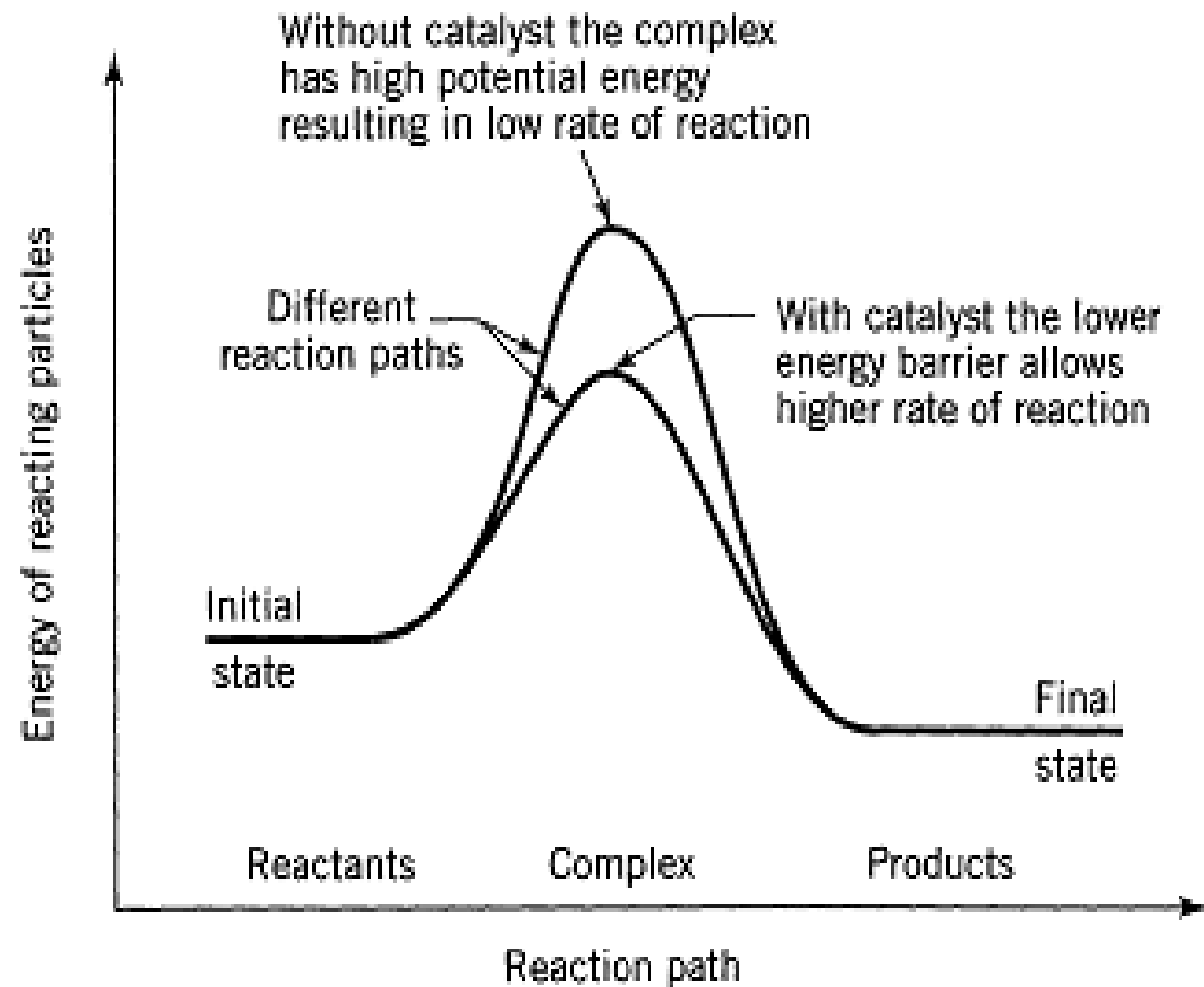
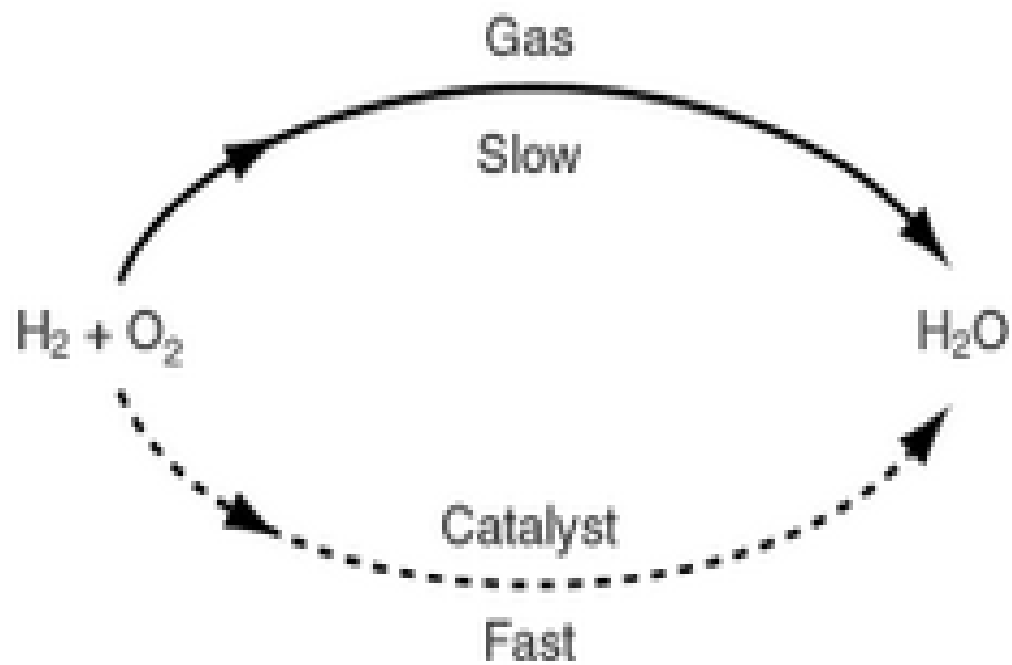


Figure 18.1 Representation of the action of a catalyst.

Promoter

Promoters are generally defined as substances **added during preparation of catalysts that improve the activity or selectivity or stabilize the catalytic agents.**

The promoter is present in a small amount and by itself has little or no activity.

For example, addition of small **quantities of alumina** to an **iron catalyst** employed in ammonia synthesis **prevents sintering of the iron crystallites.**

Thus, for this catalyst, alumina is a physical promoter.

The addition of K_2O to the same catalyst increases the intrinsic activity of the iron crystallites and therefore acts as a chemical promoter.

The promoter can be added during catalyst preparation or during reaction

Negative Promoter/Inhibitor

- Inhibitors act opposite to promoters.
- When added in small amounts, these can reduce catalyst activity, selectivity or stability.
- Inhibitor is particularly useful for reducing the activity of a catalyst for undesirable side reactions.
- In oxidation of ethylene, ethylene dichloride is added to inhibit CO_2 formation thus acting as an inhibitor.

Selectivity

- The selectivity of a reaction is the fraction of the starting material that is converted to the desired product.
- It is expressed by the ratio of the amount of desired product to the reacted quantity of a reactant and therefore gives information about the course of the reaction.

Stability

The **chemical, thermal, and mechanical stability** of a catalyst determines its lifetime in industrial reactors.

Catalyst stability is influenced by numerous factors, including **decomposition, coking, and poisoning.**

Catalyst deactivation can be followed by measuring activity or selectivity as a function of time.

Catalysts that lose activity during a process can often be regenerated before they ultimately have to be replaced.

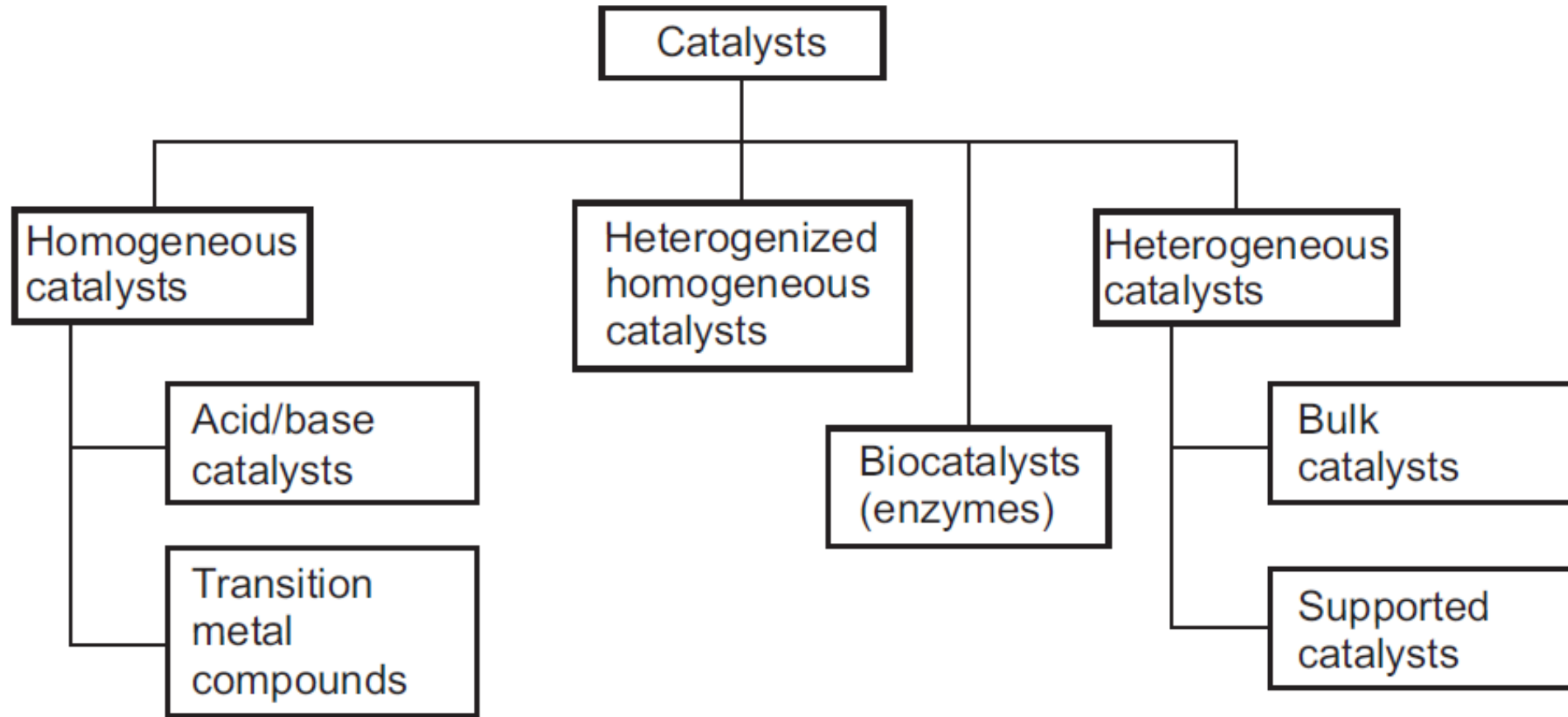
The total catalyst lifetime is of crucial importance for the economics of a process.

What is the active site of catalyst?

Active site is a point on the catalyst surface that can form strong chemical bonds with an adsorbed atom/molecule.

These sites are unsaturated atoms in the solid resulting from:
Surface irregularities, dislocations, edges of crystals and cracks along grain Boundaries

Classification of catalyst



Scheme 1-3 Classification of catalysts

Classification of catalyst

Industrial catalysts can be broadly grouped into three categories:

1. Bulk catalysts : When the **entire catalyst consists of the catalytically active substance** ,then the solid catalyst is called a bulk catalyst.

Examples include silica- alumina catalysts for catalytic cracking; iron- molybdate for oxidation of methanol to formaldehyde; iron doped with alumina and potassium oxide for the synthesis of ammonia.

2. Supported catalysts: In supported catalysts, the catalytically active materials are dispersed over the high surface area support material. For example, hydrodesulphurization is carried out over molybdenum oxide supported on alumina.

Mixed agglomerates : These catalysts are agglomerated mixture of active substance and support. These type of catalysts are used less frequently.

Homogeneous catalysis

Catalytic processes that take place in a uniform gas or liquid phase are classified as **homogeneous catalysis**. Homogeneous catalysts are generally well-defined chemical compounds or coordination complexes, which, together with the reactants, are molecularly dispersed in the reaction medium. **Examples of homogeneous catalysts include mineral acids and transition metal compounds (e. g., rhodium carbonyl complexes in oxo synthesis).**

Heterogeneous catalysis

- **Heterogeneous catalysis** takes place between several phases.
- Generally the catalyst is a solid, and the reactants are gases or liquids.
- Examples of heterogeneous catalysts are Pt/Rh nets for the oxidation of ammonia to nitrous gases (Ostwald process), supported catalysts such as nickel on kieselguhr for fat hardening , and amorphous or crystalline aluminosilicates for cracking petroleum fractions.

Biocatalysts (enzymes)

Of increasing importance are the so-called biocatalysts (enzymes). Enzymes are protein molecules of colloidal size [e. g., poly(amino acids)]. Some of them **act in dissolved form in cells, while others are chemically bound to cell membranes or on surfaces.**

Enzymes can be classified somewhere between **molecular homogeneous catalysts and macroscopic heterogeneous catalysts.**

Enzymes are the driving force for biological reactions . They exhibit remarkable activities and selectivities.

For example, the enzyme catalase decomposes hydrogen peroxide 10^9 times faster than inorganic catalysts

Preparation of solid catalyst

The catalyst preparation methods can broadly categorized as follows :

1. Bulk preparation process:

Bulk catalysts and supports are prepared by this method. Bulk preparation is mainly done by the following methods :

- a. Precipitation process
- b. Sol gel process

2. Impregnation process:

Supports are first prepared by bulk preparation methods and then impregnated with the catalytically active material.

The active materials can be deposited on the supports by various methods.

Most of the methods involve aqueous solutions and liquid solid interface.

In some cases, deposition is done from the gas phase and involves gas- solid interface

3. Physical mixing :

Mixed agglomerated catalysts are prepared by this method.

These catalysts are prepared by physically mixing the active substances with a powdered support or precursors of support in ball mill.

The final mixture is then agglomerated and activated.

Catalyst preparation

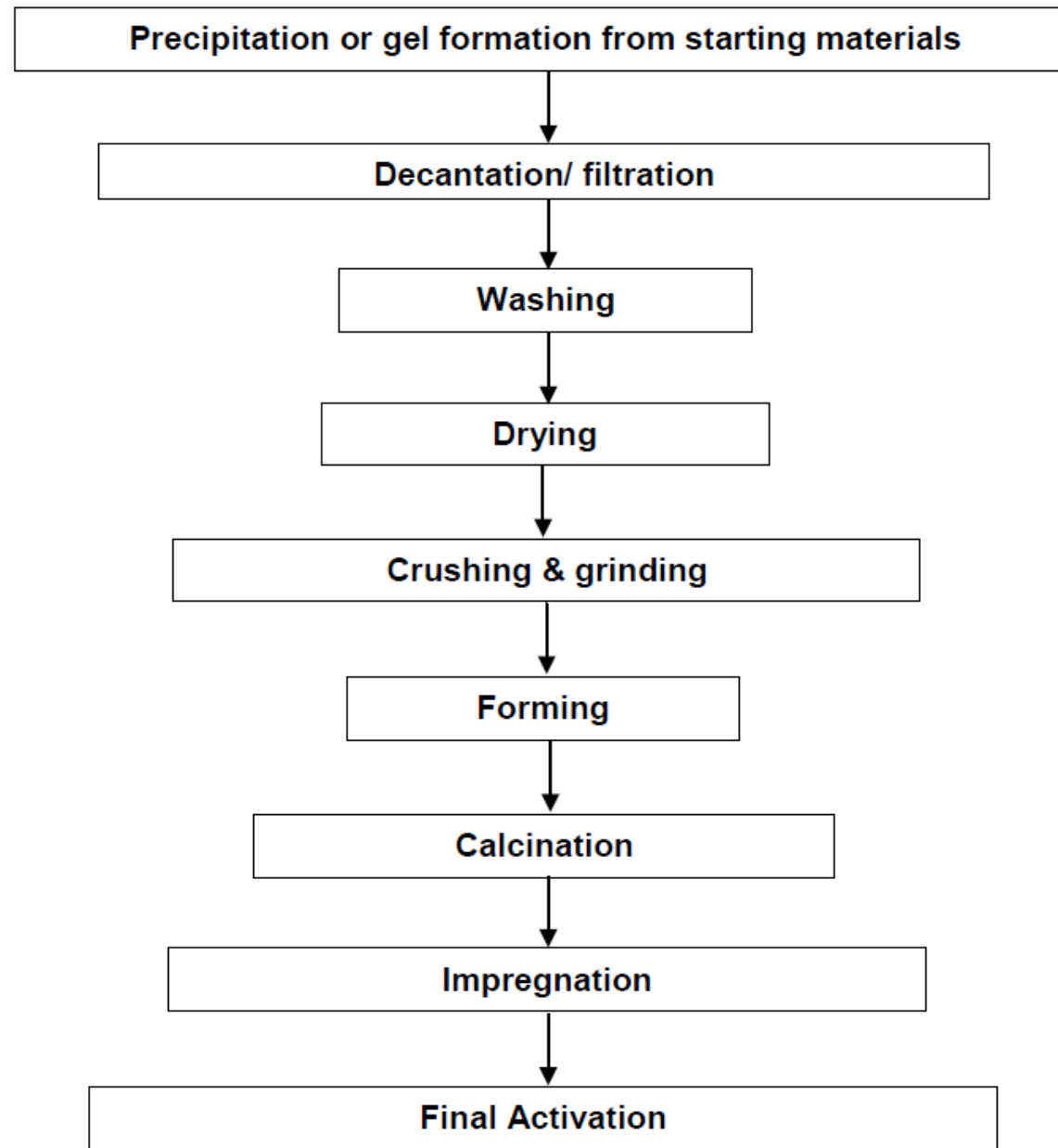


Fig: Basic unit operations in solid catalyst preparation

Precipitation and co-precipitation

1. In this process, the desired component is precipitated from the solution.
2. Co - precipitation is used for simultaneous precipitation of more than one component.
3. Catalysts based on more than one component can be prepared easily by co precipitation.
4. The precipitation process is used for preparation of bulk catalysts and support material such as Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 etc

Process

- In general, the metal hydroxides are precipitated from their precursor salt solution because of their low solubility.
- **The precipitation of hydroxides can be performed either by starting from an alkaline solution which is acidified or from acidic solution by raising the pH.**
- However, most hydroxides for technical application are precipitated from an acidic solution by the addition of an alkaline precipitating agent.
- **Usually, ammonia or sodium bicarbonate is used as the precipitating agent.**
- Highly soluble inorganic salts such as nitrates, carbonates or chlorides are generally used as metal precursors.
- **For example, preparation of alumina is done by precipitating aluminium hydroxide from aluminium nitrate solution by addition of ammonium hydroxide.**



During precipitation, several processes occur and the major steps are :

- Liquid mixing / super saturation
- Nucleation
- Crystal growth to form primary products
- Aggregation of the primary particles

Initial mixing or interdispersing of components in the solution has a significant effect on the precipitation.

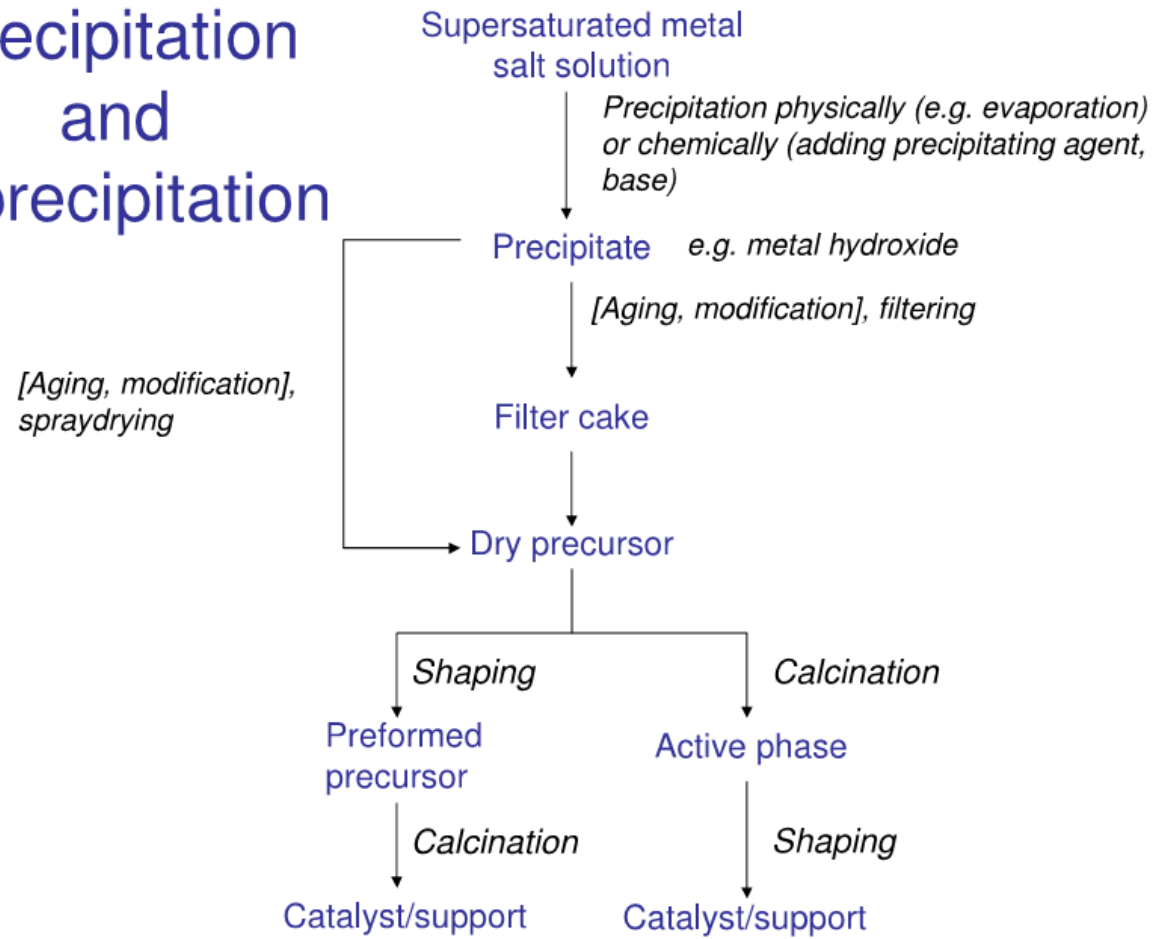
Good mixing result in a more homogeneous product particularly in case of co-precipitation.

Rate of stirring primarily affects the nucleation whereas growth rate is much less influenced by this factor.

Stirring rate also affect the aggregation. Aggregate size can be influenced by changing the stirring rate and the manner of mixing

Overview of catalyst preparation...

Precipitation and coprecipitation



Sol gel method

- In the sol gel process, initially a stable colloidal solution called **sol is formed**.
- The sol is a liquid suspension of solid particles ranging in size from **1 nm to 1 micron**. It can be obtained by hydrolysis and partial condensation of precursors such as **an inorganic salt or a metal alkoxide**.
- The further condensation of sol particles into a three dimensional network produces a gel material.
- The gel is a diphasic material in which the solids encapsulate the solvent. The molecular weight of the oxide species produced continuously increases.
- The materials are referred to as **aqua sol or aqua gels** when water is used as a solvent and **aquosol or alcogel** when alcohol is used.
- The general scheme of preparation by sol gel method is shown in **Fig. 1**

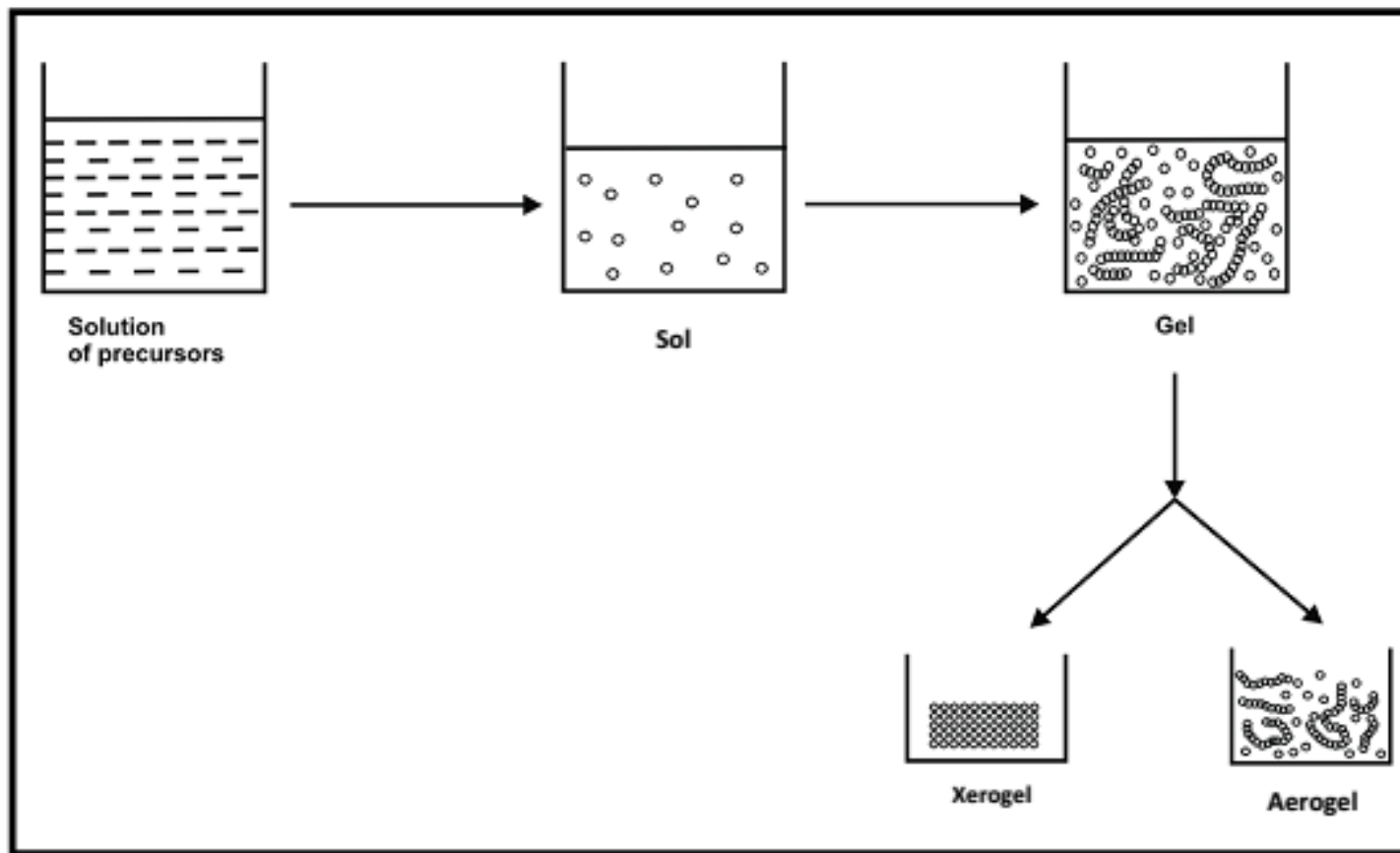


Fig. 1. General scheme of preparation by sol gel method

The encapsulated liquid can be removed from a gel by either evaporative drying or with supercritical drying /extraction.

The resulting solid products are known as xerogel and aerogel, respectively.

When gels are dried by evaporation, the dried product is called xerogel.

When the gels are dried by supercritical drying, the dried gel is called aerogels.

The aerogel retains high porosity and has very high pore volume.

The sol gel method is distinguished from other routes of material preparation from solutions or melts such as precipitation and crystallization by two main characteristics:

1. Formation of clear colloidal solution due to primary condensation of dissolved molecular precursors.
2. These colloidal particles merge during subsequent gelation stage into polymeric chains by chemical bonding between local reactive groups at their surface.

Both stages are controlled by condensation chemistry that can include as a first step, hydrolysis of hydrated metal ions or metal alkoxides molecules. The condensation chemistry in this case is based on olation/oxolation reactions between hydroxylated species. Olation is a condensation process in which a hydroxyl bridge “**-OH-**” **bridge** is formed between two metal centers.

the oxolation is a condensation reaction in which an **oxo bridge** “**-O-**” is formed between two metal centers.

The steps in sol gel processing are shown in Fig. 2 and discussed below.

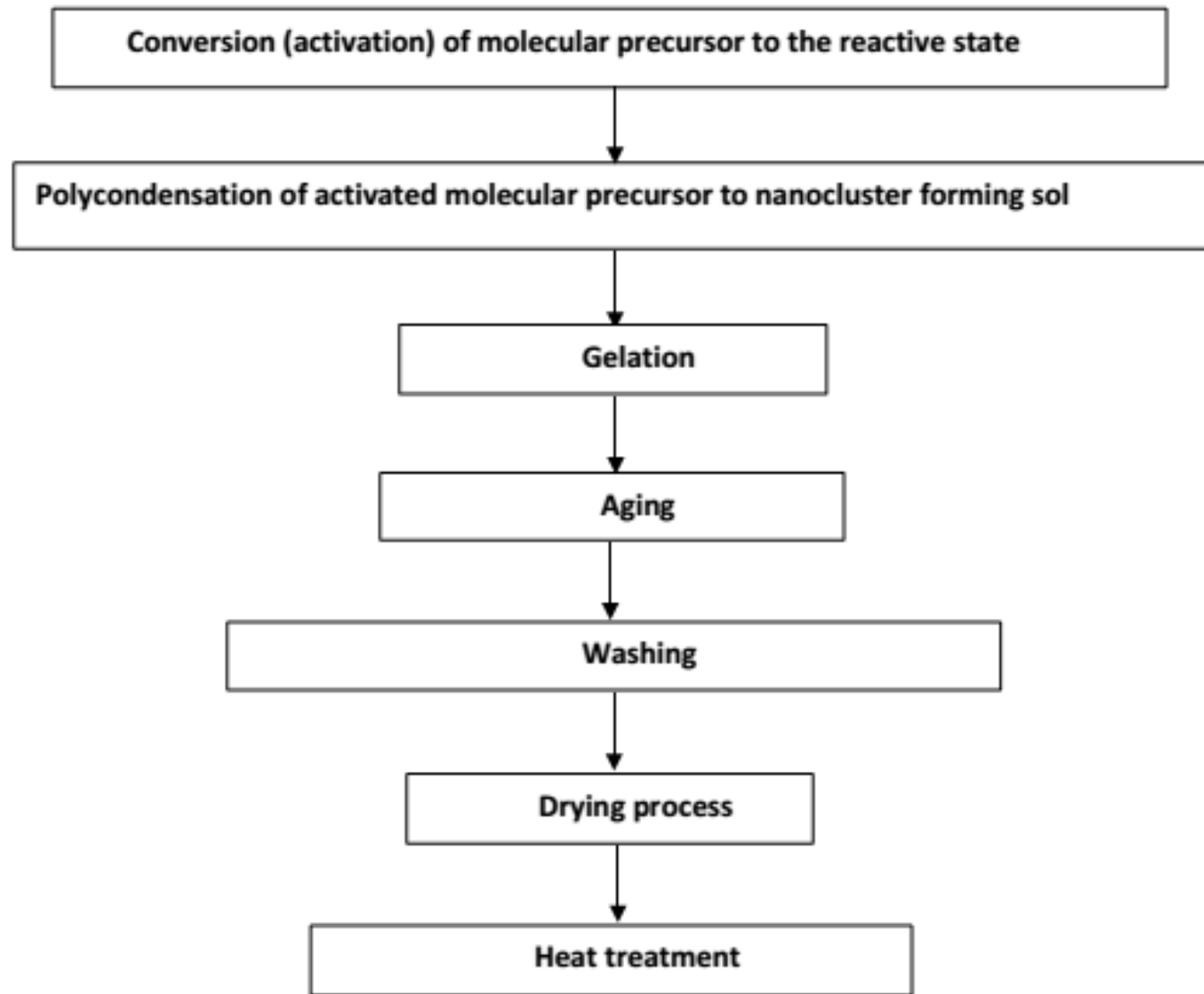


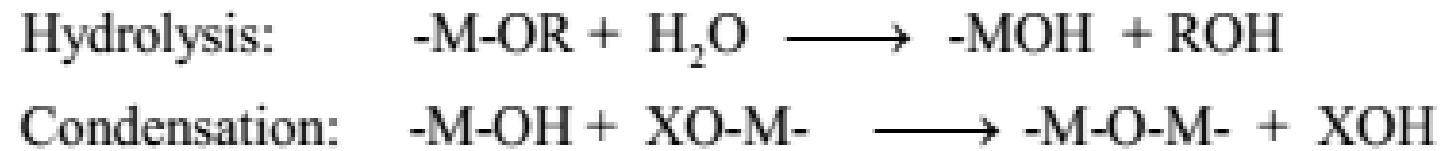
Fig. 2. Basic steps in sol gel processing

Activation and polycondensation :

Metal alkoxides are used as precursors in sol-gel operation. Metal alkoxides are most extensively used as these are commercially available in high purity and their solution chemistry is well documented.

For preparation of alumina and zirconia, aluminium propoxide and zirconium propoxide are used respectively as precursors.

The metal alkoxides are hydrolysed in alcohol solution containing a controlled amount of water. The sol gel chemistry can be represented by following two reactions



Where M= metal ; X = H or R (alkyl group)

Parameters affecting any of the two reactions will affect the properties of the final product.

Two of the main parameters that affect are :

(1) amount and rate of water addition and (2) pH of the solution.

Gelation :

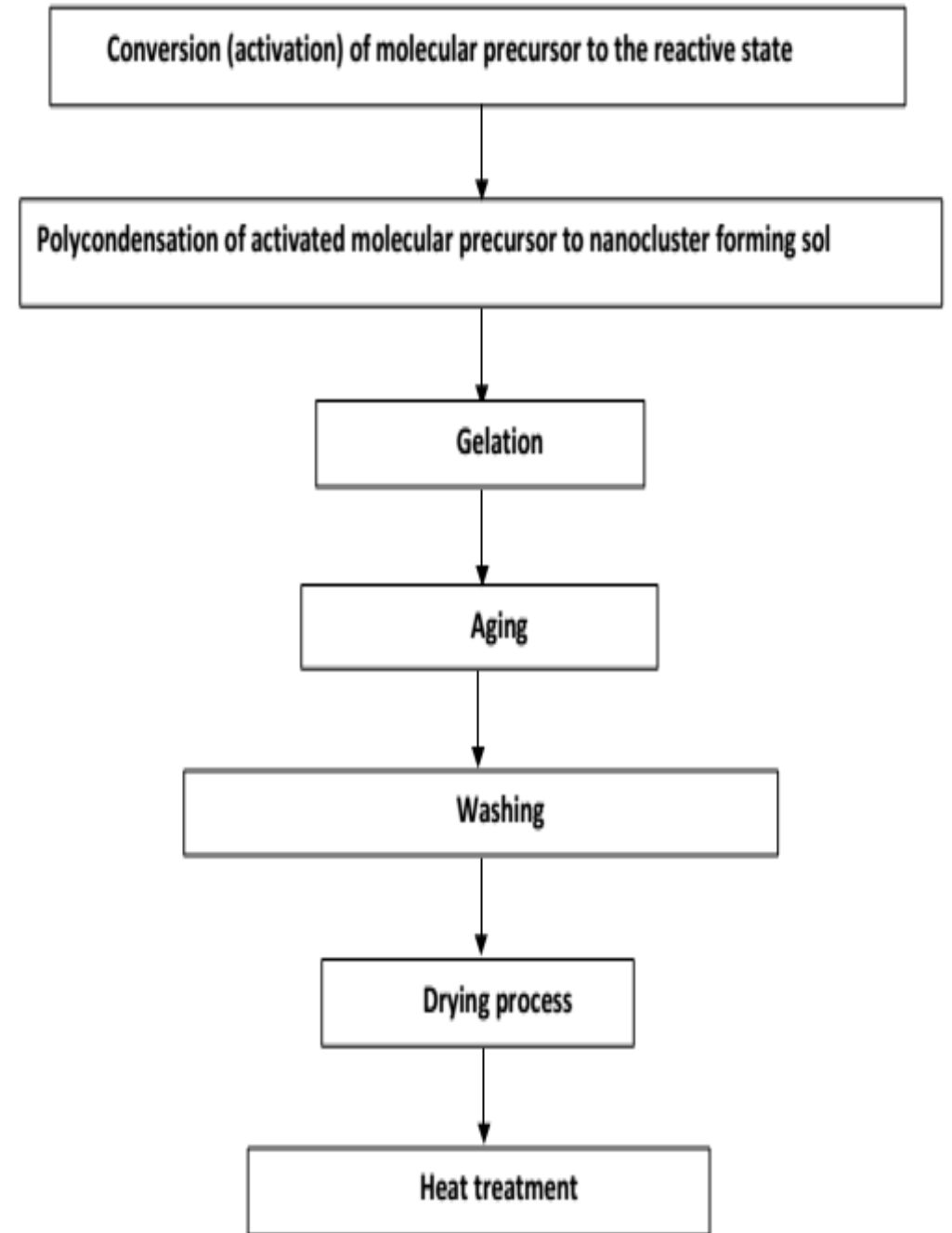
After a period of time the sol experiences a transition from liquid solution to a cross-linked gel state where it can support an elastic stress.

This period of time is known as gel time or gelation time, and during this time the viscosity of the solution undergoes a rapid increase corresponding to the transition from a viscous fluid to an elastic gel.

At the end of gelation there is a continuous phase containing a structure that reflects formation and branching of particles under specific growth conditions.

The formation of a network results in entrapping of the solution.

The gel structure is determined by the ionic character of the M-O bond and the relationship between the hydrolysis and condensation rate.



Aging :

After visible formation of gel, processing proceeds to the aging step where the structure and the properties of the formed network continue to change up to the point that yields the target density.

It represents the time between the formation of the gel and the removal of solvent. As long as the pore liquid remains in the matrix, a gel is not static and can undergo many transformations.

This step includes four processes : polycondensation , syneresis, coarsening , and phase transformation

Polycondensation between surface functional groups continues to occur after the gel point. This process is actually desirable as it leads to a more cross-linked network that is mechanically stronger and consequently easier to handle.

However, extensive condensation can lead to shrinking of the gel to such an extent that the solvent is actually expelled in a phenomenon called syneresis. Parameters that affect this process include temperature, time, and pH of the pore liquid. However, studies off these effects are still very qualitative.

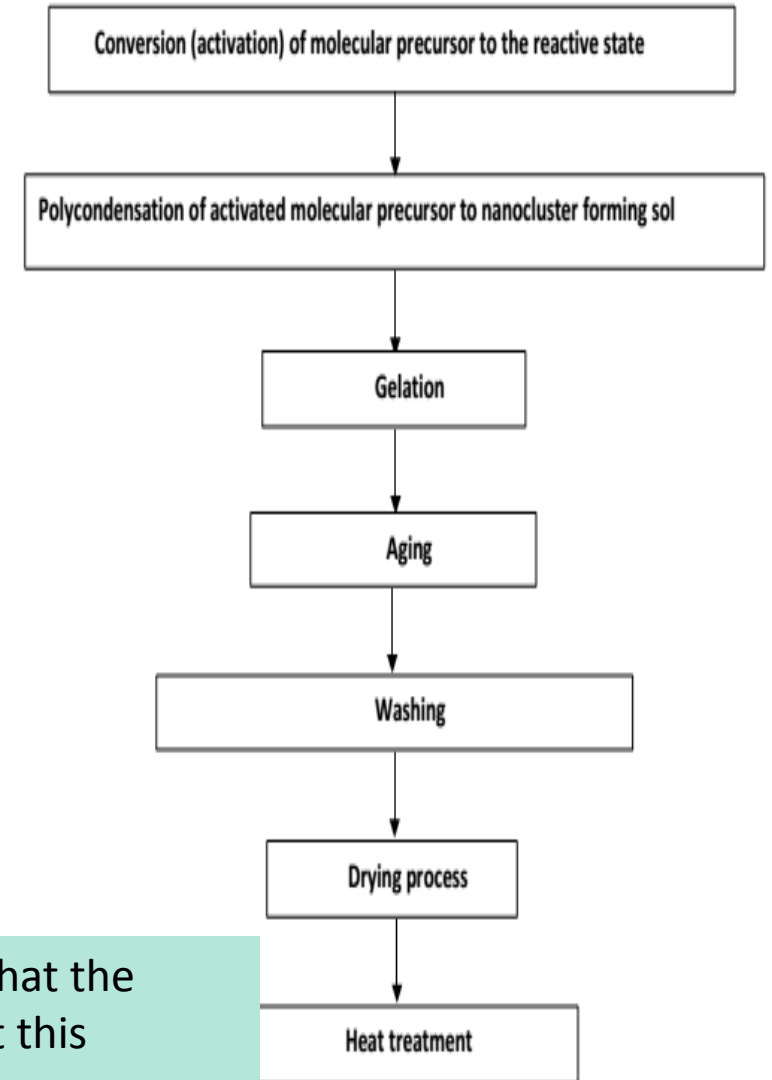


Fig. 2. Basic steps in sol gel processing

After the aging process, material is goes for treatment (washing , drying, heat treatment to get desired catalyst partical.

Characterization of catalyst

Characterization of catalyst

Characterization of heterogeneous catalyst refers to the determination of its **physical and chemical characteristics**, which are responsible for its performance in a reaction. Characteristics of catalysts include:

- Chemical composition of the **bulk and surface of the solids**
- **Surface area and porosity** (micro, meso and macro)
- **Bulk solid structure, phase composition, crystallite size**
- **Surface morphology**
- Surface chemical properties such as:
 1. location and oxidation state of active metals
 2. acid-base property
 3. reducible – oxidizable property
- Aggregate properties such as aggregate or **particle size, density, mechanical strength and attrition resistance**
- Catalytic properties : **activity , selectivity, stability**

BET theory/Method - Determination of surface area

Principle of the method

The **BET** (Brunauer, Emmet and Teller) method involves the determination of the amount of the adsorbate or adsorptive gas required to **cover the external and the accessible internal pore surfaces of a solid with a complete monolayer of adsorbate.**

This monolayer capacity can be calculated from the adsorption isotherm by means of the BET equation.

The gases used as adsorptives have to be **only physically adsorbed by weak bonds** at the surface of the solid (van der-Waals forces) and can be desorbed by **a decrease of pressure at the same temperature.**

The most common gas is **nitrogen at its boiling temperature (77.3 K).**

In the case of a very small surface area (below $1 \text{ m}^2 / \text{g}$), the sensitivity of the instruments using nitrogen is insufficient and krypton at 77.3 K should be used.

In order to determine the adsorption isotherm volumetrically, known amounts of adsorptive are admitted stepwise into the sample cell containing the sample previously dried and outgassed by heating under vacuum

BET theory / Method

Determination of surface area using BET Equation

The BET (Brunauer, Emmet and Teller) equation describes the relationship between **volume adsorbed at a given partial pressure and the volume adsorbed at monolayer coverage**. BET equation can be written in the form :

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \frac{p}{p_0} \quad \text{----- (1)}$$

p = partial pressure ; p_0 = saturation pressure at the experimental temperature ; v = volume adsorbed at p ; v_m = volume adsorbed at monolayer coverage ;
 c = constant

Monolayer coverage is determined using BET equation. The $\frac{P}{v(p_0 - P)}$ is plotted as a

function of $\frac{P}{P_0}$. The plot is linear in the range of relative pressures $\frac{P}{P_0} = 0.05 - 0.3$. At

higher relative pressure p/p_0 , the BET plot deviates from linearity as non-ideality or pore condensation was not accounted for the derivation of BET equation.

Slope and intercept of this linear plot is used for determination of monolayer capacity v_m .

The intercept and slope from the plot is given as

$$\text{Intercept} = \frac{1}{cv_m} \qquad \text{Slope} = \frac{(c-1)}{cv_m}$$

Then the monolayer volume v_m is given as , $v_m = \frac{1}{\text{slope} + \text{intercept}} (STP)$

The total number of N_2 molecules adsorbed corresponding to monolayer volume v_m can be calculated as

$$\text{No. of } N_2 \text{ molecules} = \frac{v_m (m^3) \times 6.02 \times 10^{23} (\text{molecules} / \text{mol})}{0.0224 (m^3 / \text{mol})}$$

Now, each adsorbed N_2 molecule occupies an area of surface comparable to its cross section area of 0.162 nm^2 .

$$SA(m^2) = \left[\frac{v_m (m^3) \times 6.02 \times 10^{23} (\text{molecules} / \text{mol})}{(0.0224 m^3 / \text{mol})} \right] \times 16.2 \times 10^{-20} (m^2 / N_2 \text{ molecule})$$

$$\text{Or } SA(m^2) = v_m (m^3) \times 4.36 \times 10^6 (m^{-1}) = 4.36 \times 10^6 v_m$$

“GTU- Q-paper –

1. Discuss about “Determination of Surface area for catalysts”
2. Write a short note on “Determination of Surface area for catalysts”

Catalyst Deactivation –(fogler-712)

A catalyst can be deactivated in three ways

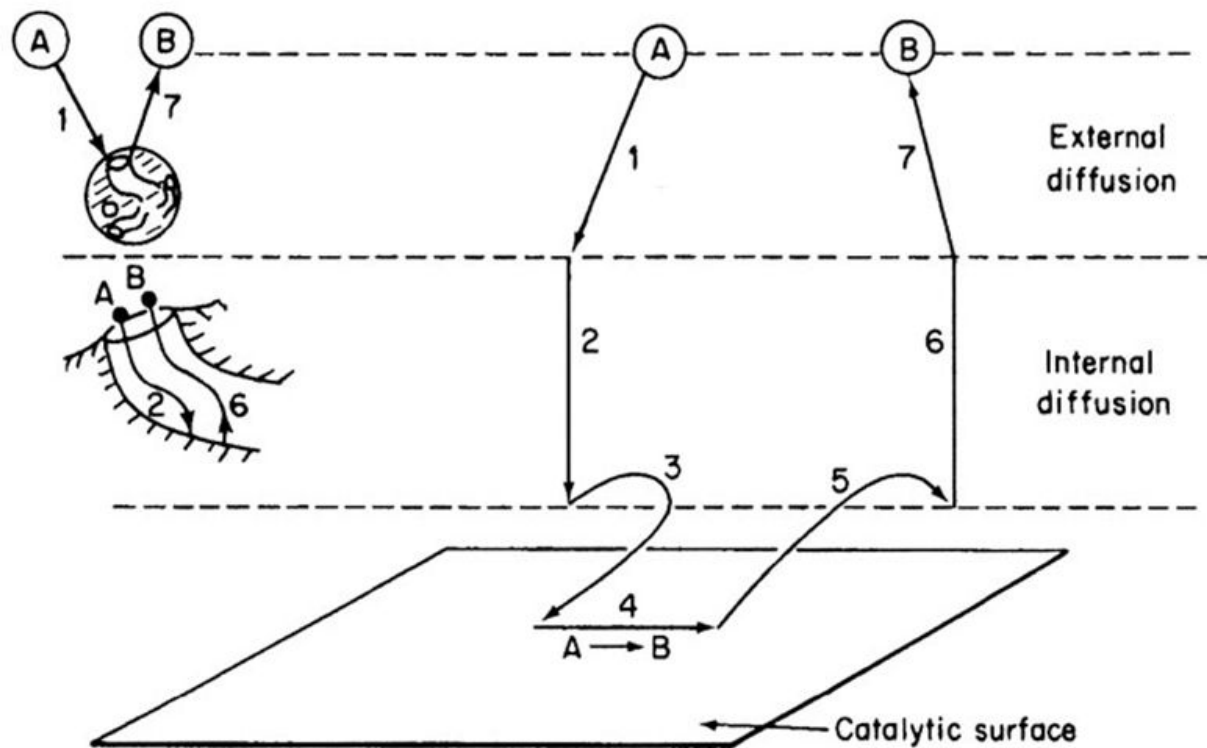
- I. Poisoning : chemisorptions of reactants or products or feed impurities on the active sites of the catalyst surface
- II. Fouling : deposition of coke material on active sites
- Iii. Sintering or phase transformation: because of local high temperature, support of catalysts or catalyst itself may undergo structural modification

Nature or characteristics of catalysed reaction

1. A catalyst remains unchanged in its amount and chemical composition at the end of the reaction.
2. A small amount of a catalyst is often sufficient to catalyse a reaction.
3. A catalyst does not change the state/position of chemical equilibrium (since it does not depend on the pathway of the reaction).
4. A catalyst is usually specific in nature.
5. A catalysed reaction generally has a lower activation energy than non-catalysed reaction. Consequently, the catalysed reaction proceeds at a faster rate.

Mechanism of solid catalysed reaction

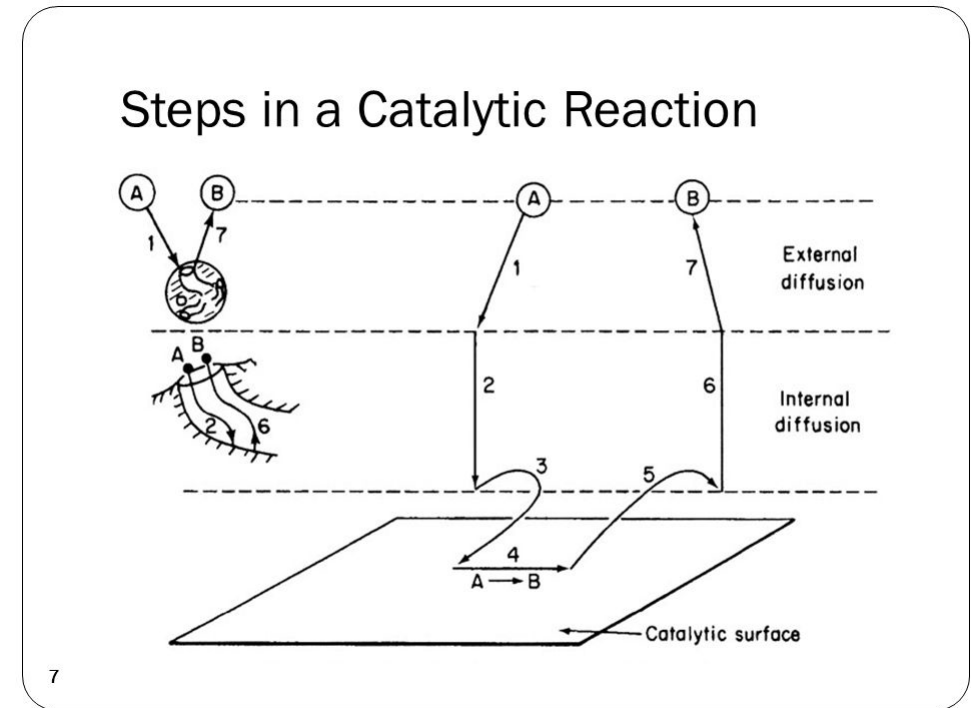
Steps in a Catalytic Reaction



1. External diffusion of reactant
2. Internal Diffusion of reactant
3. **Adsorption** of reactant A
4. **Reaction on the surface of the catalyst $A \rightarrow B$**
5. **Desorption** of the products from the surface
6. Internal diffusion of products
7. External diffusion of products

Mechanism of solid catalysed reaction

1. Mass transfer (diffusion) of the reactant(s) from the bulk fluid to the external surface of the catalyst Pellet
2. Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface
3. **Adsorption** of reactant A onto the catalyst surface
4. **Reaction** on the surface of the catalyst $A \rightarrow B$
5. **Desorption** of the products from the surface
6. Diffusion of the products from the interior of the pellet to the pore mouth at the external surface
7. Mass Transfer of the products from the external pellet surface to the bulk fluid



Step 1,2,6 & 7 are diffusion steps

Steps : 3 4 & 5 are reaction steps

The overall rate of reaction is equal to the slowest step in the mechanisms

Chapter 06

Solid catalyzed reaction : kinetics

Adsorption

Adsorption may be defined as the selective concentration or retention of one or more components of a mixture on a solid surface. The solid that adsorbs a component is called the adsorbent and the component adsorbed is called adsorbate.

The adsorption process is a result of **interaction between the adsorbate molecules and the surface of the adsorbent.**

Type of Adsorption

Physical adsorption	Chemical adsorption
<ol style="list-style-type: none"><li data-bbox="257 272 1281 411">1. The forces operating in this case are weak Vander wall's forces.<li data-bbox="257 411 1281 549">2. The heat of adsorption is low about 20-40 KJ mol⁻¹<li data-bbox="257 549 1281 753">3. The process is reversible, desorption can be occur by increasing tem. Or decreasing pressure.<li data-bbox="257 753 1281 821">4. It does not require any activation energy.<li data-bbox="257 821 1281 1025">5. It takes place at the low temperature and decreases with increase in the temperature.<li data-bbox="257 1025 1281 1163">6. It is not specific in nature all gases adsorbes on all solids to same extent.<li data-bbox="257 1163 1281 1302">7. It increases with the increase insurface area of the adsorbent.<li data-bbox="257 1302 1281 1359">8. It forms multimolecular layer.	<ol style="list-style-type: none"><li data-bbox="1281 272 2308 411">1. The Forces operating are chemical bonds (ionic or covalent bond).<li data-bbox="1281 411 2308 549">2. The heat of absorption are high about 40-400 KJ mol⁻¹<li data-bbox="1281 549 2308 753">3. The process is irreversible. Efforts to free the adsorbed gas give different Compounds.<li data-bbox="1281 753 2308 821">4. It requires activation chergy.<li data-bbox="1281 821 2308 959">5. This type of adsorption first increases with increase in temperature<li data-bbox="1281 959 2308 1163">6. It is highly specific in nature occurs only by the possibility of formation of chemical bond.<li data-bbox="1281 1163 2308 1302">7. It also increases with the increases with the increase in surface area of adsorbent.<li data-bbox="1281 1302 2308 1359">8. It forms unimolecular layer.

Adsorption isotherms

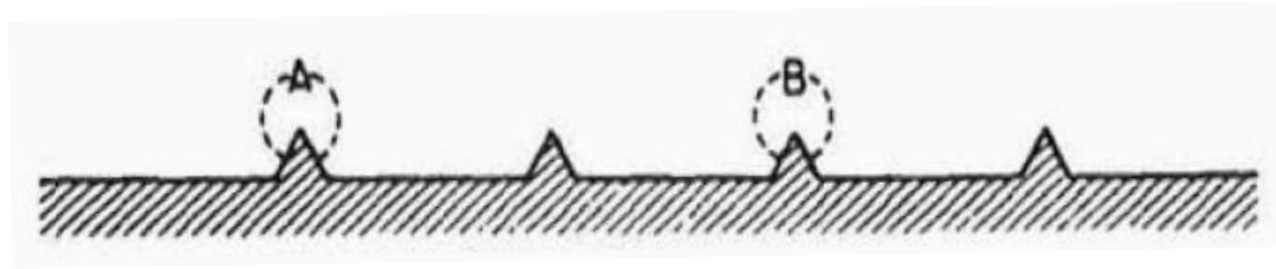


Figure: vacant and occupied sites

Let, S represent active site, & A species to be adsorbed

Further more

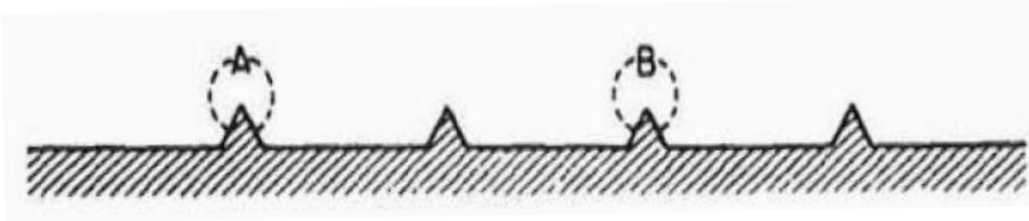
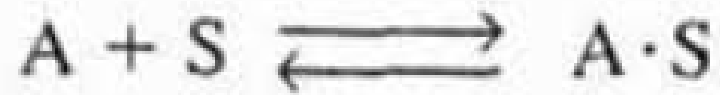
S = vacant site,

$A.S = A$ is adsorbed on the site S .

Species A can be an atom, molecule, or some other atomic combination. Depending on the circumstances.

Adsorption isotherm

The adsorption of **A** on a site **S** is represented by



The **total** molar concentration of active **sites** per unit **mass** of catalyst is labeled **C_t** , (**mol/g.cat**).

P_i , partial **pressure** of species **i** in the gas phase. atm or **kPa**,

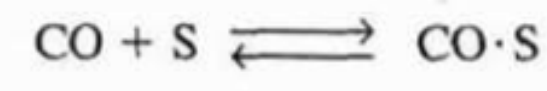
$C_{i,S}$, surface concentration of **sites** occupied by species **i** , **mol/g cat**

Total concentration of sites is $C_t = C_v + C_{A,S} + C_{B,S}$

This equation is referred to as site balance

Adsorption Models

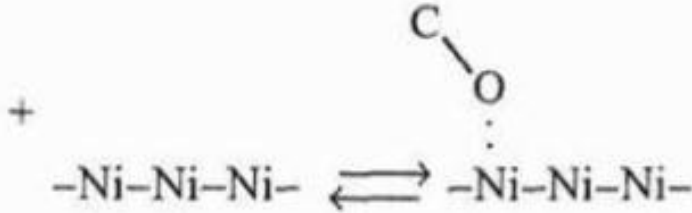
- 1. **Molecular or nondissociated adsorption** (e.g., CO) and
- 2. **Dissociative adsorption** (e.g., C and O).



as is the case on nickel

CO

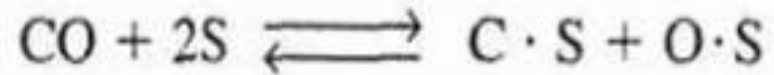
Molecular or nondissociated adsorption



Adsorption Models

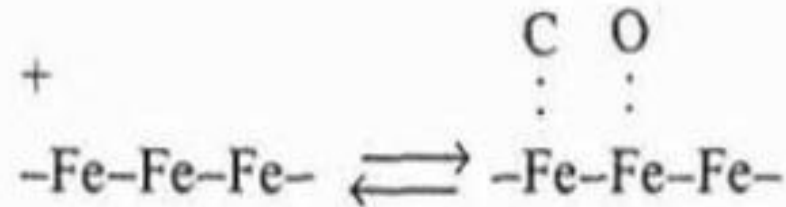
2. *Dissociative adsorption* (e.g., C and O).

In the other, carbon monoxide is adsorbed as oxygen and carbon atoms instead of molecular CO.



as is the case on iron⁸

CO



Dissociative adsorption

