

## Lecture 5

### Solid catalysts

#### Catalyst components

A solid catalyst consists of mainly three components :

1. Catalytic agent
2. Support /carrier
3. Promoters and Inhibitors

#### Catalytic agent:

These are the catalytically active component in the catalyst. These components generate the active sites that participate in the chemical reaction. Activity of any catalyst is proportional to the concentration of these active sites. Though concentration of the active sites depends on the amount of catalytically active component, however, it is not always directly proportional. Availability of active sites depends mainly on the dispersion of catalytic agent. The dispersion is defined as ratio of total number of exposed atoms/molecules of catalytic agent available for reaction to total number of atoms/molecules of catalytic agent present in the catalyst sample.

Catalytic agents may be broadly divided in the following categories:

- i. Metallic conductors ( e.g Fe, Pt, Ag, etc.)
- ii. Semiconductors (e.g. NiO, ZnO,etc.)
- iii. Insulators (e.g. Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>,MgO etc.)

**Metallic conductors:** The metals that have strong electronic interaction with the adsorbates are included in this category. The metals are used in various catalytic reactions such as methanol synthesis, oxidation , hydrogenation and dehydrogenation processes.

### Examples of metal catalysts :

Cu for water gas shift reaction and methanol synthesis ; Ag for oxidation of ethylene to ethylene oxide, Au for oxidation of methanol to formaldehyde; Fe for ammonia synthesis; Pd and Pt for hydrogenation of olefins, dienes, aniline or nitriles as well as dehydrogenation of alkanes, alcohols, cyclohexanes, cyclohexanols etc.

### Semiconductors :

The oxides and sulfides of transition metals that have catalytic activity are included in this category. Similar to conducting metals, they are also capable of electronic interaction with adsorbed species and catalyze the same type of reactions. Usually the lower valence band electrons participate in bonding. The upper conduction band separated by band gap energy is empty unless electrons are promoted by heat or radiation. Semiconductor characteristics may be intrinsic or induced by addition of foreign ion, creating cationic or anionic vacancies. Common transition oxides and sulfides such as CuO, AgO, NiO, CoO, Fe<sub>2</sub>O<sub>3</sub>, MnO, Cr<sub>2</sub>O<sub>3</sub>, FeS, V<sub>2</sub>O<sub>5</sub> show conductivity. These materials participate in catalytic reactions and reaction occurs through acceptance or donation of electrons between the reactant material and catalysts. Few applications of semiconductor catalysts are : CuO for oxidation of nitric oxides, NiO for dehydrogenation of alkanes, MnO<sub>2</sub> for oxidation of alcohols, and V<sub>2</sub>O<sub>5</sub> for oxidation of hydrocarbons.

**Insulators** : Catalytic functions of insulators are different from that of conductor and semi conductor materials. Insulators have large values of band gap energy and very low concentration of impurity levels. The electrons remain localized in valence bonds and redox type reactions involving electronic interaction as observed for metal or semiconductor catalysts does not occur. However, insulators have sites that generate protons, thereby, promote carbonium ion based reactions such as cracking, isomerization or polymerization. Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, zeolites, MgO, CaO, MgAl<sub>2</sub>O<sub>4</sub>, SiO-MgO are few examples of the insulators used as catalysts.

### **Support or carrier**

Support or carrier provides large surface area for dispersion of small amount of catalytically active agent. This is particularly important when expensive metals, such as platinum, ruthenium, palladium or silver are used as the active agent. Supports give the catalysts its physical form, texture, mechanical resistance and certain activity particularly for bifunctional catalysts. Area of the support can range from 1 - 1000 m<sup>2</sup>/gm. Common supports are alumina, silica, silica-alumina, molecular sieves etc. The surface area of  $\alpha$  - alumina is in the range 1-10 m<sup>2</sup>/gm whereas the surface area for  $\gamma$  or  $\eta$  - alumina can be in the range 100 – 300 m<sup>2</sup>/gm.

Support may be inert or interact with the active component. This interaction may result in change in surface structure of the active agent and thereby affect the catalyst activity and selectivity. The support may also exhibit ability to adsorb reactant and contribute to the reaction process.

### **Promoters :**

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.

Promoters are termed as physical or chemical promoter depending on the manner they improve the catalyst performance.

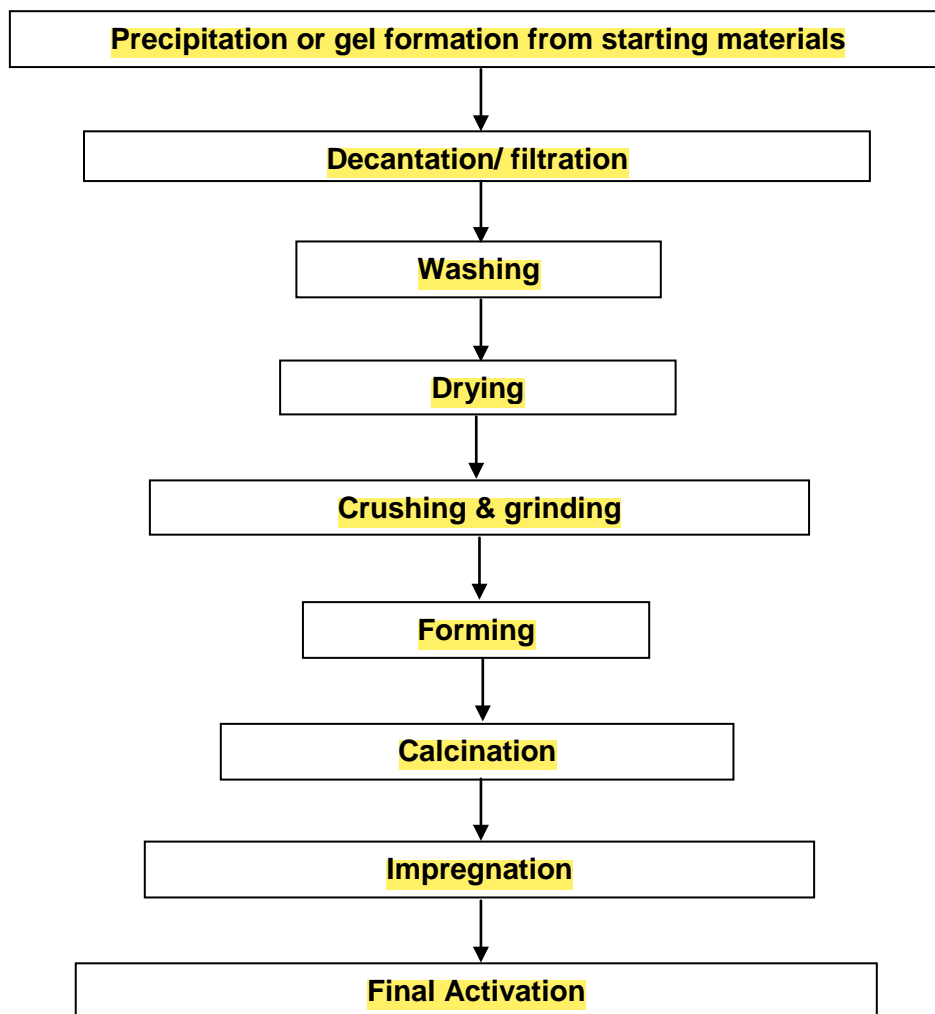
The additives that maintain physical integrity of the support and/or deposited catalytic agents are termed as physical promoters. For example, addition of small quantities of alumina to an iron catalyst employed in ammonia synthesis prevents sintering of the iron crystallites. Thus, for this catalyst, alumina is a physical promoter. The addition of K<sub>2</sub>O 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 promoters or inhibitors:** 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<sub>2</sub> formation thus acting as an inhibitor.

### **Industrial catalysts**

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



**Fig. 1. Basic unit operations in solid catalyst preparation**

## **Preparation of solid catalyst**

The catalyst preparation methods can broadly be 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.

Basic unit operations involved in preparation of solid catalyst is shown in Fig 1. Each step is discussed in detail in the following sections.