

## Lecture 8

### Supported catalysts

Supported catalysts are prepared by deposition of the active metal on the support materials. The main purpose of using a support is to achieve an optimal dispersion of the catalytically active component and to stabilize it against sintering. But in many reactions the support is not inert and the overall process consists of two catalytic functions both for active components and support.

Supported catalysts are prepared in two main steps:

1. Deposition of the precursor of the active component on the support.
2. Transformation of this deposited precursor to catalytically active site.

The final active component can be in metallic state, oxide form or reduced form depending on the requirements.

There are various deposition methods. Most of these involve aqueous solutions and liquid solid interface. In some cases, deposition is also done from the gas phase and involves gas- solid interface. The methods most frequently used are:

- a. impregnation
- b. ion exchange

#### Impregnation

Impregnation can be classified in two categories according to the volume of solution used.

##### Dry or incipient impregnation

In this method, a previously dried support is contacted with volume of solution equal to its pore volume. The solution contains the required amount of the precursors of the active phase. As soon as the support is placed in contact with the solution, the solution is drawn into the pores by capillary suction. In case of proper wetting, no excess solution remains outside the pore space. Part of the air present in the pores is imprisoned and compressed under the effect of capillary forces. The pressure developed inside the imprisoned gas

bubbles depends on the radius,  $r$ , of the curve of the liquid -gas meniscus and may reach several MPa when  $r < 100$  nm as a result of Young - Laplace law,  $\Delta P = P - P' = \frac{2\gamma}{r}$ , where  $\gamma$  is the liquid- gas interfacial tension. Considerable forces will thus be exerted on the portions of the pore walls in contact with these bubbles. The walls that are not strong enough may break down causing a degradation of the mechanical properties. Occasionally, even bursting of the catalyst grains occurs. However, the development of the high pressure is a transitory phenomenon. Under highly compressed conditions, air dissolves and progressively escapes from the solid.

#### Wet / diffusional impregnation

In this method, the pore space of the support is first filled with the same solvent as used in the impregnating precursor solution. The wetted support is then treated with the impregnating precursor solution. Here the actual impregnation takes place in diffusional condition when solvent filled support is dipped in the precursor solution.

The first phase of saturation of the support by solvent involves the characteristics of dry impregnation. But in the second phase, when solvent saturated support is added to the impregnating solution, high pressure is not developed within the pores. The precursor salt migrates progressively from the solution into the pores of the support. The driving force at all times is the concentration gradient between the bulk solution and the solution within the pores. The impregnation time is much longer than for dry impregnation.

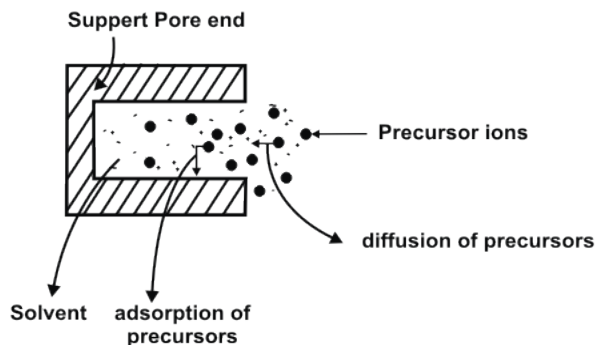
Wet impregnation should be avoided when the interaction between the precursors and the support is too weak to guarantee the deposition of the former.

**Mechanism of impregnation:** The mechanism of wet impregnation is simpler compared to dry impregnation. In wet impregnation, the distribution of the solute inside the pores is assumed to be governed by two phenomena (Fig 1):

1. Diffusion of the solutes within the pores. It is described by Fick's law
2. Adsorption of the solute onto the support. This depends on the adsorption capacity of the surface and on the adsorption equilibrium constant.

The distribution of the precursors within the pellets depends on the balance between these diffusion and adsorption phenomena.

#### (a) Wet impregnation



#### (b) Dry impregnation

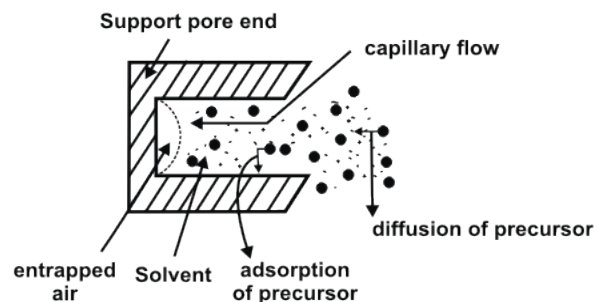


Fig. 1. Schematic representation of basic processes involved during impregnation of precursors on porous support.

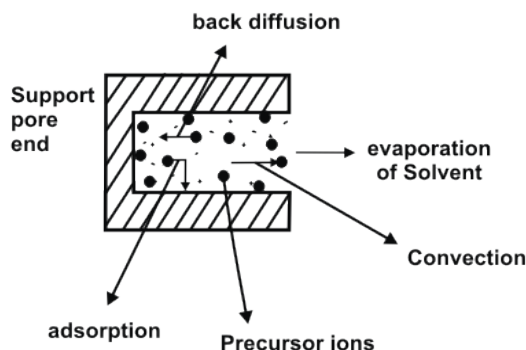
In case of dry impregnation, in addition to diffusion and adsorption processes, another phenomenon occurs, which is the pressure driven capillary flow of the solution inside the empty pores. This can be represented by Darcy's law. An important parameter from introduction of Darcy law is the solution viscosity ' $\mu$ '. In case of aqueous solution and in the common range of concentration used for impregnation, viscosity increases almost proportionally with concentration. It also increases with the presence of organic ligands attached to the metal ions. Viscosity and concentration have opposite effects on precursor diffusion; a high concentration tends to favor the diffusion of the solute towards the centre of the pellet, while a high viscosity tends to hinder the diffusion.

#### Drying

Impregnation is followed by elimination of the solvent. The impregnated sample is heated in an oven in a flow of gas, as discussed earlier. The gas may be air, oxygen, nitrogen or any other gas depending on the requirement. The temperature is generally maintained slightly higher than the boiling point of the solvent e.g 110-120 °C for water. The elimination of water from the pores leads to the increase of precursor concentration

up to saturation and consequent crystallization, preferably on the seeds resulting from the interaction with the support. Apart from temperature, heating rate affects the drying process.

**(a) Constant rate period of drying**  
**drying**



**(b) Falling rate period of**

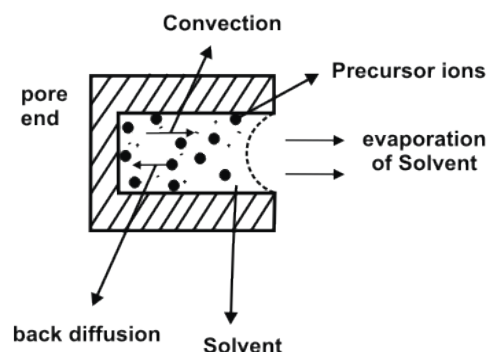


Fig. 2. Schematic representation of drying process during impregnation method

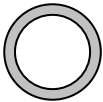
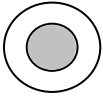
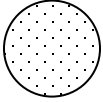
**Drying Mechanism:** The drying process can be modeled considering the outward convective flow of liquid towards the pore mouth at pellet surface where the solvent evaporation occurs. This convective flow can be described by Darcy's law and is associated with the outward flow of the precursors that is favored by a low viscosity of the solution. As the precursor concentration increases near the outer surface of the pellet due to this outward flow, an inward back diffusion of precursors, which can be modeled by Ficks law, takes place. Apart from these two flows in opposite directions, another factor that needs to be considered is the interaction between the precursor and support surface. Schematic representation of drying process during impregnation method is shown in Fig. 2.

The distribution of the precursor phase in the pellet or its segregation at the outer surface depends on the relative contribution of adsorption, convection and back-diffusion as long as the flow of solvent is high. This corresponds to constant rate period of drying.

As the solvents recedes inside the pores, evaporation occurs within the pores corresponding to the falling rate period. The drying regime is defined as slow if the constant rate period predominates and as fast if it is falling- rate period controlled.

**Precursor distribution:** The distribution of precursors within the pores of support depends on various factors. The different conditions of impregnation and drying can result in broadly three types of precursor distribution as described in Table 1. In Egg shell type distribution the precursors are preferentially accumulated near the pore wall. This type of distribution is obtained if during impregnation precursors are strongly adsorbed on the pore wall. High viscosity of the solution also tends to result in egg shell distribution. For slow drying, egg shell distribution can result even in low viscosity and weak adsorption conditions. In egg yolk type distribution the precursors are accumulated in the interior core of the pores. Egg yolk distribution is obtained if during impregnation, the competing ions are present that have stronger interaction with the pore wall of supports. Fast drying regime with predominant back diffusion also results in egg yolk distribution. In uniform precursor distribution, precursors are uniformly distributed across the pores. If the adsorption of the solutes is weak and the time is long enough, distribution tends to be uniform. Uniform distribution also results when precursors and competitors interact equally with the surface or the impregnating solution is concentrated and viscous. Room temperature drying with weakly adsorbing precursors also tends to give uniform precursor distribution. For powders, the equilibrium is reached within few minutes. However, in case of pellets it may take up to several hours to reach a uniform distribution of the precursors.

Table 1. Distribution of precursor at different conditions of impregnation and drying.

Precursor distribution	Conditions of Impregnation and drying
Egg shell distribution 	<ol style="list-style-type: none"> <li>1. Strong adsorption of precursors during impregnation</li> <li>2. High viscosity of impregnating solution</li> <li>3. Slow drying regime for low concentration, low viscosity and weak adsorption conditions</li> </ol>
Egg yolk distribution 	<ol style="list-style-type: none"> <li>1. In presence of competitor ions that have stronger interaction with the supports</li> <li>2. Fast drying regime with predominant back diffusion</li> </ol>
Uniform distribution 	<ol style="list-style-type: none"> <li>1. Precursors and competitors interact equally with the surface.</li> <li>2. Impregnating solution is concentrated and viscous</li> <li>3. Room temperature drying with weakly adsorbing precursors</li> </ol>

### Parameters affecting the impregnation process

The pH of the solution is an important parameter in the impregnation process. On liquid side, pH determines the most abundant species in solution to be deposited on to the support.  $\text{HNO}_3$ , carboxylic acids, ammonia are usually used for adjusting the pH because these can decompose during thermal treatment. On solid side, pH controls the nature of surface charge and the number of charged sites, in other words, the zeta potential. During impregnation, the extent of interaction between the metal complex and the support is controlled by parameters such as isoelectric point of oxide support, temperature and nature of support and dopants.