Solid catalysts

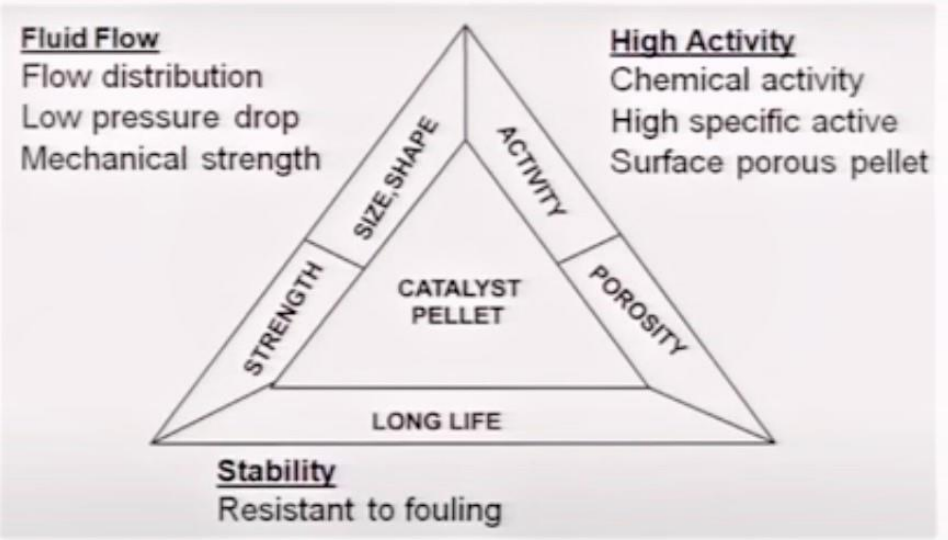
Book: *Chemical Engineering Kinetics*, J. M. Smith, 2nd Edition (Chapter 8), 3rd Edition (Chapter 8)

General requirements for a good catalyst

- **Activity**
  - should be able to **promote the rate of the desired reaction**
  - needs to adsorb the reactant molecules strongly enough for them to react, but not so strongly that the product molecules stick more or less permanently to the surface
- **Selectivity**
  - should be able to **promote only the rate of the desired reaction** and retard the undesired reaction
  - selectivity is sometimes considered to be more important than activity and may be more difficult to achieve
- **Stability**
  - should be able to **resist deactivation** caused by impurities, thermal deterioration or attrition

Shape, size and porosity

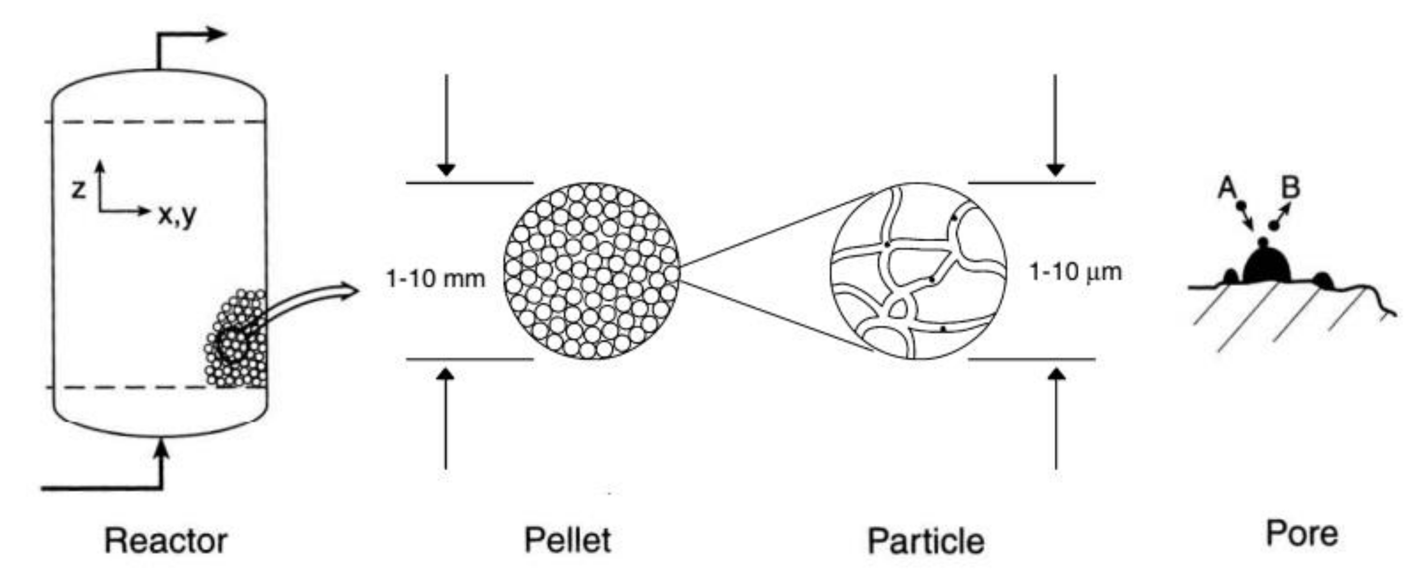
- **Porous catalysts** provide **high internal surface area**, larger **number of active sites**, chances of **better dispersion**
- Catalyst shape and size should be such that to **provide low pressure drop** – large particles provide low pressure drop but has high internal mass transfer resistance
- Catalyst should have **sufficient mechanical strength** to avoid breakage during reaction and loading



https://nptel.ac.in/courses/103/102/103102012/

Porous catalyst pellet

- Solid catalysts are **normally porous** – it is difficult to obtain large outer surface area (> 1 m^2/g) by sub dividing non-porous solids into smaller particles
- Size of the **catalyst pellet** used in a commercial reactor can **typically range from 1–10 mm**
- The pellet is usually composed of **smaller particles** frequently on **the order of 1 μm** that are held together by a binder added during the catalyst preparation process
- These **smaller particles** are usually porous and **contain micropores** (pore diameter ≤ 2 nm) and **mesopores** (2 nm < pore diameter ≤ 50 nm)
- **Macropores** (pore diameter > 50 nm) can **also exist** which can be dependent on the size and packing density of these small particles



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Catalyst preparation

Bulk or unsupported catalysts

- **Entire catalyst** consists of the **catalytically active substance**
- Catalysts are prepared by (i) precipitation or (ii) gel formation

Precipitation – method of obtaining solid material in a porous form

Involves (a) adding a precipitating agent to solutions of desired component

(b) washing (c) drying

(d) calcination (e) activation (in some cases)

Example: MgO catalyst is prepared by precipitating Mg salt from a nitrate solution by adding sodium carbonate

$$Mg(NO_3)_2 + Na_2CO_3 \rightarrow MgCO_3 \downarrow + 2NaNO_3$$

↓

washed with water to remove all traces of sodium

↓ filtration

wet paste dried at room temperature

↓

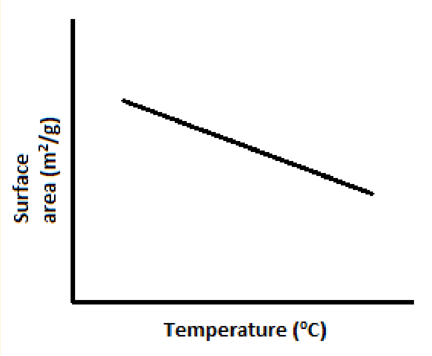
calcined (treatment at high temp; $MgCO_3$ decomposes to MgO and CO_2)

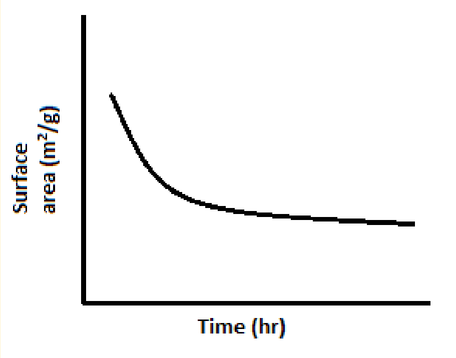
Calcination is an important step in catalyst preparation

Calcination, often **the last step in catalyst preparation** is the **heating** of solids **to a high temperature** after the drying process

The process of calcination is carried out to –

- **Decompose the precursor** and **remove volatile materials** – leads to the formation of a well determined porous structure
- The hydroxide form is converted to oxide form; chemically bound water is removed at higher temperature
- **Attain thermal stability** – catalyst sample is subjected to a more severe heating treatment than that is likely to encounter in a reactor to ensure the stability of its textural and structural properties during reaction
- **Surface area** often **decreases with temperature and time** - material calcined beyond reaction temperature so there is no collapse of surface area during reaction





- Higher temperature cause material to **crystallize into different structural forms**

$$Al_2O_3(\delta)_{cubic} \rightarrow Al_2O_3(\theta)_{monoclinic} \rightarrow Al_2O_3(\alpha)_{hexagonal}$$

Bulk or unsupported catalysts

Sol-gel method

- This is a special case of precipitation method for **catalysts containing silica and alumina** – precipitate is **colloidal nature**
- Main steps involved are:

Metal salts (alkoxides) or precursors are dissolved in a solvent (sol formation)

↓

Water and acid/base is added for pH adjustment

↓

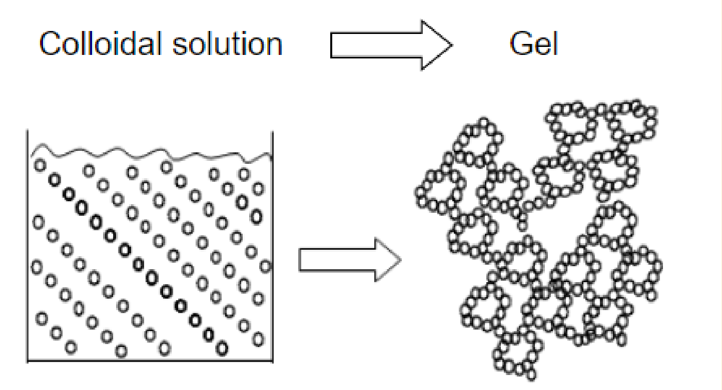
Forms self supporting gel with porous structure

↓

Gel allowed to age

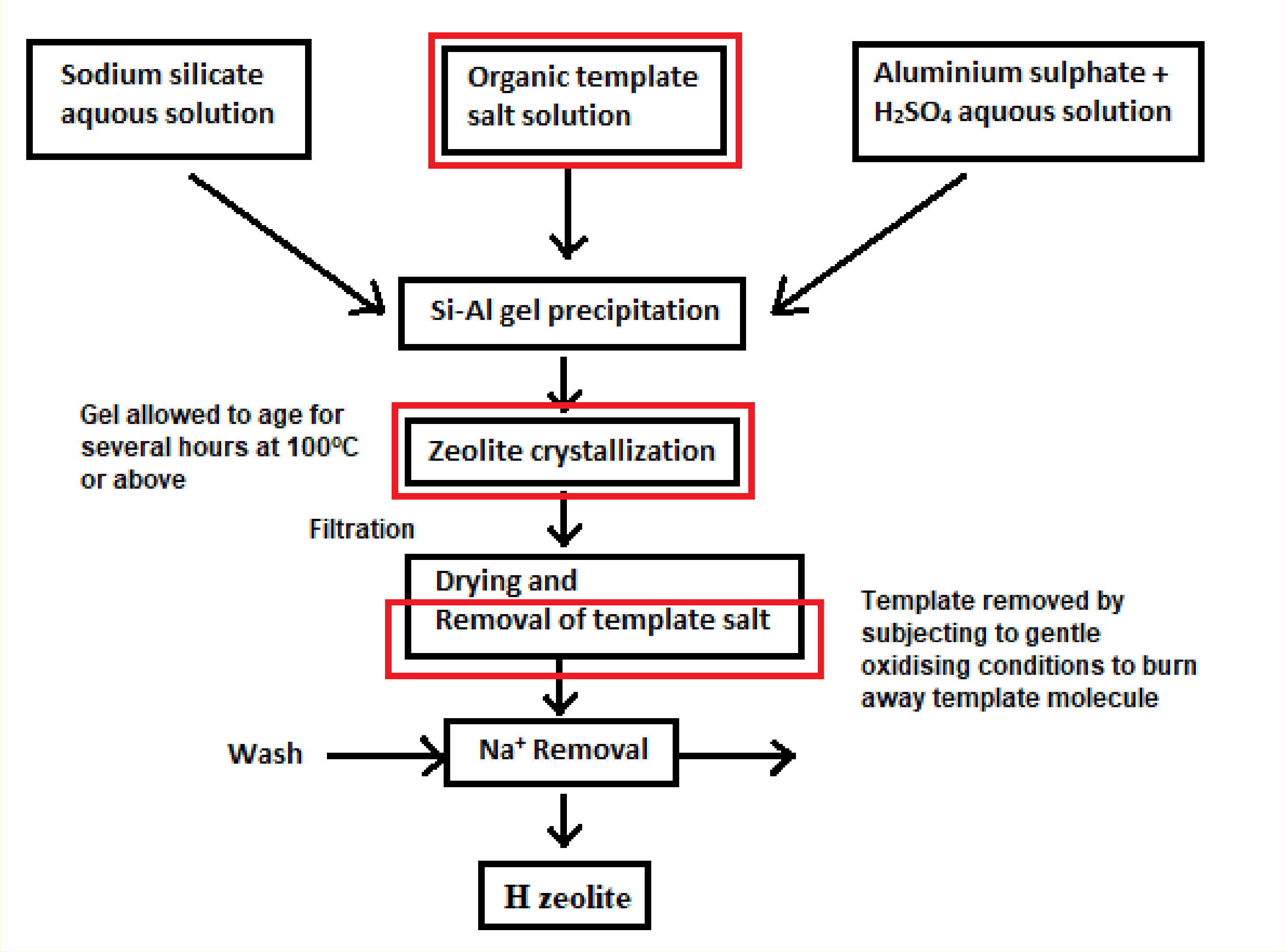
↓

Dried to remove solvents



- Drying step needs to be carried out carefully so that porous structure does not collapse
- Special methods such as supercritical extraction and use of cryogenic conditions are used for drying of liquid in gels

Preparation of silica-alumina bulk catalysts (amorphous) or zeolites (crystalline)



Sodium silicate aqueous solution

Organic template salt solution

Aluminium sulphate + H_2SO_4 aqueous solution

Si-Al gel precipitation

Gel allowed to age for several hours at 100°C or above

Zeolite crystallization

Filtration

Drying and Removal of template salt

Template removed by subjecting to gentle oxidising conditions to burn away template molecule

Wash

Na^+ Removal

H zeolite

All the steps are used for preparation of crystalline product (zeolite)

For amorphous product, the steps indicated by red boxes are removed

Catalyst preparation

Supported or impregnated catalysts

- Prepared by **impregnation of preformed supports** with **solution of active catalytic species**
- Main **purpose of using a support** is to achieve a **large surface area** with **optimal dispersion of the catalytically active component** and to **stabilize it against sintering**
- Supported catalysts are prepared in two main steps :
  1. <u>Deposition of precursors of active catalytic species</u> on the support
  2. <u>Transformation</u> of this deposited precursors <u>to catalytically active site</u>
- The final active component can be in **metallic state**, **oxide form** or **reduced form** depending on the requirements
- Active catalytic species are deposited using three methods – **(i) ion exchange**

  (ii) wet and dry impregnation

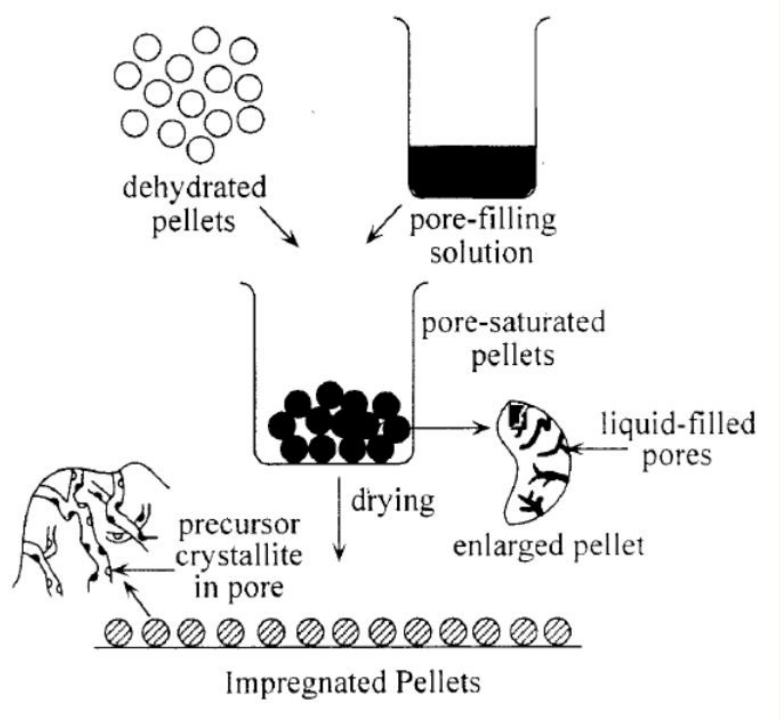
  (iii) deposition - precipitation

Ion exchange method

- Ion exchange consists of **replacing an ionic species by another ionic species** in electrostatic interaction of the precursors with the surface of a support
- **Support** (containing the ion A)is **dipped into a solution of metal precursor** (containing ion B) for a sufficient amount of time
- Ion B gradually **penetrates into the pore space of the support** and takes the place of ion A, which passes into the solution
- This **continues until an equilibrium is established** corresponding to a given distribution of the two ions between the solid and solutions
- The **support** is then **removed from solution, dried and calcined**
- The **position of the metal ions are fixed**, there is **no maldistribution during the drying process**
- The **achievable loading** is limited by **(i) ion-exchange capacity or/and (ii) saturation concentration of solution**
- Important method for microporous supports or the pores may get clogged

Impregnation method (Wet and Dry)

- Support is **dehydrated (evacuated) of adsorbed moisture** and **impurities** by treating at high temperatures
- It is then **immersed in the solution of precursor** (metal salt solution) and the **pores of the support** are allowed to be **filled up by this metal salt solution** of a given concentration depending on the loading desired
- Impregnation is followed by elimination of the solvent. The **excess solution is dried** (for wet impregnation) and then the **dried catalyst is calcined**
- In some cases, the **calcination step may be followed by activation**

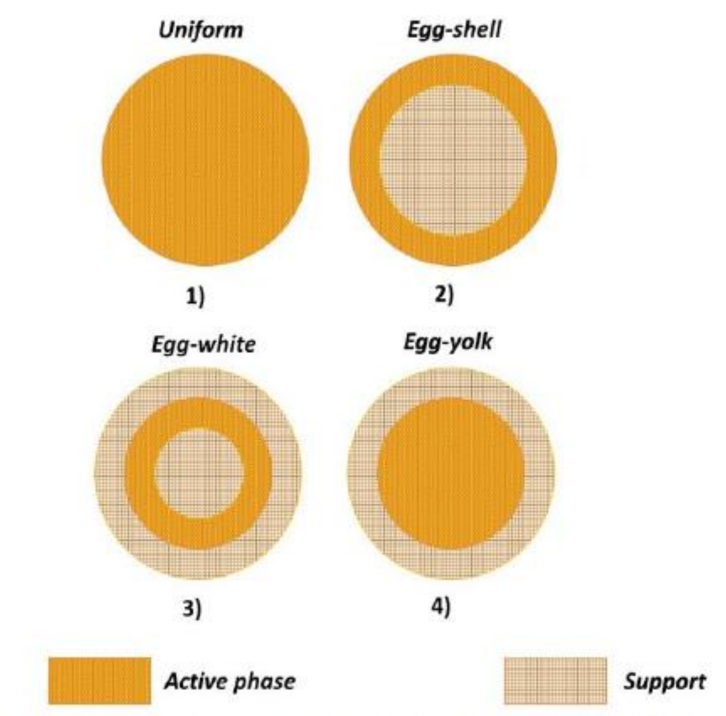


CH_4 Reforming for Synthesis Gas Production over Supported Ni Catalysts, Hoon Sub Song

- Example: Ni/Al_2O_3 hydrogenation catalyst is prepared by soaking the evacuated Al_2O_3 in $Ni(NO_3)_2$ solution, drying the excess solution and calcining it to form NiO from $Ni(NO_3)_2$.The final step is to convert NiO to Ni by reducing it in situ in H_2 just before the reaction
- **Dry impregnation or Incipient Wetness Impregnation** – the evacuated support is contacted with **as much active metal precursor solution to just fill the pores in the support** (solution volume = pore volume of support), then **dried at room temperature, and finally calcined**

Deposition-Precipitation

- Method involves **dispersing the support in solution** and then **adding the precipitation agent** for precipitating the active material
- The **active component can be homogeneously distributed** throughout the support particles (uniform) or **form an egg-shell on the outer surface**
- Other **possibilities of distribution** of the active agent is the **egg white and the egg yolk type**
- **Active phase distribution profile** can be obtained by proper selection of impregnation parameters like **choice of precursor, pH, time of contact, drying process**
- **Uniform distribution** of active agent is **usually desired when transport limitations are not expected**
- **Egg-shell distribution** is useful when the **active phase is expensive, transport limitations are present or when secondary reaction needs to be avoided**



Active phase distributions for a spherical catalyst particle

Russo et. Al., ChemEngineering **2020**, *4*(2), 24

- If the **reactant feed consists of catalytic poisons**, it is better to deposit the active component inside the subsurface layer, and have an **egg white distribution**
- Catalyst effectiveness factors larger than one can be achieved for exothermic reactions, if the **active metal is located inside the support (egg yolk) making advantage of heat transport resistances**

Catalyst preparation

Mixed agglomerated (co-precipitated) catalyst

- Involves the **co-precipitation** of both **support precursor** and **catalytic species precursor**
- Often used to prepare non-precious metal catalysts

  Eg., $Ni(NO_3)_2 + Al(NO_3)_3 + \ Na_2CO_3 \rightarrow NiCO_3 \downarrow + Al(CO_3)_3 + NaNO_3$

- **Maintaining the pH** is very important in this process – pH determines whether precipitation occurs **simultaneously (desired) or sequentially**
- A **flocculated multi-component precipitate** is formed in which the **catalytic metal microcrystals** are each surrounded by **support precursor crystals**
- The surrounding support crystals **prevent the metal crystals from coming together** and sintering
- Precipitate is then **thoroughly washed**, **filtered**, **dried and calcined** (to form oxides from hydroxides and carbonates)