

# REACTION ENGINEERING-II (HETEROGENEOUS SYSTEMS) (CH31009)

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# COURSE CONTENT:

## 1. Catalysis and Catalytic Reactions

a) Steps in Reaction

b) Synthesizing rate law, mechanism and rate limiting steps

## 2. External Resistance to Mass Transfer on Heterogeneous Reactions

3. Diffusion and Reaction in a Catalyst Pellet : Internal Diffusion to the Mass Transfer on Reaction

## 4. Solid Catalysts and their Characterisation

# BOOKS TO BE FOLLOWED

1. Chemical Reaction Engineering *by* Octave Levenspiel
2. Elements of Chemical Reaction Engineering *by* H. Scott Fogler
3. Chemical Engineering Kinetics *by* J. M. Smith

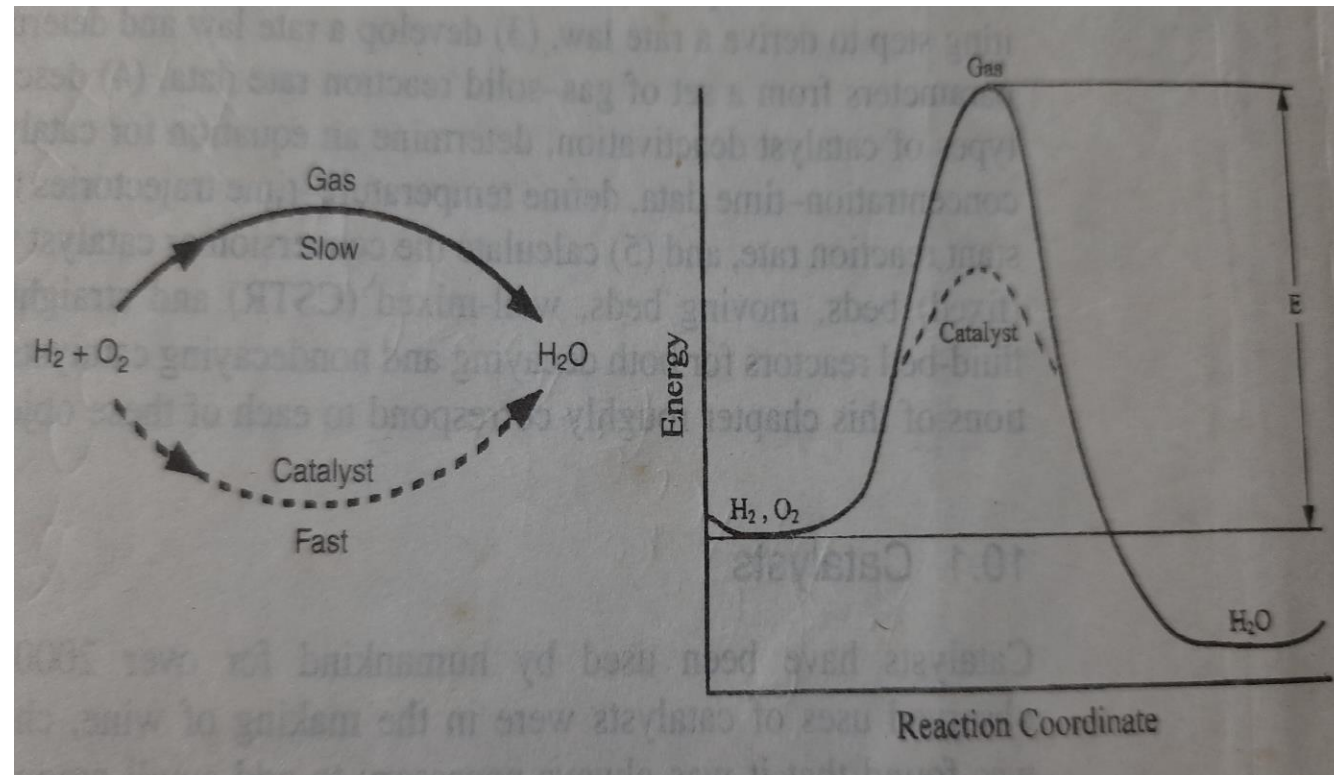
# CATALYSIS AND CATALYTIC REACTIONS:

Objectives:

- Definition of catalyst and description of its properties
- To describe the steps of a catalytic reaction and apply the concept of rate-limiting step to derive a rate law
- To develop a rate law and determine the rate law parameters from a set of gas-solid reaction rate data
- To describe the catalyst deactivation

# CATALYST AND ITS PROPERTIES IN A CHEMICAL REACTION

- ❑ Catalyst is a reagent which either accelerate or retard a chemical reaction without being consumed or converted.
- ❑ It changes the reaction rate by promoting a different molecular pathway but can not affect equilibrium
- ❑ It lowers the activation energy of a reaction



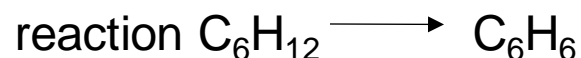
# CATALYSIS

❑ Homogeneous Catalysts: Soluble to one of the reactants

➤ Examples: HCl or H<sub>2</sub>SO<sub>4</sub> used as catalysts in Liquid phase Friedel Crafts Alkylation reaction, the catalyst is soluble in reaction medium, reaction:  $\text{C}_6\text{H}_6 \longrightarrow \text{C}_6\text{H}_5\text{CH}_3$

❑ Heterogeneous Catalysts: The catalyst remains in separate phase to the reaction medium. Usually the catalysts are solid.

➤ Platinum on alumina catalyst used in dehydrogenation of cyclohexane to produce benzene,



# HETEROGENEOUS CATALYSIS:

Heterogeneous catalysts are more common.

Advantages of heterogeneous catalysts:

- ❖ Simple and complete separation of the solid catalysts from reaction medium
- ❖ Separation of catalysts makes the process economical as no wastage of valuable catalysts
- ❖ Separation makes the reuse of the catalysts possible

In this part of study, only heterogeneous catalysis will be considered

## CONTD...

- **Supported catalyst:** Minute particles of active catalysts are dispersed on a less active support. Active particles are mostly metal/ metal-alloy particles, Examples: *Pt on alumina ( $Pt/Al_2O_3$ )* for reforming reaction,  *$V_2O_5$  on silica* for sulfur dioxide oxidation used for sulfuric acid preparation.
- **Unsupported catalyst:** No support is required, the material is as a whole a catalyst with similar activity throughout its area. Examples: *Silica-alumina* in dehydrogenation reaction for butadiene preparation
- **Porous catalyst:** The catalyst that has a large area resulting from its pores. More surface area catalysts are more active, as reaction occurs on the surface of the catalyst. Example: *Raney Ni* used in the hydrogenation of vegetable or animal oils, *Fe* in ammonia synthesis.
  - **Molecular sieves:** Pore structure is such that they allow some molecules and prevent others to enter into the pores of the catalyst, this way they act as sieves. The molecules which can enter into the pores can react with each other to produce products. Examples: *Certain clays and zeolites*. These are selective catalysts.



## CONTD....

- ❑ Heterogeneous catalytic reaction occurs at fluid-solid interface
- ❑ Hence, a large interfacial area can be helpful or be essential for attaining a significant reaction rate
- ❑ A porous catalyst has larger surface area resulting from its pore than a non-porous catalyst, example: Raney Ni has surface area up to  $1200 \text{ m}^2/\text{g}$ .
- ❑ Not all catalysts need the extended surface provided by a porous structure, some are sufficiently active.
- ❑ Most of the catalysts do not maintain their activity at the same level for indefinite period of time, they get deactivated either slowly or rapidly, depending on the nature of catalyst and reaction
- ❑ Deactivation may be caused by ageing phenomenon, such as gradual change in surface crystal structure or deposition of foreign material on the active portions of the catalyst

# GAS PHASE SOLID CATALYTIC REACTION:

Gas phase solid catalytic reaction needs the reactants to attach to the surface of the catalyst.

1. This attachment is called adsorption, which may be of two types, 1. Physical adsorption 2. Chemical adsorption
2. Physical adsorption : Force of attraction between the gas molecules and solid catalyst surface is weak, either van der Waals type, between a permanent dipole and an induced dipole or neutral atom or molecule. Heat of adsorption is small, 1-15 Kcal/gmol.
3. Chemical adsorption: Force of attraction is strong, the reactant atoms or molecules are bound to the surface atoms of the catalyst by valence bond type force. Chemical adsorption is required for reactants to perform a chemical reaction. Due to chemical adsorption, the electronic structure of reactant molecules are disturbed significantly, making them extremely reactive. Heat of adsorption is in similar magnitude to heat of reaction, i.e., 10-100 Kcal/gmol.

## CONTD...

- The reaction is not catalyzed by the entire solid surface of the catalyst
- Adsorption of reactant molecules occurs on specific active centres or sites on the catalyst surface.
- The active centres on the surface are originated from: 1. Surface irregularities 2. Dislocations 3. Edges of crystals 4. Cracks along grain boundaries.
- So, active centres on the catalyst surface are able to make strong bonds with the reactant molecules and stabilise them.
- The parameter to quantify catalyst activity: Turnover frequency—Number of molecules reacting per active sites per second at the condition of experiment
- Dispersion D of catalyst: Fraction of the metal ions present on the surface of the catalyst

# STEPS IN A SOLID CATALYTIC GAS PHASE REACTION:

**The steps involved in the overall process by which a fluid phase reaction with solid porous catalyst happens :**

- ✓ Mass transfer (diffusion) of the reactants from the bulk fluid to the external surface of the catalyst pellet
- ✓ Diffusion of the reactant from external surface to the internal pore surface through the catalyst pores
- ✓ Adsorption of the reactant on the internal surface
- ✓ Reaction on the surface to form product
- ✓ Desorption of the product from the surface
- ✓ Diffusion of the product from internal surface to pore mouth/external surface of the catalyst
- ✓ Mass transfer of the product from external surface to the bulk of the fluid

## CONTD...

- ❑ The overall rate of the reaction is equal to the rate of the slowest step of the reaction.
- ❑ When diffusion/ mass transfer steps are very fast compared to the reaction step, the concentration of reactant/product in the immediate vicinity of the active centres are almost the same as in the bulk phase. So, then diffusion/mass transfer steps can not affect reaction rate. Chemical reaction step will be the rate limiting step.
- ❑ When rate of chemical reaction is much faster than either adsorption/desorption or diffusion steps, then the rate limiting step may be the slowest step among them.