10. Catalysis & Catalytic Reaction

- **Basic Define**
  - **Catalyst, catalytic mechanism, rate limit step.**
- **Catalytic Mechanism**
  - **Describe the steps**
  - **Derive a rate law and a mechanism and rate limiting step consistent with the experimental data**
- **Use Regression to discriminate between reaction rate laws and mechanisms**

10. Catalysis & Catalytic Reaction

- Size isothermal reactors for reactions with Langmuir-Hinschelwood kinetics
- Catalyst deactivation
  - Type and the reactor types
  - Describe schemes that can help offset the deactivation
- Catalyst decay and conversion
  - CSTRs and PFRs with temperature-time trajectories, moving bed reactors, and straight through transport reactors.
- Describe the steps in Chemical Vapor Deposition (CVD)

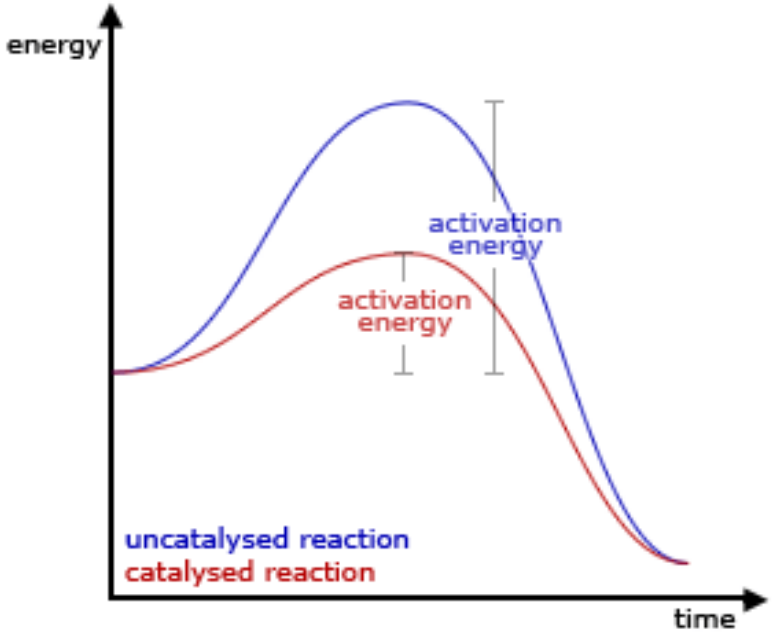
1. Catalysis I

- History
  - Over 2000 years
    - wine, cheese, bread
  - Jons Jakob Berzelius (1835)
    - small amount of foreign source could greatly affect the course of chemical reactions
  - Wilhelm Ostwald (1894)
    - substances accelerating the rate of chemical reactions without being consumed

☞ USD 3.5 billion/ yr, 2007

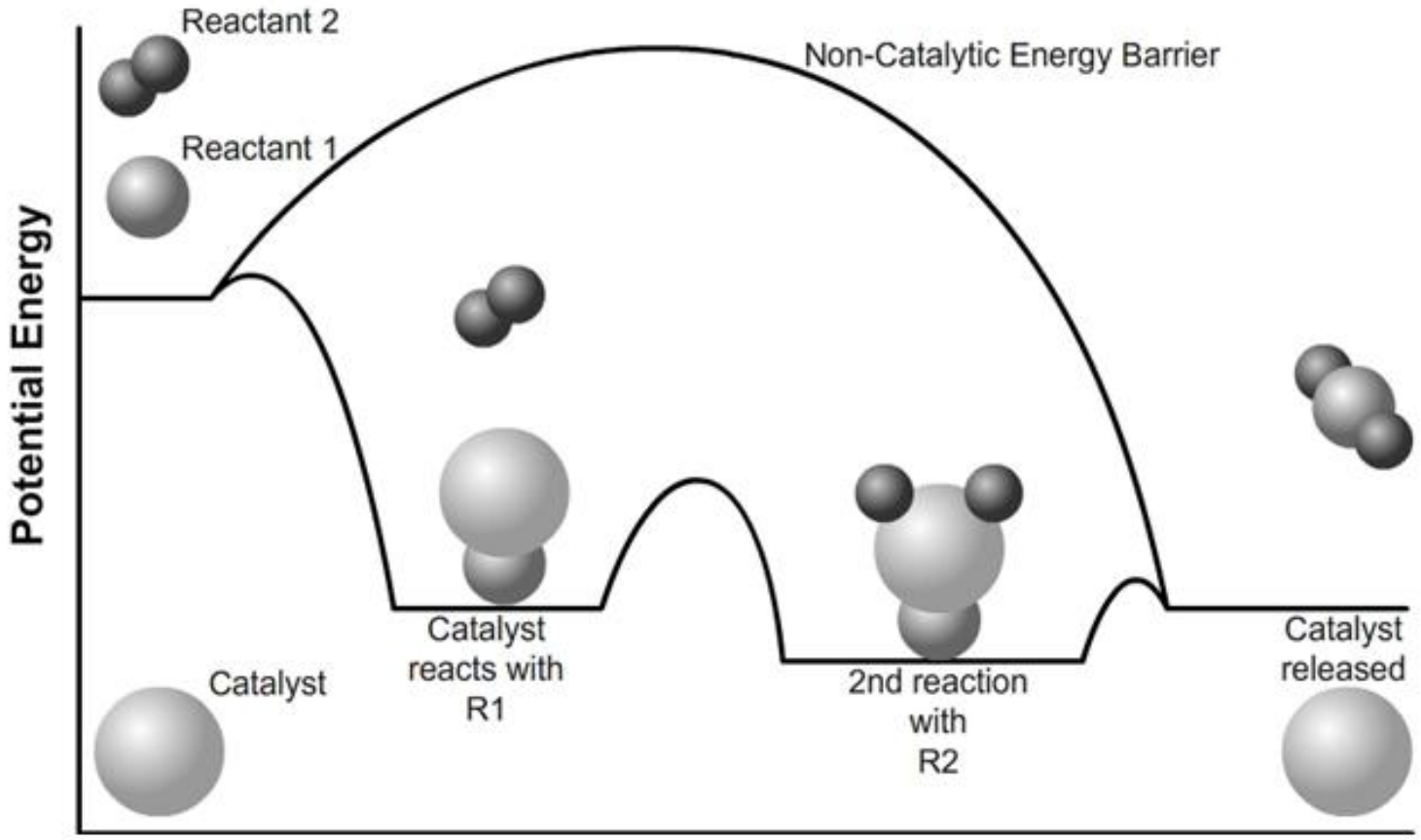
1. Catalysis II

- **Definitions**
  - **Catalyst**
    - **a substances affecting the rate of reactions but emerges from the process unchanged**
    - **usually by promoting a different mechanism**
  - **Catalysis**
    - **the occurrence, study, and use of catalysts and catalytic process**



1. Catalysis III

- **Definitions 2**



1. Catalysis IV

- **Catalyst Properties**
  - **Large interfacial area**
    - **reaction occurs at the fluid-solid interface**
  - **Typical catalysts**
    - **inner porous structure**

    ex) silica-alumina cracking catalyst
    - **pore volume of 0.6 cm^3/g with avg diameter of 4 nm**

      ≡ 300 m^2/g
    - **Raney nickel catalyst for hydrogenation**
  - **Molecular sieves - zeolite ☞ very high selectivity**
  - **Monolithic catalyst - sufficient active**

1. Catalysis V

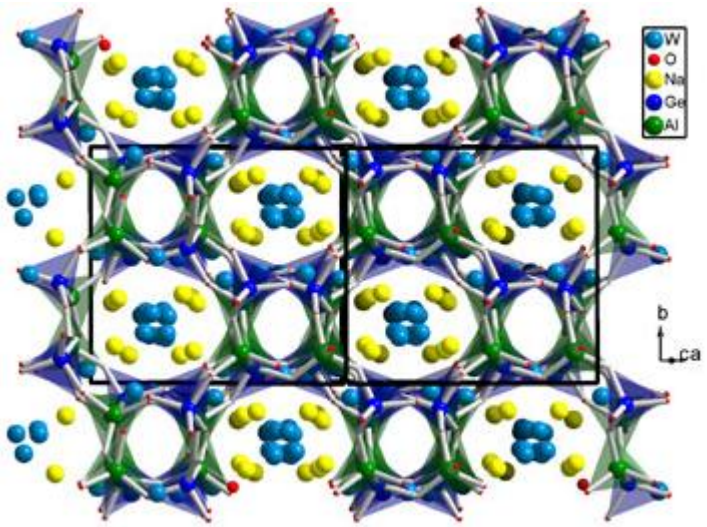
- **Molecular Sieve 1**

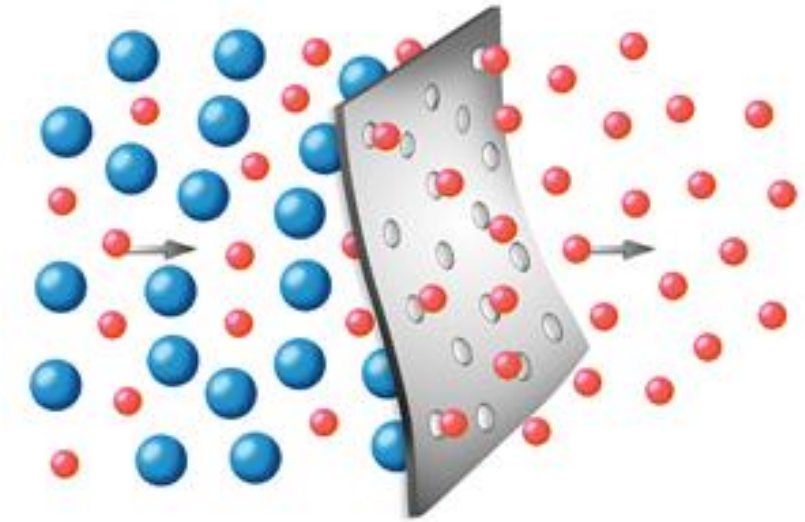
Molecular Sieve Type A

Molecular Sieve Type X

1. Catalysis VI

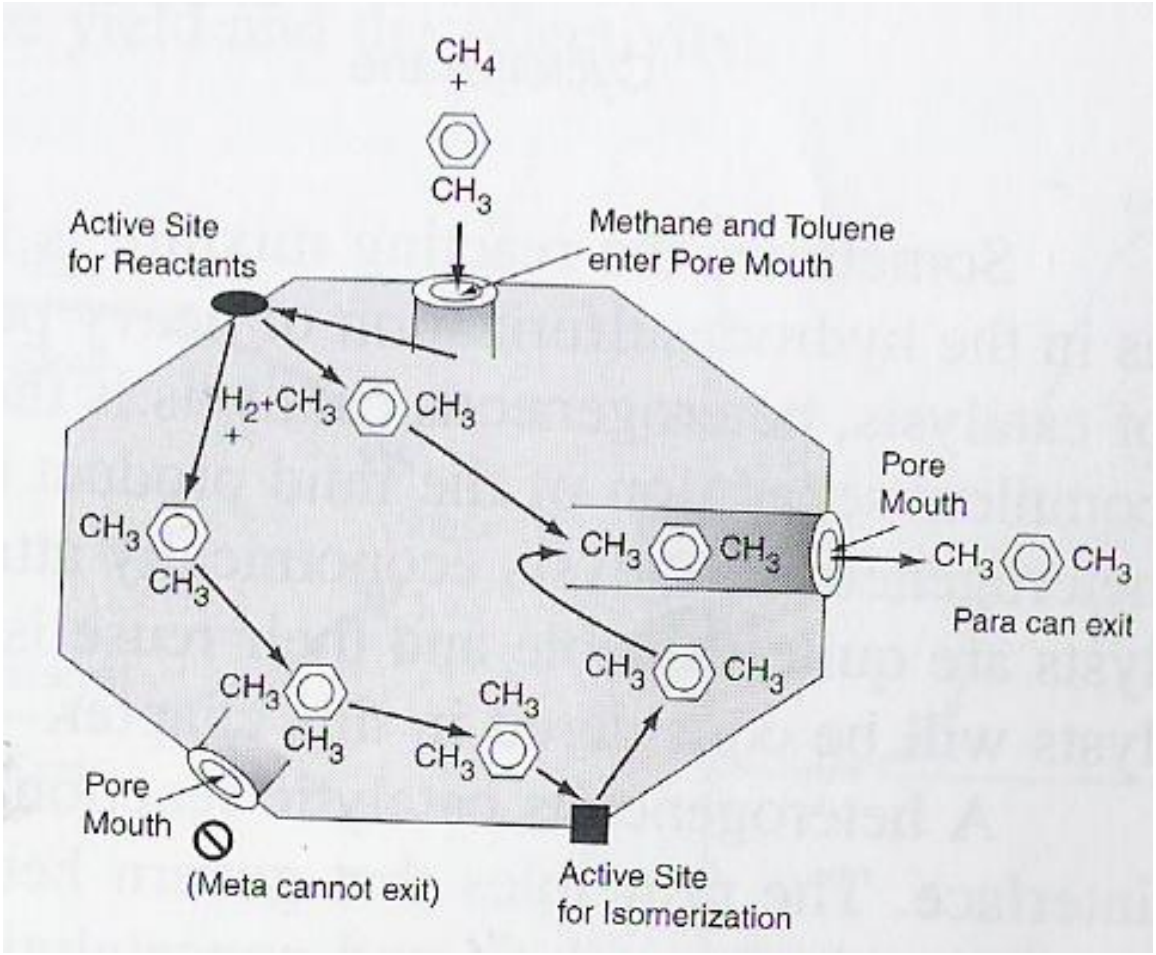
- **Molecular Sieve 2**





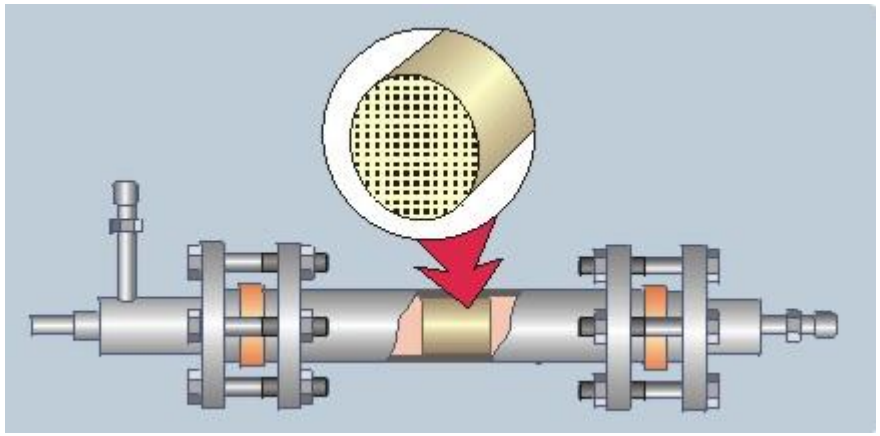
1. Catalysis VII

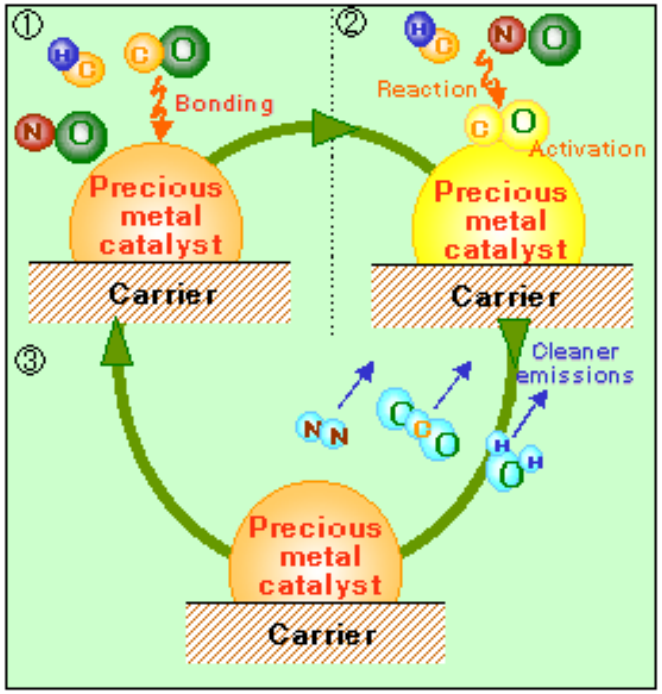
- **Molecular Sieve 3**

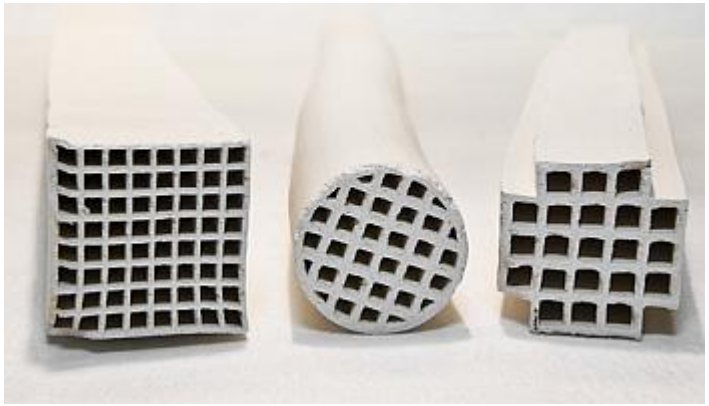


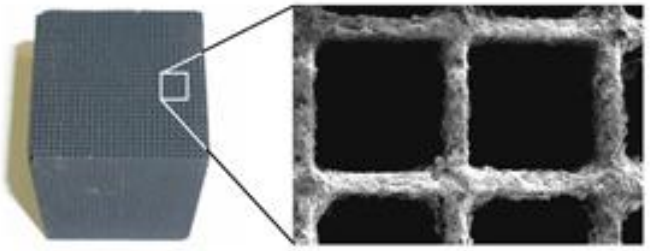
1. Catalysis VIII

- **Monolithic Catalyst**



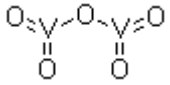


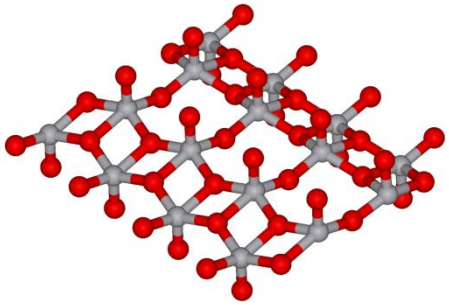




1. Catalysis IX

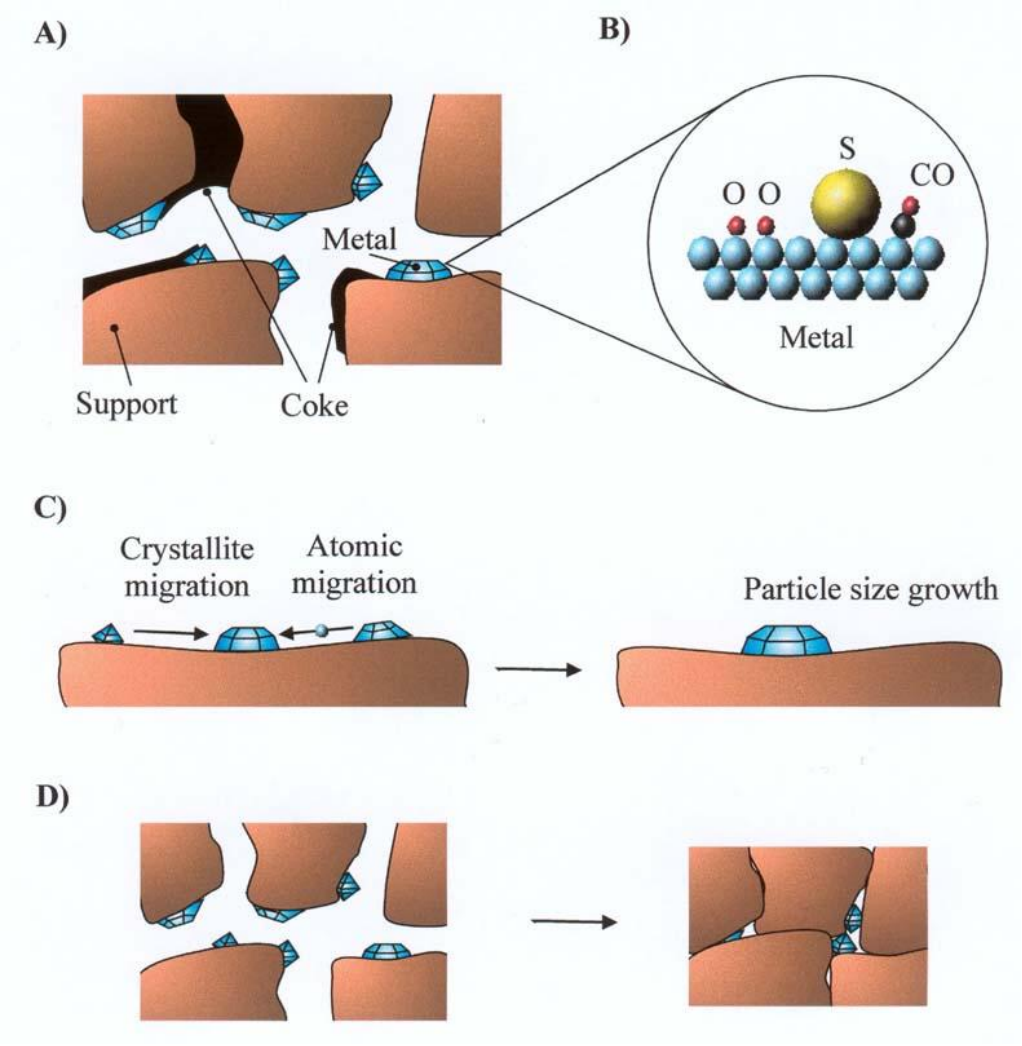
- **Supported Catalyst**
  - **Support**
    - **structural part of less active material(s)**
  - **Promoters**
    - **small amount of ingredients, increase activity**
  - **Examples**
    - **Pt-on-Al for petroleum reforming, Vanadium peroxide on silica for producing sulfuric acid**





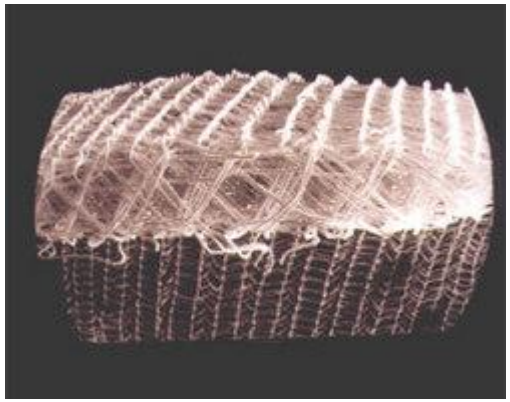
1. Catalysis X

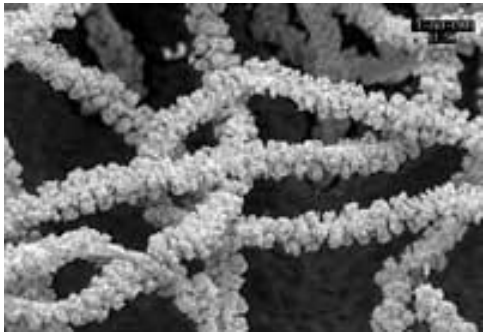
- **Supported Catalyst 2**

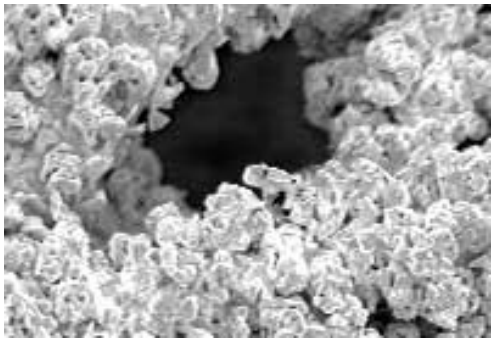


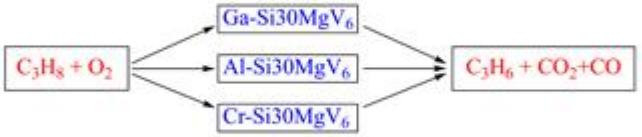
1. Catalysis XI

- **Unsupported Catalyst**
  - **Platinum gauze for ammonia oxidation, the promoted iron for ammonia synthesis, silica-alumina dehydrogenation catalyst**









1. Catalysis XII

- Deactivation
  - Aging
    - gradual change in surface crystal structure
  - Poisoning
    - irreversible deposition of substances on the active site
  - Fouling (Coking)
    - deposit of material on the entire surface

☞ very fast

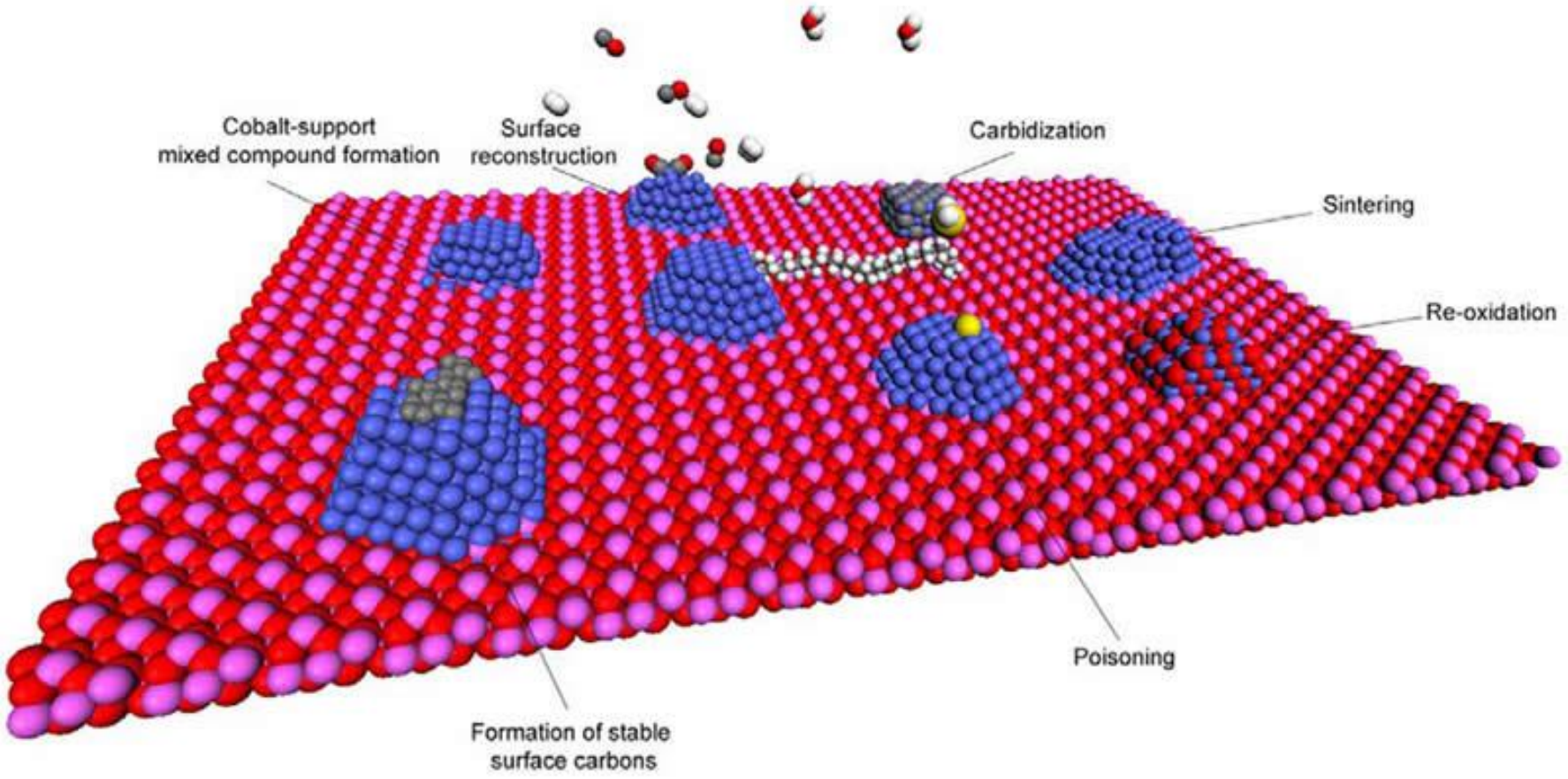
- 2~3 minutes for catalytic cracking of nathpha

☞ very slow

- automotive exhaust catalyst

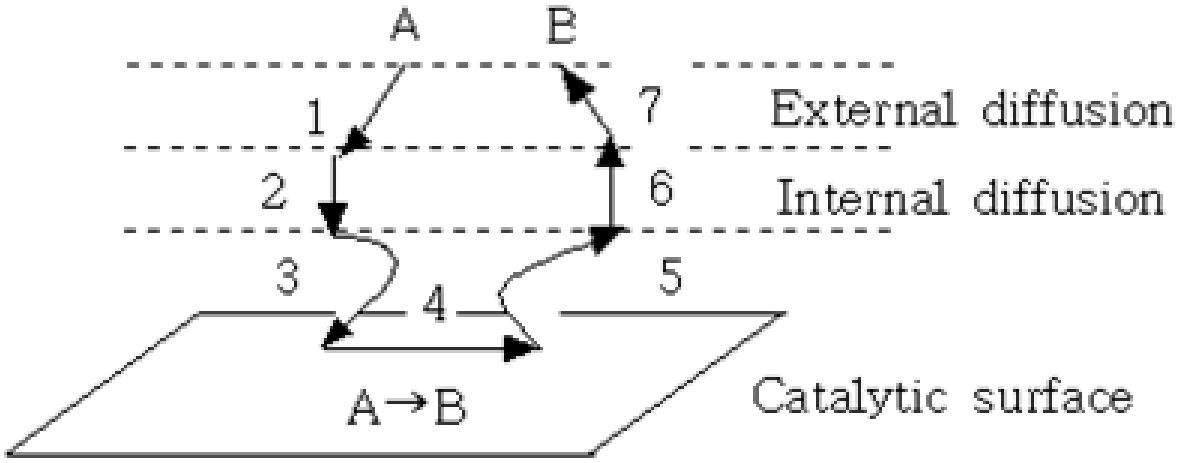
1. Catalysis XIII

- **Deactivation 2**



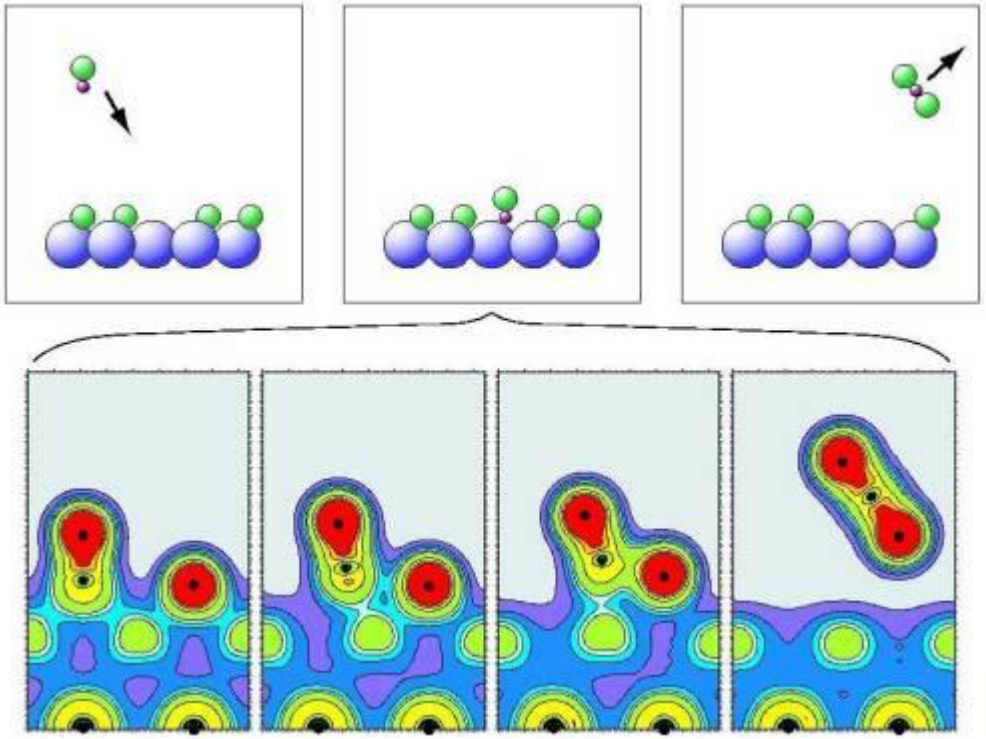
1. Catalysis XIV

- **Gas Phase Reaction with Solid Catalyst**
  - **Adsorption**
    - **physical adsorption (physisorption)**
      4~ 60 kJ/mol, similar to condensation
    - **chemical adsorption (chemisorption)**
      40 ~ 400 kJ/mol, similar to heat of rxn



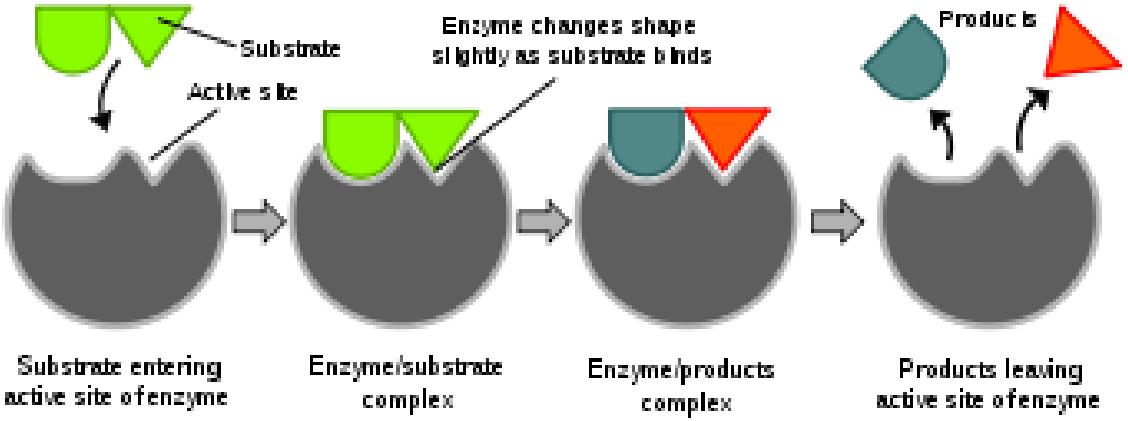
1. Catalysis XV

- **Gas Phase Reaction with Solid Catalyst 2**
  - **Adsorbed molecule has rich in electron density enough to be reactive**



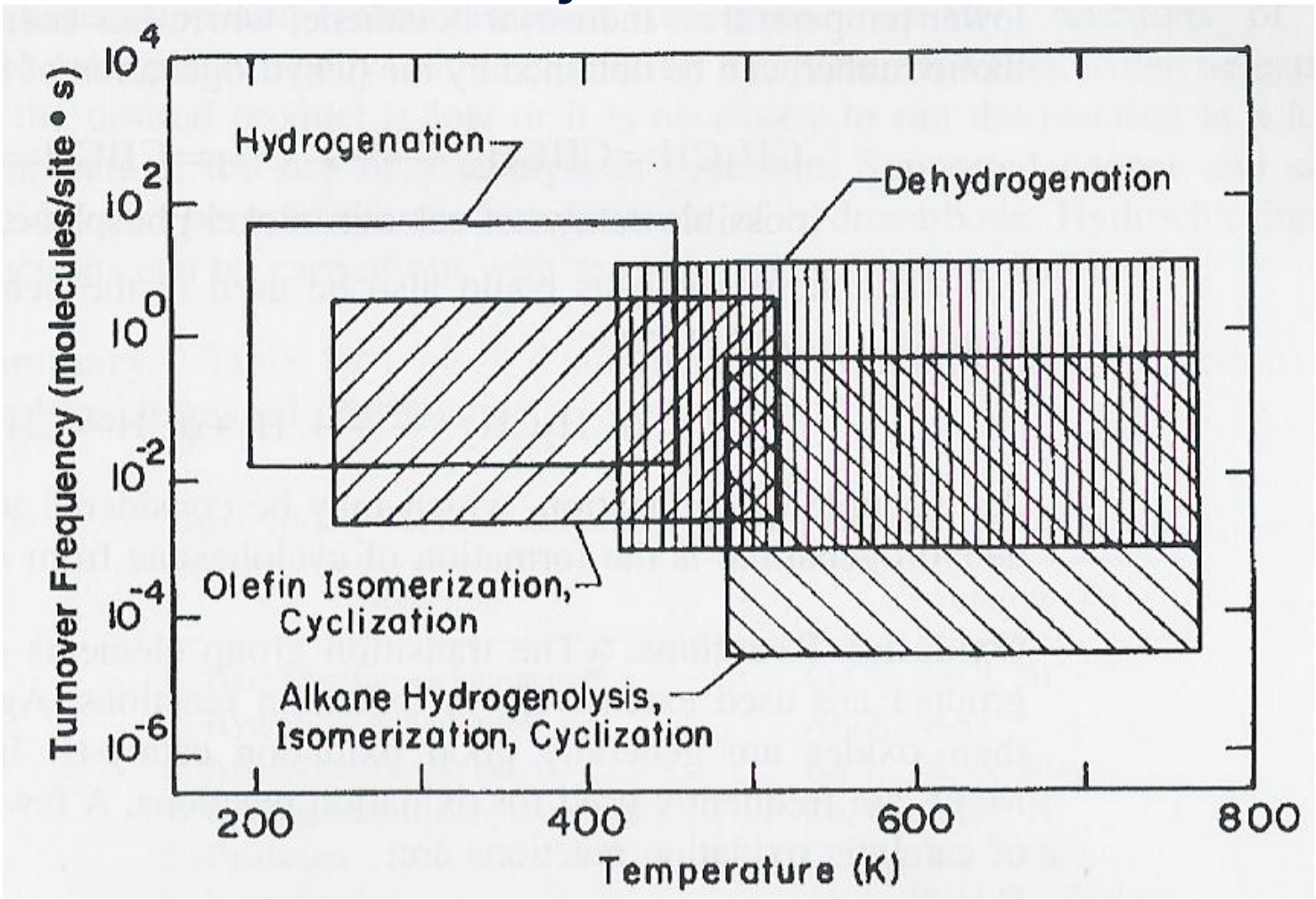
1. Catalysis XVI

- **Active Site**
  - **H. S. Taylor**
  - **Reaction is not catalyzed over the entire solid surface but only at certain active site or center**
    - **surface irregularities, dislocations, edges of crystals, cracks along grain boundaries**



1. Catalysis XVII

- **Classification of Catalyst**



1. Catalysis XVIII

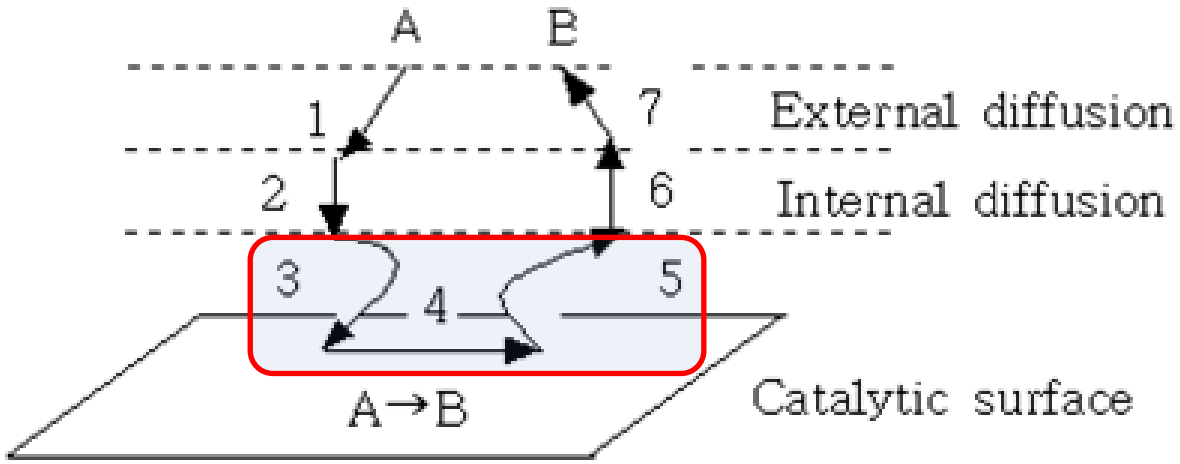
- **Classification of Catalyst**

TABLE 10-1. TYPES OF REACTIONS AND REPRESENTATIVE CATALYSTS

Reaction	*Catalysts*
1. Halogenation–dehalogenation	$CuCl_2$, AgCl, Pd
2. Hydration–dehydration	Al_2O_3, MgO
3. Alkylation–dealkylation	$AlCl_3$, Pd, Zeolites
4. Hydrogenation–dehydrogenation	Co, Pt, Cr_2O_3, Ni
5. Oxidation	Cu, Ag, Ni, V_2O_5
6. Isomerization	$AlCl_3$, Pt/Al_2O_3, Zeolites

1. Steps in a Catalytic Reaction I

○ **Main Interests**

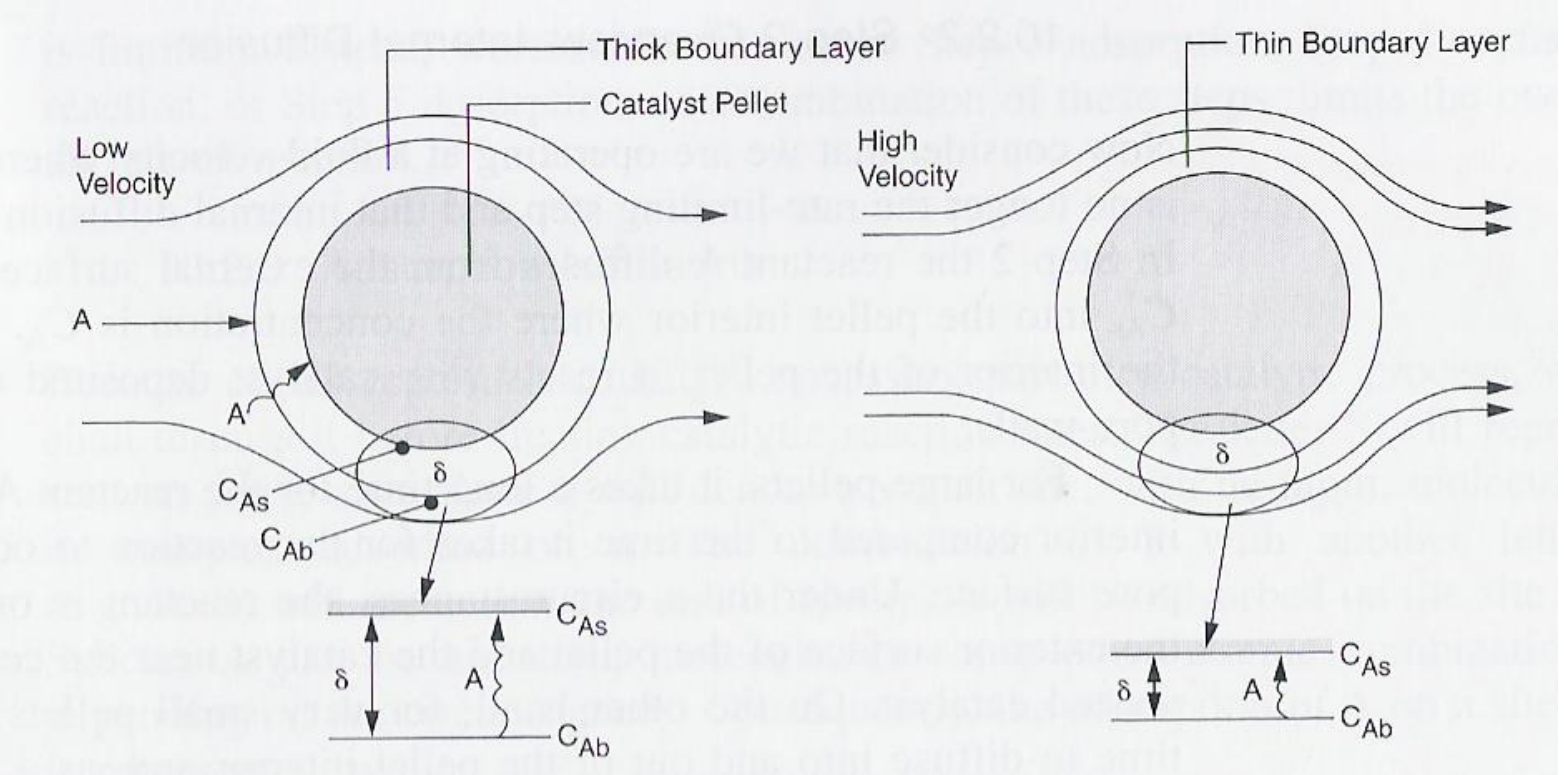


- **③Adsorption of reactant(s)**
- **④Surface reaction**
- **⑤Desorption of product(s)**

☞ **Determine the most slow (rate determining) step**

1. Steps in a Catalytic Reaction II

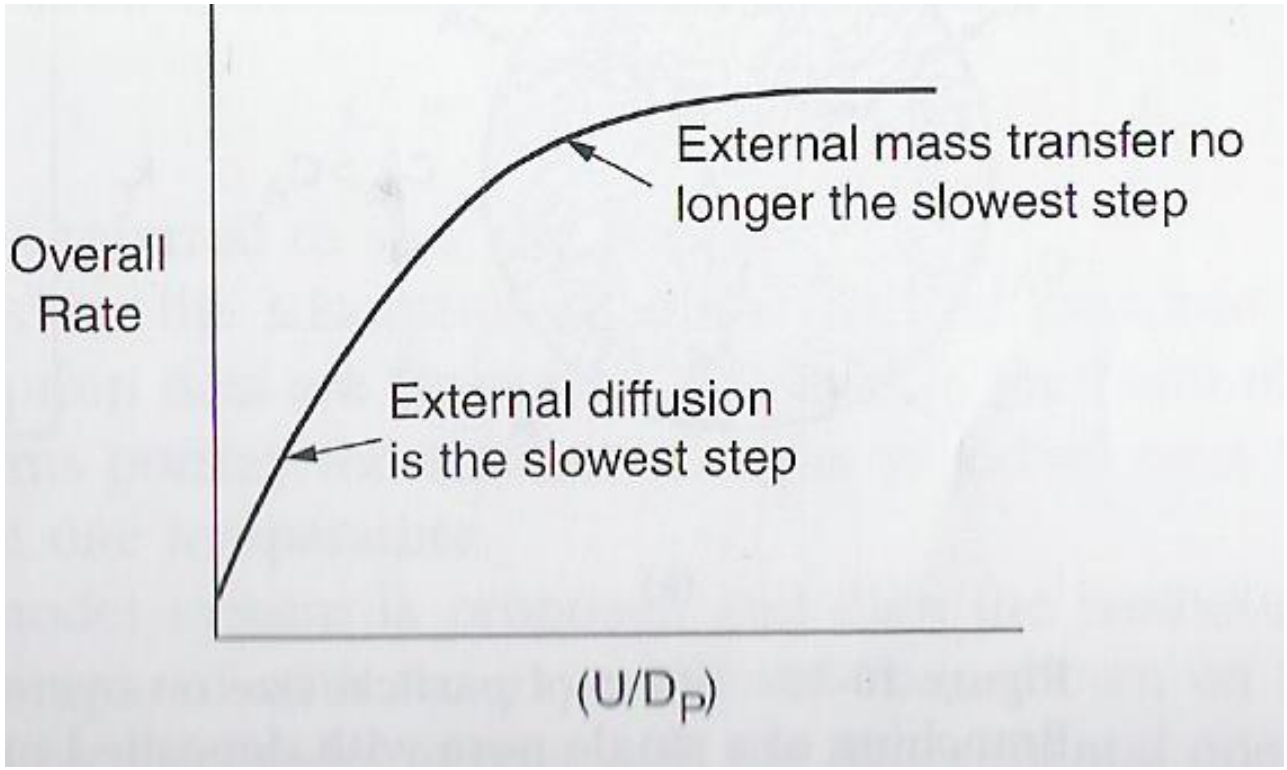
- **Step 1 Overview: External Diffusion**



$$\text{Rate} = k_C(C_{\text{Ab}} - C_{\text{As}}) \text{ where} k_C = \frac{D_{\text{AB}}}{\delta}$$

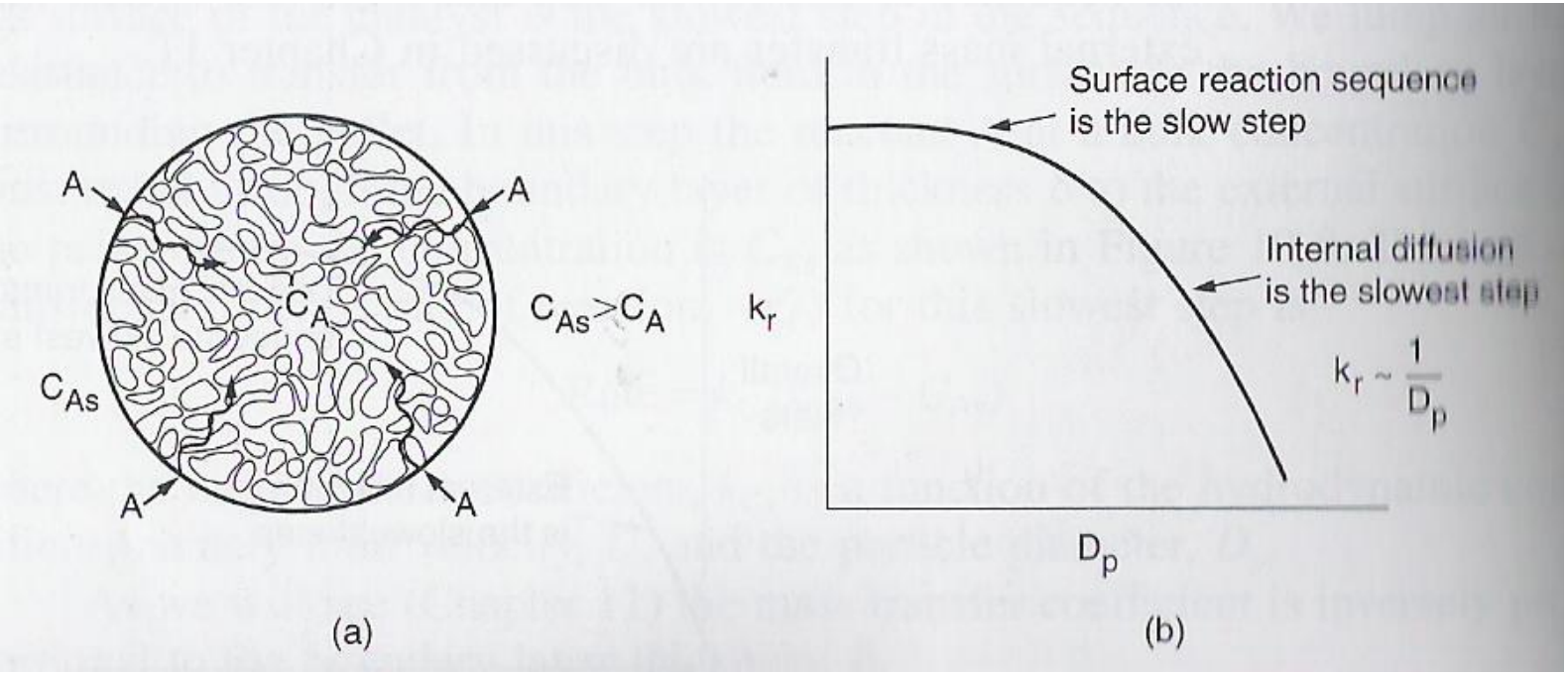
1. Steps in a Catalytic Reaction III

- **Step 1 Overview : External Diffusion 2**



1. Steps in a Catalytic Reaction IV

- **Step 2 Overview: Internal Diffusion**



$$\text{Rate} = k_r C_{As}$$

For a large pellet, near the center might not be used when reaction ⇒ Waste!!

1. Steps in a Catalytic Reaction V

- **Step 3 : Adsorption**
- **Adsorption isotherms**

$$A + S \leftrightarrow A \cdot S$$

- Total molar concentration of active sites

$$C_t = C_v + C_{A \cdot S} + C_{B \cdot S}$$

- **adsorption as molecules (on nickel)**

$$CO + S \leftrightarrow CO \cdot S$$ ☜ **nondissociated adsorption**

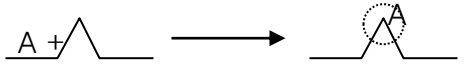
- **adsorption as atoms (on iron)**

$$CO + 2S \leftrightarrow C \cdot S + O \cdot S$$ ☜ **dissociated adsorption**

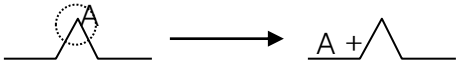
☞ **Depends on surface conditions**

1. Steps in a Catalytic Reaction VI

- **Step 3 : Adsorption 2**
- **Adsorption isotherms (Molecule) 1**
  - **Rate of attachment** $= k_{\mathrm{A}} P_{\mathrm{CO}} C_v$



  - **Rate of detachment** $= k_{-\mathrm{A}} P_{\mathrm{CO \cdot S}}$



  - **Rate of adsorption**

$$r_{\mathrm{AD}} = k_{\mathrm{A}} P_{\mathrm{CO}} C_v - k_{-\mathrm{A}} C_{\mathrm{CO \cdot S}}$$

  - **Adsorption constant**

$$K_{\mathrm{A}} = k_{\mathrm{A}} / k_{-\mathrm{A}}$$

$$r_{\mathrm{AD}} = k_{\mathrm{A}} \left(P_{\mathrm{CO}} C_v - \frac{C_{\mathrm{CO \cdot S}}}{K_{\mathrm{A}}} \right)$$

1. Steps in a Catalytic Reaction VII

- **Step 3 : Adsorption 3**
- **Adsorption isotherms (Molecule) 2**
  - **CO is the only adsorbed one**

$$C_t = C_v + C_{\mathrm{CO\cdot S}}$$

  - **At equilibrium**

$$C_{\mathrm{CO\cdot S}} = K_{\mathrm{A}} C_v P_{\mathrm{CO}}$$

  - **In terms of attached CO**

$$C_{\mathrm{CO\cdot S}} = K_{\mathrm{A}} C_v P_{\mathrm{CO}} = K_{\mathrm{A}} P_{\mathrm{CO}} (C_t - C_{\mathrm{CO\cdot S}})$$

$$C_{\mathrm{CO\cdot S}} = \frac{K_{\mathrm{A}} P_{\mathrm{CO}} C_t}{1 + K_{\mathrm{A}} P_{\mathrm{CO}}}$$

1. Steps in a Catalytic Reaction VIII

- **Step 3 : Adsorption 4**
- **Adsorption isotherms (Atomic) 1**

- CO is the only adsorbed one

$$\mathrm{CO} + 2\mathrm{S} \leftrightarrow \mathrm{C}\cdot\mathrm{S} + \mathrm{O}\cdot\mathrm{S}$$

- At equilibrium

$$r_{\mathrm{AD}} = k_{\mathrm{A}} P_{\mathrm{CO}} C_v^2 - k_{-\mathrm{A}} C_{\mathrm{O}\cdot\mathrm{S}} C_{\mathrm{C}\cdot\mathrm{S}}$$

- In terms of attached CO

$$r_{\mathrm{AD}} = k_{\mathrm{A}} \left(P_{\mathrm{CO}} C_v^2 - \frac{C_{\mathrm{O}\cdot\mathrm{S}} C_{\mathrm{C}\cdot\mathrm{S}}}{K_{\mathrm{A}}} \right)$$

$$k_{\mathrm{A}} P_{\mathrm{CO}} C_v^2 = k_{-\mathrm{A}} C_{\mathrm{O}\cdot\mathrm{S}} C_{\mathrm{C}\cdot\mathrm{S}}$$

- For $C_{\mathrm{O}\cdot\mathrm{S}} = C_{\mathrm{C}\cdot\mathrm{S}}$

$$C_{\mathrm{O}\cdot\mathrm{S}} = C_v \sqrt{K_{\mathrm{A}} P_{\mathrm{CO}}}$$

1. Steps in a Catalytic Reaction IX

- **Step 3 : Adsorption 5**
- **Adsorption isotherms (Atomic) 2**

- Substitute for $C_{O\cdot S}$ and $C_{C\cdot S}$ in the site balance eq'n

$$C_t = C_v + C_{O\cdot S} + C_{C\cdot S}$$
$$= C_v + C_v \left(K_{CO} P_{CO}\right)^{1/2} + C_v \left(K_{CO} P_{CO}\right)^{1/2}$$
$$= C_v \left(1 + 2\left(K_{CO} P_{CO}\right)^{1/2}\right)$$

- Solving for C_v

$$C_v = C_t \,/(1 + 2(K_{CO} P_{CO})^{1/2})$$

- In terms of attached O

$$C_{O\cdot S} = \frac{\left(K_A P_{CO}\right)^{1/2} C_t}{1 + 2\left(K_A P_{CO}\right)^{1/2}}$$

1. Steps in a Catalytic Reaction XI

- **Step 4 : Surface Reaction 1**
- **Rate of adsorption of species A onto a solid surface**

$$\mathrm{A} + \mathrm{S} \leftrightarrow \mathrm{A} \cdot \mathrm{S}$$

$$r_{\mathrm{AD}} = k_{\mathrm{A}} \left(P_{\mathrm{CO}} C_v - \frac{C_{\mathrm{CO \cdot S}}}{K_{\mathrm{A}}} \right)$$

- **Single site**