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
      $\equiv 300$ m$^2$/g
    - Raney nickel catalyst for hydrogenation
  - Molecular sieves - zeolite $\equiv$ 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 naphtha
      ➨ 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

![Diagram of catalytic process]
1. Catalysis XVII

- Classification of Catalyst

![Graph showing the classification of catalysts based on turnover frequency and temperature.](image)
1. Catalysis XVIII

- Classification of Catalyst

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Halogenation–dehalogenation</td>
<td>CuCl₂, AgCl, Pd</td>
</tr>
<tr>
<td>2. Hydration–dehydration</td>
<td>Al₂O₃, MgO</td>
</tr>
<tr>
<td>3. Alkylation–dealkylation</td>
<td>AlCl₃, Pd, Zeolites</td>
</tr>
<tr>
<td>4. Hydrogenation–dehydrogenation</td>
<td>Co, Pt, Cr₂O₃, Ni</td>
</tr>
<tr>
<td>5. Oxidation</td>
<td>Cu, Ag, Ni, V₂O₅</td>
</tr>
<tr>
<td>6. Isomerization</td>
<td>AlCl₃, Pt/Al₂O₃, Zeolites</td>
</tr>
</tbody>
</table>
1. Steps in a Catalytic Reaction I

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

☞ Determine the most slow (rate determining) step
1. Steps in a Catalytic Reaction II

○ Step 1 Overview: External Diffusion

\[
\text{Rate} = k_C (C_{Ab} - C_{As}) \quad \text{where} \quad k_C = \frac{D_{AB}}{\delta}
\]
1. Steps in a Catalytic Reaction III

- **Step 1 Overview: External Diffusion**

![Graph showing the relationship between overall rate and \((U/D_p)\). The graph indicates that external diffusion is the slowest step until a certain point, after which external mass transfer becomes the slower step.](image)
1. Steps in a Catalytic Reaction IV

Step 2 Overview: Internal Diffusion

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)

  \[ CO + S \leftrightarrow CO \cdot S \]  \(\uparrow\) nondissociated adsorption

- Adsorption as atoms (on iron)

  \[ CO + 2S \leftrightarrow C \cdot S + O \cdot S \]  \(\uparrow\) dissociated adsorption

  \(\uparrow\) Depends on surface conditions
1. Steps in a Catalytic Reaction VI

- **Step 3 : Adsorption 2**

- **Adsorption isotherms (Molecule) 1**
  - Rate of attachment \( = k_A P_{CO} C_v \)
  - Rate of detachment \( = k_{-A} P_{CO\cdot S} \)
  - Rate of adsorption
    \[
    r_{AD} = k_A P_{CO} C_v - k_{-A} C_{CO\cdot S}
    \]
  - Adsorption constant
    \[
    K_A = k_A / k_{-A}
    \]

\[
\begin{align*}
    r_{AD} &= k_A \left( P_{CO} C_v - \frac{C_{CO\cdot S}}{K_A} \right)
\end{align*}
\]
1. Steps in a Catalytic Reaction VII

- **Step 3 : Adsorption 3**
- **Adsorption isotherms (Molecule) 2**
  - CO is the only adsorbed one
  
  \[ C_t = C_v + C_{CO.S} \]

- At equilibrium
  
  \[ C_{CO.S} = K_A C_v P_{CO} \]

- In terms of attached CO
  
  \[ C_{CO.S} = K_A C_v P_{CO} = K_A P_{CO} (C_t - C_{CO.S}) \]

\[ C_{CO.S} = \frac{K_A P_{CO} C_t}{1 + K_A P_{CO}} \]
1. Steps in a Catalytic Reaction VIII

- Step 3: Adsorption 4
- Adsorption isotherms (Atomic) 1
  - CO is the only adsorbed one
    \[
    \text{CO} + 2\text{S} \leftrightarrow \text{C} \cdot \text{S} + \text{O} \cdot \text{S}
    \]
  - At equilibrium
    \[
    r_{\text{AD}} = k_A P_{\text{CO}} C_v^2 - k_{-A} C_{\text{O} \cdot \text{S}} C_{\text{C} \cdot \text{S}}
    \]
  - In terms of attached CO
    \[
    r_{\text{AD}} = k_A \left( P_{\text{CO}} C_v^2 - \frac{C_{\text{O} \cdot \text{S}} C_{\text{C} \cdot \text{S}}}{K_A} \right)
    \]
    \[
    k_A P_{\text{CO}} C_v^2 = k_{-A} C_{\text{O} \cdot \text{S}} C_{\text{C} \cdot \text{S}}
    \]
  - For \( C_{\text{O} \cdot \text{S}} = C_{\text{C} \cdot \text{S}} \)
    \[
    C_{\text{O} \cdot \text{S}} = C_v \sqrt{K_A P_{\text{CO}}}
    \]
1. Steps in a Catalytic Reaction IX

- **Step 3**: Adsorption 5
- **Adsorption isotherms (Atomic)** 2
  - Substitute for \( C_{O,S} \) and \( C_{C,S} \) in the site balance eq’n

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

- Solving for \( C_v \)

\[
C_v = \frac{C_t}{1 + 2 \left( K_{CO} P_{CO} \right)^{1/2}}
\]

- In terms of attached O

\[
C_{O,S} = \frac{\left( K_A P_{CO} \right)^{1/2} C_t}{1 + 2 \left( K_A P_{CO} \right)^{1/2}}
\]
1. Steps in a Catalytic Reaction XI

- **Step 4 : Surface Reaction 1**
- **Rate of adsorption of species A onto a solid surface**
  \[
  A + S \leftrightarrow A \cdot S
  \]
  
  \[
  r_{AD} = k_A \left( P_{CO} C_v - \frac{C_{CO \cdot S}}{K_A} \right)
  \]

- **Single site**