8. Heterogeneous reaction

- **solid – fluid (liquid, gas)**
  - Dissolution of solids (e.g. MgCO$_3$(s) + HNO$_3$(l))
  - Chemical Vapor Deposition (SiH$_4$(g) → Si(s) + 2H$_2$)
  - Sublimation (U(s) + 3 F$_2$(g) → UF$_6$(g))
  - Reduction of solid oxides (NiO(s) + H$_2$(g) → Ni(s) + H$_2$O(g))
  - Metals oxidation (Zn(s) + O$_2$(g) → ZnO(s))
  - Catalytic reactions

- **liquid – gas**
  - Dissolution with chemical reaction
    Cl$_2$(s) + 2NaOH(l) → NaOCl(l) + NaCl(l) + H$_2$O(l)
    3NO$_2$(g) + H$_2$O(l) → 2HNO$_3$(l) + NO(g)

- **solid – solid**
  - CoO(s) + Al$_2$O$_3$(s) → CoAl$_2$O$_4$(s)

Heat and mass transfer phenomena affect global reaction rate.
Example

\[ \text{Si}(s) + \text{O}_2(g) \rightarrow \text{SiO}_2(s) \]

\[
\frac{\partial \text{c}_{\text{O}_2}}{\partial t} = D^{s}_{\text{O}_2} \frac{\partial^2 \text{c}_{\text{O}_2}}{\partial x^2}
\]

- \( N_{\text{O}_2} \): flux density of \( \text{O}_2 \) in gas phase (mol.m\(^{-2}\).s\(^{-1}\))
- \( J^{(D)}_{\text{O}_2} \): flux density of \( \text{O}_2 \) in \( \text{SiO}_2 \) layer (mol.m\(^{-2}\).s\(^{-1}\))
- \( k_{c\text{O}_2} \): coefficient of mass transfer of \( \text{O}_2 \) (m.s\(^{-1}\))
- \( D^{s}_{\text{O}_2} \): diffusion coefficient of \( \text{O}_2 \) in \( \text{SiO}_2 \) (m\(^2\).s\(^{-1}\))
- \( r_s \): rate of chemical reaction (mol. m\(^{-2}\).s\(^{-1}\))
Steady state

\[
N_{O_2} = J_{O_2}^{(D)} = v_{O_2} r_s
\]

\[
k_{cO_2} [c_1 - c_o] = D_{O_2}^s \frac{[c_2 - c_1]}{\delta} = -k c_2
\]

c_1 \text{ a } c_2 \text{ calculation :}

\[
\left( k_{cO_2} + \frac{D_{O_2}^s}{\delta} \right) c_1 - \frac{D_{O_2}^s}{\delta} c_2 = k_{cO_2} c_o
\]

\[
- \frac{D_{O_2}^s}{\delta} c_1 + \left( k + \frac{D_{O_2}^s}{\delta} \right) c_2 = 0
\]

SiO\textsubscript{2} layer thickness and Si conversion:

\[
\delta = \omega_o X_{Si}
\]

\[
\omega_o = \frac{\delta_o}{2} \frac{M_{SiO_2}}{M_{Si}} \frac{\rho_{Si}}{\rho_{SiO_2}}
\]

reaction rate

\[
r_s = \frac{c_o}{\frac{1}{k_{cO_2}} + \frac{\delta(t)}{D_{O_2}^s} + \frac{1}{k}}
\]

Molar weights and densities of SiO\textsubscript{2} a Si

\[
\delta_o \quad \text{Initial thickness of Si slab}
\]
3 limiting cases

1. Rate determining step is the external mass transfer of oxygen towards interface (gas - SiO₂)

\[
\frac{1}{k_{cO_2}} \gg \frac{\delta}{D_{O_2}^s}, \quad \frac{1}{k_{cO_2}} \gg \frac{1}{k} \Rightarrow r_s = k_{cO_2} c_o, \quad \delta = k_{cO_2} c_o \frac{M_{SiO_2}}{\rho_{SiO_2}} t
\]

2. Rate determining step is the internal mass transfer of oxygen in porous SiO₂ layer

\[
\frac{\delta}{D_{O_2}^s} \gg \frac{1}{k_{cO_2}}, \quad \frac{\delta}{D_{O_2}^s} \gg \frac{1}{k} \Rightarrow r_s = \frac{D_{O_2}^s}{\delta} c_o, \quad \delta = \sqrt{2 D_{O_2}^s c_o \frac{M_{SiO_2}}{\rho_{SiO_2}} t}
\]

3. Rate determining step is chemical reaction taking place on the interface (SiO₂ - Si)

\[
\frac{1}{k} \gg \frac{\delta}{D_{O_2}^s}, \quad \frac{1}{k} \gg \frac{1}{k_{cO_2}} \Rightarrow r_s = k c_o, \quad \delta = k c_o \frac{M_{SiO_2}}{\rho_{SiO_2}} t
\]

Discussion: \( r_s = f(\text{composition}), \quad r_s = f(\text{temperature}) \)
External heat and mass transfer

Combustion of the spherical carbon particle

\[ O_{2(g)} + C_{(s)} \rightarrow CO_{2(g)} \]
\[ v_1 A_{1(g)} + v_2 A_{2(s)} \rightarrow v_3 A_{3(g)} \]
Oxygen molar flux at steady state

\[ \dot{N}_1 = k_c a (c_1^o - c_1^s) = -v_1 r_V = -(\frac{1}{k(T_s)})c_1^s = \]

\[ = A \exp \left( -\frac{E}{RT_s} \right) c_1^s \]

Energy flux at steady state

\[ \dot{N}_H = h a (T_s - T_o) = (-\Delta H_r) r_V \]
Surface temperature and concentration of oxygen

Two balance equations for unknown $c_1^s, T_s$

\[ h a (T_s - T_o) = (-\Delta H_r) r_V = (-\Delta H_r) k_{c_1} a (c_1^o - c_1^s) \]

\[ \frac{c_1^s}{c_1^o} = 1 - \frac{h T_o}{(-\Delta H_r) k_{c_1} c_1^o} \left( \frac{T_s}{T_o} - 1 \right) \]  

(1)

\[ k_{c_1} a (c_1^o - c_1^s) = k(T_s)(c_1^s)^n \]

\[ n = 1 \]

\[ \frac{c_1^s}{c_1^o} = \frac{k_{c_1} a}{k_{c_1} a + k(T_s / T_o)} \]  

(2)
Multiple steady state solutions as in the case of CSTR!
Molar material balances

\[ \varepsilon_p \gamma V_p \frac{dC_i}{dt} = S_t k_j (c_i^g - c_i^S) + \rho_j (1 - \varepsilon_p) \gamma V_p \sum_{j=1}^{N_p} Y_j r_{M,j} \]

Enthalpy balance

\[ \left[(1 - \varepsilon_p) \rho_j V_p c_{ps} + \varepsilon_p V_p \frac{P}{RT_p} c_{ps}\right] \frac{dT}{dt} = S_h (T_G - T_S) + (1 - \varepsilon_p) \gamma p_j V_p \sum_{j=1}^{N_p} (\Delta_h H) r_{M,j} \]

\[ (1 - \varepsilon_p) \rho_j V_p c_{ps} \frac{dT}{dt} = S_h (T_G - T_S) + (1 - \varepsilon_p) \gamma p_j V_p \sum_{j=1}^{N_p} (\Delta_h H) r_{M,j} \]

\[ \text{NH}_3 + 1.25 \text{O}_2 \rightarrow \text{NO} + 1.5 \text{H}_2 \text{O} \quad \Delta H_1 = -226.66 \text{ kJ mol}^{-1} \]  \hfill (1)

\[ \text{NH}_3 + 0.75 \text{O}_2 \rightarrow 0.5 \text{N}_2 + 1.5 \text{H}_2 \text{O} \quad \Delta H_2 = -275.22 \text{ kJ mol}^{-1} \] \hfill (2)

\[ \text{NH}_3 + \text{O}_2 \rightarrow 0.5 \text{N}_2 \text{O} + 1.5 \text{H}_2 \text{O} \quad \Delta H_3 = -317.10 \text{ kJ mol}^{-1} \] \hfill (3)

\[
\begin{array}{|c|c|}
\hline
r_{M,1} & A_1 \exp \left( -\frac{E_1}{RT} \right) P_{z,\text{NH}_3} P_{z,\text{O}_3} \text{ mol kg}^{-1} \text{s}^{-1} \\
A_1 & 4.609 \times 10^{-3} \text{ mol kg}^{-1} \text{s}^{-1} \text{Pa}^{-2} \\
E_1 & 149.1 \text{ kJ mol}^{-1} \\
\hline
r_{M,2} & A_2 \exp \left( -\frac{E_2}{RT} \right) P_{z,\text{NH}_3} P_{z,\text{O}_3} \text{ mol kg}^{-1} \text{s}^{-1} \\
A_2 & 5.00 \times 10^{-2} \text{ mol kg}^{-1} \text{s}^{-1} \text{Pa}^{-2} \\
E_2 & 61.0 \text{ kJ mol}^{-1} \\
\hline
r_{M,3} & A_3 \exp \left( -\frac{E_3}{RT} \right) P_{z,\text{NH}_3} P_{z,\text{O}_3} \text{ mol kg}^{-1} \text{s}^{-1} \\
A_3 & 2.80 \times 10^{-2} \text{ mol kg}^{-1} \text{s}^{-1} \text{Pa}^{-2} \\
E_3 & 104.0 \text{ kJ mol}^{-1} \\
\hline
\end{array}
\]
Catalytic reactions

- **homogeneous catalysis**
  - Ozone decomposition in the presence of Cl
  - SO₂ oxidation by NOₓ
  - Esterification catalyzed by acids or bases
  - Enzymatic catalysis

- **heterogeneous catalysis**
  - NH₃, CH₃OH production
  - SO₂ to SO₃ oxidation
  - HDS, HDN processes
  - Fluid Catalytic Cracking
  - Hydrogenation
  - Polymerization (Ziegler-Natta catalysts, metallocens)

\[
\begin{align*}
O_3 + Cl & \rightleftharpoons ClO + O_2 \\
ClO + O_3 & \rightleftharpoons Cl + 2O_2 \\
2O_3 & \rightleftharpoons 3O_2
\end{align*}
\]
Catalytic cycle
Non catalytic x catalytic reaction

Activated complex of non catalytic reaction

$E_{ncat} – \text{energy of activation for non catalytic reaction}$

$E_{cat} – \text{energy of activation for catalytic reaction}$

$E_i \sim e^{E_i/RT}$

The multi-step catalytic reaction can be faster than one-step reaction
## Homogeneous x Heterogeneous Catalysts

<table>
<thead>
<tr>
<th>Active sites</th>
<th>Homogeneous</th>
<th>Heterogeneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>All atoms</td>
<td>Surface atoms</td>
</tr>
<tr>
<td>Diffusion disguises</td>
<td>Low</td>
<td>High (variable)</td>
</tr>
<tr>
<td>Reaction conditions</td>
<td>50-200 °C</td>
<td>200-1000 °C</td>
</tr>
<tr>
<td>Application</td>
<td>Limited</td>
<td>Large</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Characterization</th>
<th>Homogeneous</th>
<th>Heterogeneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure, composition</td>
<td>Well defined</td>
<td>No clear definition</td>
</tr>
<tr>
<td>Modification</td>
<td>Easy</td>
<td>Difficult</td>
</tr>
<tr>
<td>Temperature stability</td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Separation</th>
<th>Difficult</th>
<th>Easy packed beds</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Recycling</th>
<th>Feasible</th>
<th>Feasible</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactant(s)</td>
<td>Product</td>
<td>Typical catalyst(s)</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-----------------------</td>
<td>--------------------------------------</td>
</tr>
<tr>
<td>Crude oil</td>
<td>Hydrocarbon fuels</td>
<td>Platinum/silica-alumina</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Platinum/acidic alumina</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Metal-exchanged zeolites</td>
</tr>
<tr>
<td>SO$_2$, O$_2$</td>
<td>Sulphuric acid</td>
<td>V$_2$O$_5$</td>
</tr>
<tr>
<td>N$_2$, H$_2$</td>
<td>Ammonia</td>
<td>Fe</td>
</tr>
<tr>
<td>NH$_3$, O$_2$</td>
<td>Nitric acid</td>
<td>Pt/Rh</td>
</tr>
<tr>
<td>CO, H$_2$</td>
<td>Methanol</td>
<td>Cu/ZnO</td>
</tr>
<tr>
<td>C$_2$H$_4$, O$_2$</td>
<td>Ethylene oxide</td>
<td>Ag</td>
</tr>
<tr>
<td>Unsaturated vegetable</td>
<td>Hydrogenated</td>
<td>Ni</td>
</tr>
<tr>
<td>oils, H$_2$</td>
<td>vegetable oils</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>Polyethylene</td>
<td>Cr(II), Ti(III)</td>
</tr>
<tr>
<td>CH$_3$OH, O$_2$</td>
<td>Formaldehyde</td>
<td>Mixed Fe, Mo oxides</td>
</tr>
<tr>
<td>C$_3$H$_6$, NH$_3$, O$_2$</td>
<td>Acrylonitrile</td>
<td>Mixed Bi, Mo oxides</td>
</tr>
<tr>
<td>o-Xylene, O$_2$</td>
<td>Phthalic anhydride</td>
<td>V$_2$O$_5$</td>
</tr>
<tr>
<td>n-Butane, O$_2$</td>
<td>Maleic anhydride</td>
<td>V$_2$O$_5$</td>
</tr>
</tbody>
</table>
Catalytic materials

- Metals
  - Dispersed: Pt/Al₂O₃, Ni/Al₂O₃, Pd/Al₂O₃
  - Porous: Raney Nickel
  - Bulk: Pt, Pd, Ag gauze

- Oxides
  - Single: Al₂O₃, Cr₂O₃, V₂O₅
  - Dual, complex: SiO₂/Al₂O₃, CuCr₂O₄
  - Dispersed: NiO/Al₂O₃, MoO₃/Al₂O₃

- Sulphides
  - MoS₂/Al₂O₃, WS₂/Al₂O₃

- Acids
  - SiO₂-Al₂O₃; zeolites; natural clays

- Base
  - CaO, MgO, K₂O, Na₂O
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals (e.g., Ni, Pd, Pt, as powders or on supports) or metal oxides (e.g., Cr₂O₃)</td>
<td>C═C bond hydrogenation, e.g., olefin + H₂ → paraffin</td>
</tr>
<tr>
<td>Metals (e.g., Cu, Ni, Pt)</td>
<td>C═O bond hydrogenation, e.g., acetone + H₂ → isopropanol</td>
</tr>
<tr>
<td>Metal (e.g., Pd, Pt)</td>
<td>Complete oxidation of hydrocarbons, oxidation of CO</td>
</tr>
<tr>
<td>Fe (supported and promoted with alkali metals)</td>
<td>3H₂ + N₂ → 2NH₃</td>
</tr>
<tr>
<td>Ni</td>
<td>CO + 3H₂ → CH₄ + H₂O (methanation)</td>
</tr>
<tr>
<td>Fe or Co (supported and promoted with alkali metals)</td>
<td>CO + H₂ → paraffins + olefins + H₂O + CO₂ (+ other oxygen-containing organic compounds) (Fischer-Tropsch reaction)</td>
</tr>
<tr>
<td>Cu (supported on ZnO, with other components, e.g., Al₂O₃)</td>
<td>CO + 2H₂ → CH₃OH</td>
</tr>
<tr>
<td>Re + Pt (supported on ƞ-Al₂O₃ or γ-Al₂O₃ promoted with chloride)</td>
<td>Paraffin dehydrogenation, isomerization and dehydrocyclization</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Reaction</td>
</tr>
<tr>
<td>---------------------------------------------------------------</td>
<td>--------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Solid acids (e.g., SiO$_2$-Al$_2$O$_3$, zeolites)</td>
<td>Paraffin cracking and isomerization</td>
</tr>
<tr>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>Alcohol $\rightarrow$ olefin + H$_2$O</td>
</tr>
<tr>
<td>Pd supported on acidic zeolite</td>
<td>Paraffin hydrocracking</td>
</tr>
<tr>
<td>Metal-oxide-supported complexes of Cr, Ti or Zr</td>
<td>Olefin polymerization, e.g., ethylene $\rightarrow$ polyethylene</td>
</tr>
<tr>
<td>Metal-oxide-supported oxides of W or Re</td>
<td>Olefin metathesis, e.g., 2 propylene $\rightarrow$ ethylene + butene</td>
</tr>
<tr>
<td>Ag(on inert support, promoted by alkali metals)</td>
<td>Ethylene + 1/2 O$_2$ $\rightarrow$ ethylene oxide (with CO$_2$ + H$_2$O)</td>
</tr>
<tr>
<td>V$_2$O$_5$ or Pt</td>
<td>2 SO$_2$ + O$_2$ $\rightarrow$ 2 SO$_3$</td>
</tr>
<tr>
<td>V$_2$O$_5$ (on metal oxide support)</td>
<td>Naphthalene + 9/2O$_2$ $\rightarrow$ phthalic anhydride + 2CO$_2$ +2H$_2$O</td>
</tr>
<tr>
<td>Bismuth molybdate</td>
<td>Propylene + 1/2O$_2$ $\rightarrow$ acrolein</td>
</tr>
<tr>
<td>Mixed oxides of Fe and Mo</td>
<td>CH$_3$OH + O$_2$ $\rightarrow$ formaldehyde (with CO$_2$ + H$_2$O)</td>
</tr>
<tr>
<td>Fe$_3$O$_4$ or metal sulfides</td>
<td>H$_2$O + CO $\rightarrow$ H$_2$ + CO$_2$</td>
</tr>
</tbody>
</table>
Catalytic reaction

- Raw materials (impurities, ..,)
- Operation conditions (T, P, ..)
- Reactors - continuous, batch
- Equilibrium
- Hydrodynamics
- Kinetics
- Properties of Catalyst, Preparation procedure
- Heat and mass transfer
**Steps in a catalytic reaction**

1) Mass transfer of reactants to the external surface of catalyst
2) Mass transfer of reactants in porous structure of catalyst
3) *Adsorption of reactants*
4) *Surface reaction (+ migration)*
5) *Desorption of products*
6) Mass transfer of products in porous structure of catalyst
7) Mass transfer of reactants from the external surface of catalyst

The transport steps (1,2,6,7) depend on T, P, composition, flow rates, pore size, ....

The chemical steps (3,4,5) are dependent on T, P, composition.
Elementary steps of catalytic reaction

- Fluid phase
- Reactants
- Products
- Desorption
- Adsorption
- Dissociation
- Surface reaction
- Migration
Mechanisms in heterogeneous catalysis

Langmuir-Hinshelwood

Rideal-Eley

Adsorption

Desorption

Migration

Surface reaction

We run a kinetic experiment in a batch reactor

Here are the experimental points

Here is the kinetic model
Adsorption x Chemisorption

2A + 2[*] ⇄ 2A*

A₂ + 2[*] ⇄ 2A*

Adsorption (physical phenomenon)

Chemisorption (chemical phenomenon)

Energy of biatomic molecule A₂

Distance from catalyst surface

E_{mc}, E_{mp} – activation energy of migration in adsorbed and chemisorbed state

E_D – energy of dissociation of molecule A₂

E_d – energy of desorption of A₂

E_a – energy of activation of transition from adsorbed to chemisorbed state
### Adsorption x Chemisorption

<table>
<thead>
<tr>
<th></th>
<th>Adsorption</th>
<th>Chemisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Principal</td>
<td>van der Waals forces</td>
<td>covalent or ionic bonds</td>
</tr>
<tr>
<td></td>
<td>no electron transfer!</td>
<td>electron transfer</td>
</tr>
<tr>
<td>Adsorbent</td>
<td>all solids</td>
<td>specific sites</td>
</tr>
<tr>
<td>Adsorbat</td>
<td>gases $T &lt; T_c$</td>
<td>reactive components</td>
</tr>
<tr>
<td>Temperature</td>
<td>low</td>
<td>higher</td>
</tr>
<tr>
<td>Enthalpy</td>
<td>10-40 kJ/mol</td>
<td>80-600 kJ/mol</td>
</tr>
<tr>
<td>Rate</td>
<td>high</td>
<td>depends on $T$</td>
</tr>
<tr>
<td>Activation energy</td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td>Occupancy</td>
<td>multilayer</td>
<td>monolayer</td>
</tr>
<tr>
<td>Reversibility</td>
<td>YES</td>
<td>YES but …</td>
</tr>
<tr>
<td>Use</td>
<td>BET method</td>
<td>surface concentration</td>
</tr>
<tr>
<td></td>
<td>pore size distribution</td>
<td>of active sites</td>
</tr>
</tbody>
</table>
Chemisorption of fluid phase molecule (adsorbat)

Surface occupancy ($\Theta$)

$$\Theta_i = \frac{\text{Number of sites occupied by } i\text{-th component}}{\text{Total number of sites}}$$

$$0 < \Theta_i < 1$$

Associative x Dissociative chemisorption

Adsorption (chemisorption) isotherm – Surface occupancy as a function of partial pressure of given component at constant temperature

Henry isotherm

$$\Theta_i = H_i \cdot p_i$$
Irving Langmuir

1920 - adsorption isotherm
- kinetics of catalytic reactions on ideal surfaces

1932 - Nobel Prize
**Langmuir adsorption isotherm**

**Brunauer-Emmett-Teller (BET) adsorption isotherm**
**Associative adsorption**

\[ \text{M}_\text{(g)} + * \xrightleftharpoons{k_a \leftrightarrow k_d} \text{M}^- * \]

* - active site, \( k_a \) a \( k_d \) – kinetic constants for adsorption and desorption

**Adsorption rate**  
\[ \text{Adsorption rate} = k_a \cdot p \cdot (1 - \Theta) \quad p = \text{partial pressure of adsorbat} \]

**Desorption rate**  
\[ \text{Desorption rate} = k_d \cdot \Theta \]

**Equilibrium**

\[ k_a \cdot p \cdot (1 - \Theta) = k_d \cdot \Theta \]

**Langmuir adsorption isotherm**

\[ \Theta = \frac{N_s}{N} = \frac{K \cdot p}{(1 + K \cdot p)} \quad (K = \frac{k_a}{k_d}) \]
Asociative chemisorption

Langmuir adsorption (chemisorption) isotherm
**Multicomponent associative chemisorption**

\[
A_{(g)} + * \xleftrightarrow{k_a/k_d} A^- \quad \text{Occupancy of A}
\]

\[
B_{(g)} + * \xleftrightarrow{k_b/k_d} B^- \quad \text{Occupancy of B}
\]

\[
\Theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B}
\]

\[
\Theta_B = \frac{K_B p_B}{1 + K_A p_A + K_B p_B}
\]

\[
K_A = \frac{k_a}{k_d} \quad \text{Irreversible chemisorption}
\]

\[
K_B = \frac{k_b}{k_d} \quad \text{catalyst poisoning}
\]
Dissociative chemisorption

\[ M_{2(g)} + 2 * \xrightleftharpoons{k_a}{k_d} 2 M^- * \]

Rate of chemisorption = \( k_a \cdot p \cdot (1 - \Theta)^2 \)

Rate of desorption = \( k_d \cdot \Theta^2 \)

\[ k_a \cdot p \cdot (1 - \Theta)^2 = k_d \cdot \Theta^2 \quad (K' = \frac{k_a}{k_d}) \]

\[ \frac{\Theta^2}{(1 - \Theta)^2} = K' \cdot p \quad \Rightarrow \quad \Theta = \frac{\sqrt{K' \cdot p}}{1 + \sqrt{K' \cdot p}} \]
Isotherms

Langmuir
(chemisorption, adsorption, monolayer, micropores)

\[ \frac{n_{ads}}{n^*} = \Theta = \frac{K.p}{1+K.p} \]

Henry
(chemisorption, adsorption, low occupancy)

\[ \frac{n_{ads}}{n^*} = \Theta = H.p \]

Freundlich
(chemisorption, adsorption, non ideal)

\[ \frac{n_{ads}}{n^*} = \Theta = K_p^n \]

Temkin
(chemisorption, non ideal

\[ \Theta = A ln [B.p] \]

Brunauer-Emmett-Teller (BET)
(adsorption, multilayer)

\[ \frac{p}{n_{ads}(p_0-p)} = \frac{1}{n_{m}C} + \frac{(C-1)p}{n_{m}C_p_0} \]

Virial
(adsorption, multilayer)

\[ \frac{p}{R.T} = \Theta (1+a_1\Theta+a_2\Theta^2+...) \]
Brunauer-Emmett-Teller (BET)

Extension of Langmuir model

Assumptions:

- Adsorption in multilayer s, 1st layer interaction between adsorbent and adsorbat, in 2nd and further layers condensation-like interaction

\[
\frac{p}{n_{ads}(p_0-p)} = \frac{1}{n^m C} + \frac{(C-1)p}{n^m C p_0}
\]
Mesoporous alumina

Temperature of calcination: 3.3 nm (450 °C) - 4.5 nm (600 °C) - 5.1 nm (800 °C)
Reaction rate per mass

\[
\frac{1}{m} r = \frac{1}{m} \frac{d \xi}{dt} = \frac{1}{m} \frac{1}{\nu_i} \frac{dn_i}{dt} \quad \text{mole.kg}^{-1}.s^{-1}
\]

\[
\frac{1}{m} r_k = \frac{1}{m} \frac{d \xi_k}{dt}
\]

Reaction rate per surface

\[
\frac{1}{S} r = \frac{1}{S} \frac{d \xi}{dt} = \frac{1}{S} \frac{1}{\nu_i} \frac{dn_i}{dt} \quad \text{mole.m}^{-2}.s^{-1}
\]

\[
\frac{1}{S} r_k = \frac{1}{S} \frac{d \xi_k}{dt}
\]
Reaction rate per active center (turnover number)

\[ r_{RS} = \frac{1}{n_{RS}} r = \frac{1}{n_{RS}} \frac{d\xi}{dt} = \frac{1}{n_{RS}} \frac{1}{\nu_i} \frac{dn_i}{dt} \quad \text{s}^{-1} \]

\[ r_{RS,k} = \frac{1}{n_{RS}} r_k = \frac{1}{n_{RS}} \frac{d\xi_k}{dt} \]

**Reaction rate of catalytic reactions**

Langmuir-Hishelwood ideal surface

- Rate of elementary steps
- Rate determining step x steady state hypothesis
CO oxidation on Pt

**Overall reaction** \( \Delta G^o_r < 0 \)

\[
2\text{CO}_\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)}
\]

\[
\text{nebo}
2\text{CO}_\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)}
\]
Elementary steps of catalytic CO oxidation on Pt

1. CO chemisorption

\[ \text{CO}_{(g)} + [*] \leftrightarrow \text{CO}^* \]

\[ r_1 = k_{f,1} P_{\text{CO}} \Theta_\text{CO}^* - k_{b,1} \Theta_{\text{CO}} \]

2. O\textsubscript{2} dissociative chemisorption

\[ \text{O}_{2(g)} + 2[*] \leftrightarrow 2\text{O}^* \]

\[ r_2 = k_{f,2} P_{\text{O}_2} \Theta_\text{O}^*^2 - k_{b,2} \Theta_\text{O}^2 \]

3. Surface reaction between CO\textsuperscript{*} and O\textsuperscript{*}

\[ \text{CO}^* + \text{O}^* \leftrightarrow *\text{CO}_2 + * \]

\[ r_3 = k_{f,3} \Theta_{\text{CO}} \Theta_{\text{O}} - k_{b,3} \Theta_{\text{CO}_2} \Theta_* \]

4. CO\textsubscript{2} desorption into gas phase

\[ *\text{CO}_2 \leftrightarrow \text{CO}_{2(g)} + * \]

\[ r_4 = k_{f,4} \Theta_{\text{CO}_2} - k_{b,4} P_{\text{CO}_2} \Theta_* \]

\( p_i \) – partial pressures of gaseous components [Pa]

\( \Theta_i \) - occupancy (coverage) of the i-th species [-]

\( k_{f,j}, k_{b,j} \) - reaction rate constants

\( r_j \) – rate of the j-th elementary step [mol/kg katalyzátoru/s, mol/molPt/s= 1/s]
Rate determining step in steady state

\[ r = \frac{r_i}{\sigma_i} \]

Forward reaction rate

\[ r_i = \tilde{r}_i - \tilde{r}_i \]

Backward reaction rate

\[ \tilde{r}_i \]

Fast step

\[ \tilde{r}_i \cong \tilde{r}_i \Rightarrow \text{step is close to the equilibrium} \]

\[ \tilde{r}_{i+1} \]

\[ r = \frac{r_i}{\sigma_i} \]

Slow step =

Rate determining step
Relation between overall reaction rate and the rate of i-th elementary step determines the stoichiometric number $\sigma_i$ (do not confuse with stoichiometric coefficient !)

$$r = \frac{r_i}{\sigma_i}$$

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$\sigma_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO}_{(g)} + [<em>] \leftrightarrow \text{CO}^</em>$</td>
<td>2</td>
</tr>
<tr>
<td>$\text{O}_2(g) + 2[<em>] \leftrightarrow 2\text{O}^</em>$</td>
<td>1</td>
</tr>
<tr>
<td>$\text{CO}^* + \text{O}^* \leftrightarrow \text{CO}_2 + *$</td>
<td>2</td>
</tr>
<tr>
<td>$\text{CO}<em>2 \leftrightarrow \text{CO}</em>{2(g)} + *$</td>
<td>2</td>
</tr>
<tr>
<td>$2\text{CO}_{(g)} + \text{O}_2(g) \rightarrow 2\text{CO}_2(g)$</td>
<td></td>
</tr>
</tbody>
</table>
Rate determining step: surface reaction

\[ K_{CO} = \frac{k_{f.1}}{k_{b.1}} = \frac{\Theta_{CO}}{P_{CO} \Theta_*} \quad K_{O2} = \frac{k_{f.2}}{k_{b.2}} = \frac{\Theta_{O}^2}{P_{O2} \Theta_*^2} \quad K_{CO_2} = \frac{k_{f.4}}{k_{b.4}} = \frac{\Theta_{CO_2}}{P_{CO_2} \Theta_*} \]

\[ \Theta_* + \Theta_{CO} + \Theta_O + \Theta_{CO_2} = 1 \]

\[ \Theta_* = \frac{1}{1 + K_{CO}P_{CO} + \sqrt{K_{O2}P_{O2} + K_{CO_2}P_{CO_2}}} \]

\[ \Theta_{CO} = \frac{K_{CO}P_{CO}}{1 + K_{CO}P_{CO} + \sqrt{K_{O2}P_{O2} + K_{CO_2}P_{CO_2}}} \]

\[ \Theta_{O} = \frac{\sqrt{K_{O2}P_{O2}}}{1 + K_{CO}P_{CO} + \sqrt{K_{O2}P_{O2} + K_{CO_2}P_{CO_2}}} \]

\[ \Theta_{CO_2} = \frac{K_{CO_2}P_{CO_2}}{1 + K_{CO}P_{CO} + \sqrt{K_{O2}P_{O2} + K_{CO_2}P_{CO_2}}} \]

Reaction rate as a function of measurable variables

\[ r_3 = k_{f.3} \Theta_{CO} \Theta_{O} - k_{b.3} \Theta_{CO_2} \Theta_* = \frac{k_{f.3}K_{CO} \sqrt{K_{O2}P_{CO} \sqrt{P_{O2} - k_{b.3}K_{CO_2}P_{CO_2}}}}{\left[1 + K_{CO}P_{CO} + \sqrt{K_{O2}P_{O2} + K_{CO_2}P_{CO_2}}\right]^2} \]
Example

\[
\text{C}_2\text{H}_5\text{OH}_\text{(g)} (A_1) \rightarrow \text{CH}_3\text{CHO}_\text{(g)} (A_2) + \text{H}_\text{(g)} (A_3)
\]

Catalysts: CuO, CoO a Cr\textsubscript{2}O\textsubscript{3}


Kinetics

\[
r_M = \frac{kK_1 \left( P_1 - P_2 P_3 / K_{eq} \right)}{\left( 1 + K_1 P_1 + K_2 P_2 \right)^2}
\]

\(r_M\) (mol\text{.g}^{-1}\text{.hod}^{-1}), \(P_i\) (bar), \(k\) (mol\text{.g}^{-1}\text{.hod}^{-1}), \(K_{eq}\) (bar), \(K_i\) (bar\textsuperscript{-1}).

Task: to estimate on the basis of experimental data kinetic and adsorption parameters \(k, K_1, K_2\).
EXPERIMENTAL SET-UP

Fig. 1. Apparatus: 1,2, feed burettes; 3, metering pump; 4, thermocouples; 5, ice-bath; 6, mV-recorder; 7, reactor; 8, reactor-mantle; 9,10, variable transformers; 11,13, manometers; 12, pressure regulating device; 14, cooler; 15, cooling unit; 16, circulating pump; 17, sampling flask; 18, liquid air trap; 19, saturator, eventually also absorber in periods between sampling; 20, wet test meter; 21, flowmeters for air and nitrogen.
<table>
<thead>
<tr>
<th>( \frac{W}{F_1^o} ) [g.hod/mol]</th>
<th>( P ) [bar]</th>
<th>( y_1^o ) [-]</th>
<th>( y_{y1}^o ) [-]</th>
<th>( y_{y2}^o ) [-]</th>
<th>( T ) [°C]</th>
<th>( X_1 ) [-]</th>
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<td>0,135</td>
<td>0,0</td>
<td>275,0</td>
<td>0,196</td>
</tr>
</tbody>
</table>
Solution:
Minimize the objective function:

$$\Phi(k, K_1, K_2) = \sum_{i=1}^{N_{EXP}} \left[ X_{1,i}^{\text{exp}} - X_{1,i}^{\text{mod}}(k, K_1, K_2) \right]^2$$

$X_{1,i}^{\text{mod}}(k, K_1, K_2)$ calculated from isothermal catalytic PFR model:

$$\frac{dX_1}{d\left(\frac{W}{F_1^o}\right)} = r_M(X_1) \quad W / F_1^o = 0, X_1 = 0$$

ATHENA Visual Studio.
Catalytic Ethanol Dehydrogenation Kinetics

Global x1,x2,x3,x4 As Real
Global TSEP, X1, X2, X3 As Real

\textit{Connect Variables} \\
X1 = \text{K1}(1) \\
X2 = \text{K2}(2) \\
X3 = \text{K3}(3) \\
X4 = \text{K4}(4) \\
X5 = \text{K5}(5)

\textit{Reaction rate constant}

\textit{Adsorption equilibrium constant for ethanol}

\textit{Adsorption equilibrium constant for hydrogen}

\textit{Adsorption equilibrium constant for water}

\textit{Temperature [K]}

\textit{Feed ethanol mol. fraction}

\textit{Feed water mol. fraction}

\textit{Feed acetaldehyde mol. fraction}

\textit{Initial Conditions}

X1(0) = 0.0

\textit{Model Equations}

\textit{Ethanol partial pressure}

\textit{Acetaldehyde partial pressure}

\textit{Water partial pressure}

\textit{Response Model}

Y(1) = X(1)
\[
\ln(k_1) = f\left(\frac{1}{T}\right)
\]

\[
\ln(KA_1) = f\left(\frac{1}{T}\right)
\]

\[
\ln(KA_2) = f\left(\frac{1}{T}\right)
\]
Models of catalytic reactors

- In a fixed-bed reactor the catalyst pellets are held in place and do not move with respect to a fixed reference frame.

- Material and energy balances are required for both the fluid, which occupies the interstitial region between catalyst particles, and the catalyst particles, in which the reactions occur.

- The following figure presents several views of the fixed-bed reactor. The species production rates in the bulk fluid are essentially zero. That is the reason we are using a catalyst.
Expanded views of a fixed bed reactor
The steps to consider

During any catalytic reaction the following steps occur:

1. transport of reactants and energy from the bulk fluid up to the catalyst pellet exterior surface,

2. transport of reactants and energy from the external surface into the porous pellet,

3. adsorption, chemical reaction, and desorption of products at the catalytic sites,

4. transport of products from the catalyst interior to the external surface of the pellet, and

5. transport of products into the bulk fluid.

The coupling of transport processes with chemical reaction can lead to concentration and temperature gradients within the pellet, between the surface and the bulk, or both.
Single Reaction in an Isothermal Particle

- We start with the simplest cases and steadily remove restrictions and increase the generality. We consider in this section a single reaction taking place in an *isothermal* particle.

- First case: the spherical particle, first-order reaction, without external mass-transfer resistance.
First-Order Reaction in a Spherical Particle

\[ A \xrightarrow{k} B, \quad r = kc_A \]

\[ 0 = D_j \nabla^2 c_j + R_j, \quad j = 1, 2, \ldots, n_s \]

Substituting the production rate into the mass balance, expressing the equation in spherical coordinates, and assuming pellet symmetry in \( \theta \) and \( \phi \) coordinates gives

\[ D_A \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dc_A}{dr} \right) - kc_A = 0 \]

in which \( D_A \) is the effective diffusivity in the pellet for species A.

As written here, the first-order rate constant \( k \) has units of inverse time.

Be aware that the units for a heterogeneous reaction rate constant are sometimes expressed per mass or per area of catalyst.
Boundary Conditions

- We require two boundary conditions for Equation

- In this section we assume the concentration at the outer boundary of the pellet, $c_{As}$, is known

- The symmetry of the spherical pellet implies the vanishing of the derivative at the center of the pellet.

- Therefore the two boundary conditions for Equation are

\[
\begin{align*}
    c_A &= c_{As}, & r &= R \\
    \frac{dc_A}{dr} &= 0, & r &= 0
\end{align*}
\]
Dimensionless form

At this point we can obtain better insight by converting the problem into dimensionless form. Equation has two dimensional quantities, length and concentration. We might naturally choose the sphere radius $R$ as the length scale, but we will find that a better choice is to use the pellet’s volume-to-surface ratio. For the sphere, this characteristic length is

$$a = \frac{V_p}{S_p} = \frac{4}{3} \pi R^3 = \frac{4 \pi R^3}{4 \pi R^2} = \frac{R}{3}$$

The only concentration appearing in the problem is the surface concentration in the boundary condition, so we use that quantity to nondimensionalize the concentration

$$\bar{r} = \frac{r}{a}, \quad \bar{c} = \frac{c_A}{c_{As}}$$
Dividing through by the various dimensional quantities produces

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dc}{dr} \right) - \Phi^2 c = 0$$

$$\bar{c} = 1 \quad \bar{r} = 3$$

$$\frac{dc}{dr} = 0 \quad \bar{r} = 0$$

in which $\Phi$ is given by

$$\Phi = \sqrt{\frac{ka^2}{DA}} \frac{\text{reaction rate}}{\text{diffusion rate}} \text{ Thiele modulus}$$
**Models of catalytic reactors**

Model equations involve:
- Balance equations for components of reaction mixture in both gas phase and porous catalytic particle
- Balance of energy (enthalpy)
- Balance of momentum
- Flux constitutive equations for component and energy fluxes
<table>
<thead>
<tr>
<th></th>
<th>Pseudo homogeneous</th>
<th>Heterogeneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-D</td>
<td>• without axial dispersion (pure plug flow)</td>
<td>Gradients of concentration and temperature between phases</td>
</tr>
<tr>
<td></td>
<td>• with axial dispersion</td>
<td></td>
</tr>
<tr>
<td>2-D</td>
<td>Radial dispersion</td>
<td></td>
</tr>
</tbody>
</table>
1-D pseudo homogeneous model without axial dispersion

\[ \frac{dF_i}{dz} = S \nu_i \gamma_i \]

\[ m c_p \frac{dT}{dz} = (-\Delta H_r) S \gamma_i + \frac{\pi d_i}{\pi d_i^2 / 4} K(T_m - T) = (-\Delta H_r) S \gamma_i + \frac{4}{d_i} K(T_m - T) \]

\[ - \frac{dP}{dz} = f \frac{\rho g u_s^2}{d_p} \]

\[ z = 0 \]

\[ F_i = F_i^o, T = T_o, P = P_o \]

dp effective diameter of catalytic particle
f friction coefficient
u_s mean fluid velocity
K overall heat transfer coefficient
The counter-current catalytic reactor for ammonia synthesis is depicted on above presented figure. The cold gas mixture (21.75 mol. % N₂, 65.25 mol. % H₂, 5 mol. % NH₃, 4 mol. % CH₄ a 4 mol. % Ar) is introduced into the shell side (blue arrows) and is preheated by the heat transferred from catalytic tubes.

\[ \dot{Q} = \omega \left( T_R - T_f \right) dS \]

Synthesis of ammonia is based on the high pressure gas phase catalytic reaction

\[ \text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3 \]
\[ r_v = k_f \frac{P_{N_2}P_{H_2}^{1.5}}{P_{NH_3}} - k_b \frac{P_{NH_3}}{P_{H_2}^{1.5}} \quad [\text{kmol/m}^3/\text{hr}] \]

\[ k_f = 9.88469 \times 10^5 \exp \left( -\frac{87085}{RT} \right) \quad [\text{kmol/m}^3/\text{hr/bar}^{1.5}] \]

\[ k_b = 6.751949 \times 10^{15} \exp \left( -\frac{198454}{RT} \right) \quad [\text{kmol} \times \text{bar}^{0.5}/\text{m}^3/\text{hr}] \]

\[ R = 8.31446 \quad \text{J/mol/K} \]
1-D pseudo homogeneous model with axial dispersion

\[
\varepsilon D_{ai} \frac{d^2 c_i}{dz^2} - \nu_z \frac{dc_i}{dz} + \nu_T r_T = 0
\]

\[
\lambda_{am} \frac{d^2 T}{dz^2} - \nu_z \rho_z c_{pm} \frac{dT}{dz} + (-\Delta H_r) r_T + \frac{AK}{d_z} (T_m - T) = 0
\]

Boundary conditions

\[
z = 0 \quad - \varepsilon D_{ai} \frac{dc_i}{dz} + c_i \nu_z = c_i^* \nu_z \quad - \lambda_{am} \frac{dT}{dz} + \nu_z \rho_z c_{pm} T = \nu_z \rho_z c_{pm} T_0
\]

\[
z = L \quad \frac{d c_i}{dz} = 0 \quad \frac{dT}{dz} = 0
\]

Dimensionless form

\[
x = \frac{z}{L} \quad Y_i = \frac{c_i}{c_i^*} \quad \vartheta = \frac{T}{T_0}
\]

\[
\frac{1}{Pe_{Ma}} \frac{d^2 Y_i}{dx^2} - \frac{d Y_i}{dx} + D a_i R(Y_i, \vartheta) = 0
\]

\[\frac{1}{Pe_H} \frac{d^2 \vartheta}{dx^2} - \frac{d \vartheta}{dx} + \beta R(Y_i, \vartheta) = 0\]

\[
x = 0 \quad \frac{1}{Pe_{Ma}} \frac{d Y_i}{dx} = Y_i - 1 \quad \frac{1}{Pe_{Ma}} \frac{d \vartheta}{dx} = \vartheta - 1
\]

\[
x = 1 \quad \frac{d Y_i}{dx} = 0 \quad \frac{d \vartheta}{dx} = 0
\]

\[
Pe_{Ma} = \frac{\nu_z L}{\varepsilon D_{ai}} \quad Pe_H = \frac{\nu_z L}{\lambda_{am}} \quad Da_i = \frac{L R_i (c^*_i, T_0)}{c_i^* \nu_z} \quad \beta = \frac{L R_i (c^*_i, T_0)(-\Delta H_r)}{\nu_z c_{pm} \rho_z \nu_z T_0}
\]
2-D pseudo homogeneous model with axial and radial dispersion

\[ N_i = -D_{ai} \frac{\partial c_i}{\partial z} - D_{ri} \frac{\partial c_i}{\partial r} + y_i \sum_{j=1}^{N_S} N_j = -D_{ai} \frac{\partial c_i}{\partial z} - D_{ri} \frac{\partial c_i}{\partial r} + c_i \cdot \nabla \]

\[ N_H = -\lambda_{am} \frac{\partial T}{\partial z} - \lambda_{rm} \frac{\partial T}{\partial r} + \nu \rho_s c_{pm} T \]

Balance element of volume
Balance equations

\[
\frac{D_m}{\rho} \left( \frac{\partial^2 (c_i)}{\partial r^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} \right) + D_m \frac{\partial^2 c_i}{\partial z^2} + \nu_i \frac{\partial c_i}{\partial z} + v_i \frac{\partial c_i}{\partial r} = 0
\]

\[
\lambda_m \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) + \lambda_m \frac{\partial^2 T}{\partial z^2} + \nu_i \rho_i c_{pi} \frac{\partial T}{\partial z} + (-\Delta H_c) r_T = 0
\]

Boundary and initial conditions

\[
z = 0, \quad 0 < r < r_e
\]

\[-D_m \frac{\partial c_i}{\partial z} + \nu_i c_i = \nu c_i^2 \]

\[-\lambda_m \frac{\partial T}{\partial z} + \nu \rho i c_{pi} T = \nu \rho_i c_{pi} T \]

\[
r = r_e
\]

\[
\frac{\partial c_i}{\partial r} = 0, \quad -\lambda_m \frac{\partial T}{\partial r} = h_w (T - T_h)
\]

\[
r = 0
\]

\[
\frac{\partial c_i}{\partial r} = 0, \quad \frac{\partial T}{\partial r} = 0
\]
Fluidized bed catalytic reactor

Figure 2. Forms of gas-solids fluidized beds.

Figure 7. Schematic drawing of fluidized bed and freeboard.

Figure 9. Schematic diagram of flow structure in a circulating fluidized bed.
Figure 4. Industrial gas distributors: (A) perforated plate; (B) nozzle plate; (C) bubble-cap plate.

Figure 5. Gas flow for isolated rising bubbles in the Davidson model [30].
\[ \varepsilon_b \frac{\partial C_{bi}}{\partial t} = -[u - u_{mf}(1 - \varepsilon_b)] \]
\[ \times \frac{\partial C_{bi}}{\partial h} - k_{G,i} \times a \times (C_{bi} - C_{di}) \] (26)

and, for the suspension phase

\[ (1 - \varepsilon_b)[\varepsilon_{mf} + (1 - \varepsilon_{mf})\varepsilon_i] \frac{\partial C_{di}}{\partial t} \]
\[ = -u_{mf}(1 - \varepsilon_b) \times \frac{\partial C_{di}}{\partial h} + k_{G,i} \times a \times (C_{bi} - C_{di}) \]
\[ + (1 - \varepsilon_b) \times (1 - \varepsilon_{mf})\rho_s \sum_{j=1}^{M} v_{ij} r_j \] (27)

In eqs 26 and 27 the following simplifying assumptions have been made:

(i) Plug flow through the suspension phase at an interstitial velocity \((u_{mf}/\varepsilon_{mf})\).
(ii) Bubble phase in plug flow, bubbles are solids free.
(iii) Reaction in suspension phase only.
(iv) Constant-volume reaction (Ref. 99 shows how to handle a change in the number of moles).
(v) Sorption effects are neglected (see Ref. 102 for handling sorption).

Here \(\varepsilon_i\) is the porosity of the catalyst particles, \(a\) is the local mass-transfer area per unit of fluidized-bed volume, which can be calculated as

\[ a = \frac{6\varepsilon_b}{d_v} \] (28)
Experimental determination of kinetics of heterogeneous catalytic reactions

OVERVIEW
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   2.1 Dynamical Changes in catalysts: Reaction Sites, Structure and Morphology, Surface Composition
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   2.3 Modelling and estimation: CO chemisorption on Pt, NO reduction by H₂, Electrocatalytic Ethylene Epoxidation, CO methanation
1. **Steady state techniques**

1.1 Reactors: Batch, CSTR, PFR

Screening of catalysts – high throughput methods - most promising formulation investigated in more detail – scale up of the catalytic reaction towards the industrial application starts from the knowledge of detailed reaction kinetics $\Rightarrow$ rate equation(s)

Batch reactor, CSTR, PFR

![Batch reactor diagram](image)

- reactor
- catalyst
- silica wadding
- furnace

700°C
Figure 1.17. Batch reactors: a) glass, b) high pressure, c) in parallel mode.

Figure 1.21. Multitubular reactor.

Figure 1.26. The Buss loop reactor

Figure 1.27. Berty gradientless reactors
Calculation of reaction rate $r$ [mol/kg/s]

<table>
<thead>
<tr>
<th>CSTR</th>
<th>PFR</th>
<th>BATCH</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ direct evaluation of r.r.</td>
<td>+simple setup</td>
<td>+simple setup</td>
</tr>
<tr>
<td>- outlet condition’s control</td>
<td>+variation of m/F</td>
<td>- isothermicity</td>
</tr>
<tr>
<td>- real hydrodynamics</td>
<td>- temperature and conc.gradients</td>
<td>-</td>
</tr>
<tr>
<td>differentiation</td>
<td></td>
<td>- isothermicity</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- differentiation in r.r. calculation</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
    r_M &= \frac{F_A^0 X_A}{|\nu_A| m} \\
    X_A &= \frac{F_A^0 - F_A}{F_A^0}
\end{align*}
\]

\[
\begin{align*}
    r_M &= \frac{1}{|\nu_A|} \frac{dX_A}{d(m / F_A^0)} \\
    r_M &= \frac{1}{|\nu_A|} m \frac{dX_A}{dt}
\end{align*}
\]
1.2 Transport Disguises at Particle Scale
Ideality at reactor scale (plug flow or ideal mixing), it is not sufficient to obtain accurate kinetic data

**external transfer**  detem. of mass and heat transfer coefficients

**internal transfer**  determ. of effectiveness factor

\[ Sh_i = \frac{k_i^o L}{D_{mi}} \]  \hspace{1cm} \text{external transfer}

**Deska**

\[ \text{Re}_L < 10^5 \quad Sh_i = 0,66 \text{Re}^{1/2}_L \text{Sc}_i^{1/3} \quad \text{Re}_L = \frac{uL}{\nu} \quad \text{Sc}_i = \frac{D_{mi}}{\nu} \]

\[ \text{Re}_L > 10^5 \quad Sh_i = 0,036 \text{Re}^{0.8}_L \text{Sc}_i^{1/3} \]

**Koule**

\[ Sh_i = 2,0 + 0,4(\text{Re}^{1/2}_L + 0,06 \text{Re}^{2/3}_L)\text{Sc}_i^{0,4} \]
Packed bed

\[ j_D = \frac{k_c^o M}{G} S c_i^{2/3} \]

\[ S c_i = \frac{\mu}{\rho D_{im}} \quad G = \frac{m}{S_o} \quad \text{Re} = \frac{d_p G}{\mu} \]

\[ j_D = f(\text{Re}) = C \cdot \text{Re}^n \]

\[ j_H = \frac{h}{C_p G} \Pr^{2/3} \]

\[ \Pr = \frac{C_{pm} \mu_m}{\lambda_m} \]

\[ j_H = f(\text{Re}) = C' \text{Re}^{n'} \]

\[ h a (T_s - T_o) = (-\Delta H_r) r_v = (-\Delta H_r) k_{xA} a (x_A^o - x_A^s) \]

\[ \frac{T_s}{T_o} - 1 = (-\Delta H_r) \frac{k_{xA} x_A^o}{h T_o} \left(1 - \frac{x_A^s}{x_A^o}\right) \]
\[
\frac{c_A^s}{c_A^o} = 1 - \frac{r_V}{k_{cA}ac_A^o} \quad \text{ha}(T_s - T_o) = (-\Delta H_r)r_V = (-\Delta H_r)k_{xA}a(x_A^o - x_A^s)
\]
\[
\frac{x_A^s}{x_A^o} = 1 - \frac{r_V}{k_{xA}ax_A^o} \quad \frac{T_s}{T_o} - 1 = (-\Delta H_r)\frac{k_{xA}x_A^o}{hT_o}(1 - \frac{x_A^s}{x_A^o})
\]

Criteria for the absence of transport limitations (packed bed)

\[
\left|\frac{c_A^s - c_A^o}{c_A^o}\right| \geq 0.95 \quad \frac{T_s - T_o}{T_o} \leq 0.02
\]
Experimental tests

\[
\frac{m}{F_A^o} = \text{konst}
\]

\[X_A\]

\[F_A^o\]
\[ J_i^s = -\overline{D}_i \frac{\partial c_i}{\partial x} \]
\[ J_H^s = -\overline{\lambda}_s \frac{\partial T}{\partial x} \]

\[ N_i = k_{gi}(c_i^o - c_i^s) \]
\[ N_H = h(T_o - T_s) \]

\[ \Delta T = \frac{(-\Delta H_r)\overline{D}_i c_i(r_o)}{v_i |\overline{\lambda}_s T(r_o)|} \frac{\Delta c_i}{c_i(r_o)} = \beta_i \frac{\Delta c_i}{c_i(r_o)} \]

\[ \beta_i \text{ – Prater number} \]

\[ c_i^s = c_i(r_o) \quad T_s = T(r_o) \]

\[
\overline{D}_i \left( \frac{d^2 c_i}{dx^2} + \frac{a}{x} \frac{dc_i}{dx} \right) = -v_i r_v(T, c_k) \quad 0 \text{ plate} \\
\overline{\lambda}_s \left( \frac{d^2 T}{dx^2} + \frac{a}{x} \frac{dT}{dx} \right) = (-\Delta H_r) r_v(T, c_k) \quad a = 1 \text{ cylinder} \\
\]
Experimental tests (supposing that external gradients are negligible)

\[ \frac{m}{F_A^o} = konst \]

\[ X_A \]

\[ 1 / d_p \]
1.3 Kinetic Analysis: Single Reaction, Complex Reactions, Estimation Methods

The differential or integral method of kinetic analysis

LHHW kinetics

Linearization $\Rightarrow$ linear regression

Non-linear models $\Rightarrow$ non-linear regression

$m / F_A^o$
Example
Ethanol dehydrogenation (Franckaerts, Froment, 1964)
A → R + S
C_2H_5OH \rightarrow CH_3CHO \text{ (g)} + H_2 \text{ (g)}

r.d.s.
Adsorption of A
Surface reaction
Desorption of R

\[ r_M = \frac{k_A (P_A - P_R P_S / K)}{1 + \frac{K_A}{K} P_R P_S + K_R P_R + K_S P_S + K_w P_w} \]

\[ r_M = \frac{k K_A (P_A - P_R P_S / K)}{(1 + K_A P_A + K_R P_R + K_S P_S + K_w P_w)^2} \]

\[ r_M = \frac{k_R K K_R (P_A / P_S - P_R / K)}{1 + K_A P_A + K K_R P_A / P_S + K_S P_S + K_w P_w} \]

\[ \Phi(\vec{\beta}) = \sum_{i=1}^{M} \left[ X_i - f_i(\vec{\beta}) \right]^2 \]
Air oxidation of o-xylene on V$_2$O$_5$ (Vanhove, Froment 1975)

Example

\[ \text{o-xylene} \xrightarrow{r_1} \text{tolulaldehyde} \]
\[ \text{CO, CO}_2 \]

\[ \text{r}_2 \]

\[ \text{r}_3 \]

\[ \text{phtalic anhydrid} \]
Estimation methods

\[ y = f(x, \beta) \]
\[ e_j(\beta) = y_j - f(x_j, \beta) \quad j = 1, \text{NEXP} \]

Moment matrix of residuals

\[ M(\beta) = \sum_{j=1}^{\text{NEXP}} e_j(\beta)e_j(\beta)^T \]

Objective functions

\[ \Phi(\beta) = \text{Trace}[QM(\beta)] \]
\[ \Phi(\beta) = \text{Trace}[V^{-1}M(\beta)] \]
\[ \Phi(\beta) = \text{det}[M(\beta)] \]

Gradient, Gauss-Newton

Marquardt-Levenberg

Quadratic expansion
2. Transient methods
Reaction sites - single crystal surfaces, ultra high vacuum ⇒ structure sensitive reaction rate (Dahl et al. 1999: rate of dissociative adsorption of nitrogen on Ru (0001) surface was reduced by more than nine orders.

Structure and Morphology – CO oxidation on the Pt(110) surface. Ertl (1994) has shown by photo-emission electron microscopy that surface concentrations of reacting species vary with time and 2D-space. Grunwaldt (2000) found that structure of Cu particles depend on the reduction potential of gas mixture CO+H₂.

Surface composition – surface composition of catalyst may change with gas composition – redox systems (Mars, Krevelen, 1953)