Outline

- Introduction
  - Role of the catalyst
  - Principal reaction mechanisms
  - Nature of active sites
- Acid – base catalysis
- Metal catalysis
- Redox catalysis

Definition of catalysis

Catalysis is a process in which the rate of a reaction is enhanced by a relatively small amount of a different substance (catalyst) that does not undergo any permanent change itself.

- 1835 Berzelius
- 1900 Bodenstein, Ostwald, van't Hoff

After one cycle the catalyst has to reach the same state as before the reaction.

- Opposed to surface reaction or stoichiometric reaction with a coreactant.
- Catalysts reduce the energy, which is necessary to proceed along the reaction pathway.
- Catalysts offer new reaction pathways.
- Catalysts concentrate the reactants at the surface.
Energy pathway of catalyzed reaction

THERMAL REACTION

Potential Energy

ΔH_{ads} Reactants

ΔH_{des.} Reactants adsorbed

ΔH_{react.} Products adsorbed

CATALYTIC REACTION

Elementary steps in Heterogeneous Catalysis

External diffusion

Internal diffusion

Adsorption

Surface reaction

Desorption

Internal transport of products

External transport of products
Types of elementary steps

- Langmuir Hinshelwood mechanism
- Eley - Redeal mechanism
- Mars-van Krevelen mechanism

Acid -base catalysis
Acid and bases - definitions

Brønsted – Lowry acid-base theory

**Acid:** Hydrogen containing species able to donate a proton

**Base:** Species capable of accepting a proton

\[
AH + B \rightleftharpoons A^- + BH^+
\]

Lewis acid-base theory

**Acid:** Species able to accept an electron pair to form a dative or coordinative bond

**Base:** Species possessing a non-bonding electron pair able to form a dative or coordinative bond

\[
A + B \rightleftharpoons A^\delta^- + B^\delta^+
\]

Acid solutions and solid acids

- Aqueous solutions of acids contain only one type of acid: \(H_3O^+\)
- Only the extensive factor of acidity is measured.
- On solid surfaces:
  - Every OH group is potentially a Brønsted acid site
  - Therefore, distribution of site strengths exist.

The term “acidity” may describe

- an **extensive property**, i.e., the density of acid sites on the catalyst surface (mol/g_{cat}) better called **acid site density**.
- an **intensive property**, i.e., the ability to protonate bases of different strengths. This property is better called **acid strength**.
Acidity and basicity of solids

- The intrinsic acid-base strength of a solid depends upon its average electronegativity
  - High average electronegativity – strong acid
  - Low average electronegativity – weak acid
- The average electronegativity according to Sanderson is the geometric mean of the electronegativities of the elements in a compound.
- Many existing concepts fail to predict nature and concentration of acid sites.

\[ S_{\text{int}} = \left( S_p^p \cdot S_q^q \cdot S_R^R \right)^{1/p+q+r} \]

Acid sites generated by defects and substitution

But, when substituting some Si\(^{4+}\) by Al\(^{3+}\), strong acidity develops.

OH groups in silica (SiO\(_2\)) weakly acidic
Acid and base sites in zeolites

Sorption and catalysis are governed by crystalline void space and substitution. Solid acids provide a low concentration of protons.

Acid – base catalysis

- Acid catalyzed alkane activation
- Carbenium ion based catalysis
  - Isomerization
  - Cracking
  - Oligomerization, alkylation
- Alcohol reactions
- Shape selectivity
Overall mechanism of protolytic cracking

Products in protolytic n-butane conversion
Conversion of light alkanes over H-MFI

<table>
<thead>
<tr>
<th>Bond</th>
<th>BE (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>413</td>
</tr>
<tr>
<td>C-C</td>
<td>347</td>
</tr>
</tbody>
</table>

The logarithm of the rate of cracking and dehydrogenation increases linearly with the size of the alkane.

Micropores contribute strongly to alkane sorption

Protons contribute 7 resp. 12 kJ/mol to the alkane bonding.
Reaction pathway and energy profile

反应路径和能量剖面图

\[ r_{TOF} = k_{\text{react.}} \frac{\Theta_{\text{react.}}}{\Theta_{\text{ads.}}} \]

\[ r_{TOF} = k_{\text{react.}} \frac{K_{\text{ads.}} P_{\text{react.}}}{P_{\text{ads.}}} \]

\[ r_{TOF} = Ae \frac{e^{\frac{E_a}{RT}}}{e^{\frac{\Delta G_{\text{ads.}}}{RT}}} \]

\[ r_{TOF} = Ae \frac{e^{\frac{\Delta H_{\text{ads.}}}{RT}}}{e^{\frac{\Delta S_{\text{ads.}}}{R}}} P_{\text{react.}} \]

**Conversion of light alkanes over H-MFI**

- The true energy of activation is identical for all n-alkanes.
- The activity depends upon the concentration of alkanes in the pores, their transition entropy and the concentration of Brønsted acid sites.
Acid strength and acid site concentration

Polanyi relationship

\[ E_A = E_A^0 - \gamma_R \Delta H_R \]

Borges et al., Journal of Molecular Catalysis A: Chemical 229 (2005) 127


Activation of hydrocarbons via generation of carbenium ions

- A double bond in an olefin can be attacked by a proton (Brensted acid site) forming a carbocation (carbenium ion).
- A hydride can be abstracted from a paraffin by a Lewis site (carbenium ion).
- A very strong acid site could protonate a paraffin forming a penta-coordinated carbocation (carbonium ion), which decomposes into hydrogen/alkane and a carbenium ion.
Proton addition to olefins

- Carbenium ions of small olefins exist only as transition states.
- In the ground state they form alkoxy groups.
- Carbenium ions of sterically hindered olefins are stable.

Hydride abstraction and dehydrogenation

- Lewis acid sites abstract hydride, which leads to dehydrogenation and formation of an olefin.
- The olefin is protonated at a Brønsted acid site.
Decomposition of carbonium ions

- Carbonium ions are transition states that decompose readily into alkoxy groups.
- Carbenium ions of sterically hindered olefins are stable.

Relative stabilities of carbenium ions

- Tertiary carbenium ion is more stable than secondary and secondary more stable than primary.

<table>
<thead>
<tr>
<th>Type of ion</th>
<th>Relative value of $E_*$, kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-$</td>
<td>0</td>
</tr>
<tr>
<td>CH$^+$</td>
<td>14</td>
</tr>
<tr>
<td>C(CH$_3$)$_2$</td>
<td>21</td>
</tr>
</tbody>
</table>

B. C. Golez, J. R. Katzor, and G. C. Schult
"Chemistry of Catalytic Processes"(1979) p. 11
Acid-catalyzed reactions of carbenium ions

**Elementary steps**
- Hydride Shift
- Methyl shift (via 3C- ring)
- β-scission
- Addition to carbenium ions
- Hydrogen Transfer

**Double-bond isomerization of 1-butene (hydride shift)**
- Proton addition to the double bond on the Brønsted acid site
- Internal **hydride shift**
- Proton elimination
n-Butene isomerization on acid catalysts

However, the formation of primary carbenium ion results in a high activation energy and much lower rates than for n-pentene isomerization.

n-Pentene isomerization on acid catalysts

regardless of where the ring opens
Carbenium ion cracking

- Secondary carbenium ions form at random.
- Scission of bond $\beta$ to carbon with positive charge yielding an $\alpha$-olefin and a primary carbenium ion
- Primary carbenium ion undergoes rapid hydride shift to form more stable secondary ion

Ethene hardly formed in catalytic cracking

Methane and ethane are less observed in catalytic cracking in contrast to thermal and protolytic cracking.

$\beta$ - scission

$\beta$ - scission not possible

Energetically not favored
Activation via hydride abstraction

\[
\begin{align*}
\text{O-Si-O-Si} & \quad \text{O-Si-O} \\
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{H}_2 & \quad \text{H}_2 \\
\text{C} & \quad \text{C} \\
\text{H}_3 & \quad \text{H}_3 \\
\end{align*}
\]

Alkylation – the reverse reaction to cracking

\[
C_nH_{2n} + H^+ \rightarrow [C_nH_{2n+1}]^+ \\
\text{Alkene Carbenium ion Ester} \\
\]

Initiation

\[
H_3C\text{CH}_{n}\text{CH}_4 + H_2 \rightarrow H_3C\text{CH}_{n}\text{CH}_3 \\
\text{Hydride transfer} \\
\text{iso-Butane iso-Alkane}
\]

[Alkylation – the reverse reaction to cracking](#)
Design criteria for alkylation catalysts

Sufficient space for the hydride transfer transition state

Appropriate strength of the C-O bond

High concentration of acid sites

Elimination of alcohols on acid-base catalysts

Dehydration

Dehydrogenation
Types of shape selectivity induced by zeolites

Reactant exclusion

Dewaxing

Product diffusion control

Para-directed aromatic reactions

Restricted transition state

Prevention of transalkylation

Isomerization of xylenes

- Reaction is proportional to OH coverage, if all H⁺ are equally active.
- Product selectivity determined by transition state and diffusion limitations.