Catalytic cracking, Cracking reactions, Zeolite catalysts

Catalytic Cracking Reactions:

\[
\begin{align*}
\text{Carbonium ion} & \quad \xrightarrow{\beta\text{-scission}} \quad \text{Olefin} \\
+ R^+ & \\
\end{align*}
\]

\(\Delta H\) vary depending upon the compound:

- Cracking: (+ve) endothermic
- H-Transfer: (-ve) Exothermic
- Isomerization mildly: Exothermic
- Cyclization: (-ve) Exothermic
- Cyclization: Dealkalization: (+ve)

Catalytic cracking, Main Catalysts: Acidic catalysts\[^{[1,2,6-18]}\]

![Diagram of reaction pathways](http://nptel.ac.in/courses/103102022/thermal%20and%20catalytic%20cracking/Catalytic%20cracking%20cracking%20reactions%20zeolite%20catalysts.html)

**Fig: 4.7 The typical sketch and relationship between the Acid strength of different catalyst versus different reaction carried out for different hydrocarbon products.**

Addition of Lewis Acid:

- \(\text{RCH}_2 + \text{BF}_3 / \text{AlCl}_3 / \text{FeCl}_3 \rightarrow \text{RCHF}_2 + \text{BF}_2^-\)
- Life time of a Carbonium ion may vary from a fraction of second to minutes.
- Tertiary Carbonium ion is stablest one followed by secondary and primary Carbonium ion.
- When protonation takes place, a Carbonium Ion may result.

Paraffin Reactivity:

http://nptel.ac.in/courses/103102022/thermal%20and%20catalytic%20cracking/Catalytic%20cracking%20cracking%20reactions%20zeolite%20catalysts.html
Rate of reaction increases with carbon number but rate of coke formation also increases with (carbon number) molecular weight characterized by high production of C\textsubscript{3} and C\textsubscript{4} in the cracked gas.

**Olefin Reactivity:**

These cracks at a much faster rate compared to paraffins and subject to rapid isomerization.

**Naphthene Reactivity:**

They cracks at a faster rate compared to corresponding paraffins.

**Aromatics:**

Alkyl Aromatics

\[
\begin{align*}
\text{Stable ring} \\
\text{CH}_2 & \quad \text{CH}_2 & \quad \text{CH}_2
\end{align*}
\]

**Stability of the ring:**

So ring does not crack because of alkyl group. But removal of alkyl group is easy and it is again by $\beta$-scission.

\[
\begin{align*}
\text{C} & > \text{C} - \text{C}+ \text{C} \\
\text{Tertiary} & > \text{Secondary} & > \text{Primary}
\end{align*}
\]

**Cracking reactions:**\textsuperscript{[1,2,9-20]}

Alkyl Naphthene $\rightarrow$ Naphthene + Olefin

Alkyl Aromatic $\rightarrow$ Aromatic + Olefin

N-Octane cracking, $C_8H_{18}$ (where $R=CH_3CH_2CH_2CH_2CH_2CH_2CH_2$----)

**Step1:** mild thermal cracking initiation reaction.

\[
nC_8H_{18}\rightarrow CH_4 + RCH=CH_2
\]

**Step2:** Proton shift

\[
\begin{align*}
\text{RCH=CH}_2 + \text{H}_2\text{O} + \text{Al-O-Si} & \rightarrow \text{RCH+CH}_3 + \text{H}_2\text{O} + \text{Al-O-Si} \\
\text{Carbonium}
\end{align*}
\]

**Step3:**

\[
\begin{align*}
\text{R}-\text{CH}^+\text{CH}_3 & \xrightarrow{\beta\text{-scission}} \text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
\text{olefin} & \text{carbonium ion}
\end{align*}
\]

**Step4:** Rearrangement towards more stable structure

\[
\begin{align*}
\text{stability}\rightarrow \text{tertiary} > \text{secondary} > \text{primary}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 & \leftrightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2\text{CH}_3 \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 & \leftrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \leftrightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2\text{CH}_3 \\
\text{CH}_3 & \leftrightarrow \text{CH}_2\text{CH}=\text{CH}_3
\end{align*}
\]
**Step 5:** Hydrogen ion transfer

\[
\text{CH}_2 \rightarrow \text{CH} - \left( \text{CH}_2 \right)_2 + \text{C}_8 \text{H}_{18} \quad \rightarrow \quad \text{i-C}_6 \text{H}_{10} + \text{CH}_3 \rightarrow \text{C} - \text{CH}_2 - \text{R}
\]

**Cracking Catalyst**

**Acidic catalyst: which can supply proton.**

- Acid treated natural alumino silicates.
- Amorphous synthetic silica-alumina catalyst.
- Crystalline (aluminosilicates) synthetic. Silica alumina catalyst zeolite or molecular sieve.
- Zeolites have more active sites and adsorption capacity which helps in faster cracking rate.

**Advantages of zeolite catalyst:** \(^{[1,2,8-20]}\)

1. Zeolite has tremendous advantages over amorphous silica-alumina.
2. Higher activity: factor of 100 higher than amorphous silica-alumina catalyst.
3. Higher gasoline yield at a given conversion however octane number of gasoline obtained from zeolite cracking is lower by 2-3 numbers compared to amorphous catalyst.
4. Production of gasoline containing a large number of paraffin and aromatic hydrocarbons.

**Tab: 4.2**

<table>
<thead>
<tr>
<th></th>
<th>Paraffin</th>
<th>Aromatics</th>
<th>Naphthenes</th>
<th>Olefins</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>38</td>
<td>10</td>
<td>0.45</td>
<td>10</td>
</tr>
<tr>
<td>Zeolite</td>
<td>45</td>
<td>20</td>
<td>0.15</td>
<td>20</td>
</tr>
</tbody>
</table>

Olefins are lower & paraffins and aromatics are higher. This is because of superior Transfer facility of zeolites.

- O + N → K_{H+} P + A
- O → P + A
- Cyclo-olefins → N + A

Gasoline yield is higher with zeolite. This is because of:

- \( C_{16} \rightarrow C_{16}^+ \)
- \( C_{16}^+ \xrightarrow{\beta\text{-scission}} C_{16}^+ + C_3 \)

5. Lower coke yield.
6. Increased iso- butane production. (this is again because of H- Transfer)
7. Increased iso- butane production. (this is again because of H- Transfer)
8. Lower dry gas yield. (\( C_1-C_4 \) HC’s) [more gasoline, less coke and less gas yield are its main advantages.]
Characteristics

- Residence time ~ 1 - 4 sec.
- Zeolite - Y : generally used as a cracking catalyst.
- Faujasite: naturally occurring crystalline alumino-silicates.
- Zeolite -Y : synthetic form of Faujasite.
- Composition: $0.9 \pm 0.2 \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot w\text{SiO}_2 \cdot x\text{H}_2\text{O}$ (sodium form of zeolite.)
  \[ 3 < w < 6 , x < 9 \]
  but Na is poison to cracking reaction. So it must be in ion form. So converted to acidic form.
- Cation exchange with a medium containing rare earth cation (cesium, lanthanum etc.)

Catalytic Cracking processes

- Fixed bed, Houdry
- Moving bed - Air lift - Thermofer catalytic cracking
- Fluidised bed:
  - FCC, UOP, Texaco
  - Kellog (Orthoflow)
  - Fexi cracking