Study of the ethanol-to-butadiene reaction using ethanol from renewable sources

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Historical review I.

- 1839: discovery of vulcanization
- 1910: Germany and Russia, 1st investigations
- 1915: Ostromislensky, Two step process, Al₂O₃ or clay mineral catalyst, from acetaldehyde + ethanol mixture
- 1918-1938: Ukraine, Russia, Kazakh dandelion (rubber root)
- 1928: Lebedev, One step process: ZnO-Al₂O₃ catalyst, from pure ethanol
1950: butadiene from the ethylene process, 99.9%

2011: Academic research for the ethanol-to-butadiene reaction, 0.1 % bioethanol

2015: The butadiene demand is 11 million tons in the World.

Historical review II.

- Nitrile and Polychloroprene: 9%
- Polybutadiene: 27%
- Adiponitrile: 6%
- Styrene Butadiene Rubber: 32%
- Arcylonitrile Butadiene Styrene: 18%
- Others: 8%
Reaction mechanism of ethanol to butadiene transformation

- **Ethanol** (\(\text{CH}_3\text{CH}_2\text{OH}\)) can be transformed into **acetaldehyde** (\(\text{CH}_3\text{CHO}\)) using strong acid, or into **ethylene** (\(\text{C}_2\text{H}_4\)) and **diethyl ether** (\(\text{C}_4\text{H}_10\text{O}\)) under base/acid conditions.

- **Acetaldehyde** can react with **hydrogen** (\(\text{H}_2\)) to form **3-hydroxy-butanal** (\(\text{CH}_3\text{C(OH)}\text{CH}_2\text{CH}_2\text{CH}_3\)).

- **Crotal alcohol** (\(\text{CH}_3\text{C(OH)}\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}\)) can be converted to **crotonaldehyde** (\(\text{CH}_3\text{CH(OH)}\text{CHC(=\text{O})CH}_3\)) under base/acid conditions.

- **Crotonaldehyde** can be dehydrated to form **butanal** (\(\text{CH}_3\text{CH(OH)}\text{CHC(=\text{O})}_3\)).

- **Butanal** can be converted to **isobutene** (\(\text{CH}_3\text{C(=\text{C})}_2\)), **1-butene** (\(\text{CH}_3\text{C(=\text{C})CH}_3\)), and **2-butene** (\(\text{CH}_3\text{C(=\text{C})}_2\)) under acid conditions.

- **1,3-butadiene** (\(\text{CH}_3\text{C(=\text{C})C(=\text{C})}_2\)) can also be obtained under acid conditions, and can be hydrated to form **butanol** (\(\text{CH}_3\text{CH(OH)}\text{CH}_2\text{CH}_2\text{OH}\)).
Catalytic test reactions

- Fixed-bed, continuous-flow reactor at atmospheric pressure
- On-line GC, two FID (PLOT-Fused Silica Al₂O₃/KCl – hydrocarbons; HP-PLOT-U - oxygenates) and TCD detector
- The GC was calibrated for reactant and all products separately
- Selectivities were calculated on carbon basis (number of carbon atoms in selected product divided by the summarized number of carbon atoms in all product molecules)
Tested catalysts in the ethanol-butadiene reaction

I. Stage: talc like catalysts


II. Stage: high-SSA SiO₂-MgO catalysts group

Blanka Szabó, Gyula Novodárszki, Zoltán May, József Valyon, Jenő Hancsók, Róbert Barthos: *Conversion of ethanol to butadiene over mesoporous In₂O₃ promoted MgO-SiO₂ catalysts*, Molecular Catalysis, 491 (2020) 110984

III. Stage: high-SSA MgO-SiO₂ catalysts group

<table>
<thead>
<tr>
<th>Wet-kneaded family</th>
<th>Silica-coated family</th>
<th>Internal hydrolyzed family</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-SSA MgO-SiO₂</td>
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III. Stage: high SSA MgO-SiO₂ catalysts group

1st step: Resorcinol–formaldehyde polymerisation

\[
\text{Resorcinol} + 2 \text{Formaldehyde} \rightarrow \text{Substituted resorcinol}
\]

1 day: 50 °C
3 day: 90 °C
Solvent exchange

Product of condensation

2nd step: Hard templating method for mesoporous MgO synthesis

\[
\begin{align*}
\text{Mesoporous carbon (a_s=729 m}^2\text{/g)} & \rightarrow 3 \text{ days: Mg(NO}_3\text{)}_2 \\
*\text{Internal hydrolyzed family} & \rightarrow \text{Filtrationon} \\
& \rightarrow \text{Drying, RT} \\
& \rightarrow \text{Calcination} \\
\rightarrow \text{High surface area MgO}
\end{align*}
\]

\[a_s = 40 \text{ m}^2/\text{g} \quad (a_s = 5 \text{ m}^2/\text{g})\]
Ethanol conversion over silica-coated family

Low-SSA MgO-SiO₂

- Butenes
- Butadiene
- Acetaldehyde
- DiethylEther
- Butanol
- Conversion
- Ethylene

High-SSA MgO-SiO₂

Temperature, °C

1 g catalyst, 0.5 g ethanol/(g cat * h), 30 ml/perc (4.4 ml/min ethanol + 25.6 ml/min He)
Ethanol conversion over wet-kneaded family

**Low-SSA MgO-SiO$_2$**

- Butenes
- Butadiene
- Acetaldehyde
- DiethylEther
- Butanol
- Conversion
- Ethylene

**High-SSA MgO-SiO$_2$**

Conversion, selectivity, %

Temperature, °C

1 g catalyst, 0.5 g ethanol/(g$_{\text{cat}}$ *h), 30 ml/perc (4.4 ml/min ethanol + 25.6 ml/min He)
Ethanol conversion over internal hydrolyzed family

**Low-SSA MgO-SiO$_2$**

**High-SSA MgO-SiO$_2$**

- Conversion, selectivity, %

1 g catalyst, 0.5 g ethanol/($g_{cat} \times h$), 30 ml/perc (4.4 ml/min ethanol + 25.6 ml/min He)
The role of acidic and basic sites in ethanol-butadiene reaction

High-SSA MgO

Conversion, selectivity, %

Temperature, °C

SiO₂

1 g catalyst, 0.5 g ethanol/(g cat * h), 30 ml/perc (4.4 ml/min ethanol + 25.6 ml/min He)
Conversion of the 3 intermediates over MgO-SiO$_2$ catalysts

1. 3-hydroxy-butanal
   - Unstable $\rightarrow$ hard to detect

   ![3-hydroxy-butanal](image)

2. Crotonaldehyde
   - Polymerized products
   - Molecular H$_2$

   ![crotonaldehyde](image)

3. Crotyl alcohol

   ![Conversion, selectivity %](image)

1 g catalyst, 0.125 g crotyl alcohol/(g$_{cat}$ h), 30 ml/min (6.4 ml/min crotyl alcohol + 23.6 ml/min He)
• The optimal catalyst in the ethanol-butadiene reaction:

  ✓ High surface area, porous structure,
  ✓ active in dehydrogenation,
  ✓ moderate dehydration activity.

• At comparable ethanol conversions the BD yields over the high SSA MgO-SiO$_2$ catalysts, made using carbon template, were of significantly higher than that over the low SSA MgO-SiO$_2$ catalysts.

• The favorable activity of the high SSA MgO-SiO$_2$ catalysts was explained by the more intimate interaction of the MgO and SiO$_2$ catalyst components: basic MgO sites facilitate ethanol coupling, whereas acidic mixed oxide phase provides adequate dehydration activity.

• Based on our experiments, we described the probable ethanol-butadiene pathway.

SUMMARY
Thank you for your attention!

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www.skhu.eu

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