Glycerol conversion to 1,2-propanediol in mild conditions

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COK, KULeuven, Belgium
Poitiers, March 13, 2008
• **Introduction**
  – Use of 1,2-propanediol
  – Results with better literature catalysts
  – Bifunctional mechanism

• **New bifunctional catalyst**
  – Reaction conditions & Results
  – Overall conversion results
  – Stability 1,2-propanediol
  – Hydrogenation of hydroxy acetone
  – Effect of gaseous products: CO₂ and H₂
  – Origin of acidity in bifunctional pathway

• **Reaction pathways with new bifunctional catalyst**
  – Extended scheme for the bifunctional mechanism
  – Suggested reforming mechanism

• **Conclusions**
Content

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Introduction:
Use of 1,2-propanediol

1,2-Propanediol = bulk intermediate

- direct use as moistering or softening agent, as anti-freeze, solvent or conservative
- monomer for polyesters, polyurethanes and alkyd resins
- preparation of cyclic ethers and 1,3-dioxanes used in organic synthesis as solvents or intermediates
Introduction: Results with better literature heterogeneous catalysts

- **One step processes**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (°C)</th>
<th>p H₂ (bar)</th>
<th>Results</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCr</td>
<td>270</td>
<td>200</td>
<td>Y = 85 %</td>
<td>Adkins et al., Journal of the American Chemical Society, 54: 1138-1145, (1932)</td>
</tr>
<tr>
<td>Cu/ZnO</td>
<td>180</td>
<td>80</td>
<td>S = 100 %, X = 19 %</td>
<td>Gallezot et al., Green Chemistry, 6: 359-361, (2004)</td>
</tr>
<tr>
<td>Raney Cu</td>
<td>240</td>
<td>30</td>
<td>Y = 57 %</td>
<td>Montassier et al., Heterogeneous Catalysis and Fine Chemicals: 165-170, (1988)</td>
</tr>
<tr>
<td>CuZnO/Al₂O₃</td>
<td>270</td>
<td>100</td>
<td>Y = 84 %</td>
<td>Casale et al., US Patent 5 214 219, (1993)</td>
</tr>
<tr>
<td>Ru/C</td>
<td>210</td>
<td>60</td>
<td>Y = 75 %</td>
<td>Montassier et al., Journal of Molecular Catalysis, 70 (1), 99-110, (1991)</td>
</tr>
<tr>
<td>RuS/C</td>
<td>240</td>
<td>130</td>
<td>Y = 75 %</td>
<td>Casale et al., US patent 5 276 181, (1994)</td>
</tr>
</tbody>
</table>

Y = yield, S = selectivity, X = conversion

- **Multiple step processes**

  - **Three step proces** [¹]
  
  - γ-Al₂O₃ at 300 °C + acid resin + Ni/Al₂O₃/SiO₂ at 140 °C and 40 bar H₂
  
  → Y = 60 %

  - **Two step proces** [²]

  - CuCr at 220 °C + CuCr at 300 °C and 14 bar H₂
  
  → Y = 62 %

Introduction: Bifunctional mechanism

Glycerol conversion scheme via dual function catalyst *

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  – Extended scheme for the bifunctional mechanism
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• **Conclusions**
New bifunctional catalyst: Reaction conditions & Results

Mild conditions, no additives, heterogeneous catalyst, inert atmosphere

- 100 ml batch reactor
- 230 °C, 15 h
- 40 ml 20 wt% glycerol in H₂O
- 4 wt% catalyst

**In situ** H₂ production

\[
\begin{align*}
8 \text{glycerol} + 3 \text{H}_2\text{O} \xrightarrow{\text{new catalyst}} 7 \text{1,2-propanediol} + 3 \text{CO}_2
\end{align*}
\]

\[
\begin{align*}
S_{\text{1,2-propanediol}} &= 64 \% \\
X_{\text{glycerol}} &= 85 \% \\
Y_{\text{1,2-propanediol}} &= 55 \% \\
\text{MB liquid C} &= 89 \%
\end{align*}
\]

S = selectivity, X = conversion, Y = yield, MB = carbon mass balance of liquid products
New bifunctional catalyst: Overall conversion results

<table>
<thead>
<tr>
<th>Product</th>
<th>Selectivity (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>0.9</td>
<td>2.4</td>
</tr>
<tr>
<td>ethanol</td>
<td>9.5</td>
<td>12.2</td>
</tr>
<tr>
<td>acetone + propanal</td>
<td>1.0</td>
<td>0.9</td>
</tr>
<tr>
<td>iso-propanol</td>
<td>1.4</td>
<td>1.2</td>
</tr>
<tr>
<td>n-propanol</td>
<td>7.5</td>
<td>6.4</td>
</tr>
<tr>
<td>ethylene glycol</td>
<td>2.1</td>
<td>2.6</td>
</tr>
<tr>
<td>hydroxy-acetone</td>
<td>3.0</td>
<td>2.6</td>
</tr>
<tr>
<td>1,2-propanediol</td>
<td>64.0</td>
<td>54.6</td>
</tr>
</tbody>
</table>

Conversion (%) = 85.4
Carbon mass balance of liquid products (%) = 89.4

100 ml batch reactor, 230 °C, 15 h, 40 ml 20 wt% glycerol in H₂O, 4 wt% catalyst, Yield based on mol/L

X = conversion, S = selectivity, mb = mass balance of liquid products, EtOH = ethanol, n-propOL = n-propanol, OH-AcON = hydroxy acetone
New bifunctional catalyst: Stability of 1,2-propanediol

![Graph showing stability over time]

- Via bifunctional pathway to n-propanol

\[
\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{OH} & \quad \text{OH} \\
\text{OH} & \quad \text{OH}
\end{align*}
\]

- Via dehydrogenation and cracking to ethanol and CO

\[
\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{OH} & \quad \text{OH}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Product</th>
<th>Carbon Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol</td>
<td>40,5</td>
</tr>
<tr>
<td>acetone + propanal</td>
<td>1,3</td>
</tr>
<tr>
<td>iso-propanol</td>
<td>5,7</td>
</tr>
<tr>
<td>n-propanol</td>
<td>18,6</td>
</tr>
<tr>
<td>hydroxy-acetone</td>
<td>4,7</td>
</tr>
<tr>
<td>conversion (%)</td>
<td>24,7</td>
</tr>
<tr>
<td>carbon mass balance of liquid products (%)</td>
<td>70,7</td>
</tr>
</tbody>
</table>

100 ml batch reactor, 230 °C, 24 h, 40 ml 20 wt% 1,2-propanediol in H₂O, 4 wt% catalyst, S = carbon selectivity
New bifunctional catalyst: Hydrogenation of hydroxy acetone

- Equimolar amount of $\text{H}_2$ and hydroxy acetone
  - Fast hydrogenation
  - Low selectivity for CO, $\text{CO}_2$ and $\text{CH}_4$
  - Enhanced selectivity for propane

<table>
<thead>
<tr>
<th>Product</th>
<th>Carbon Selectivity (%)</th>
<th>Carbon mass balance of liquid products (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>no $\text{H}_2$</td>
<td>42 bar $\text{H}_2$</td>
</tr>
<tr>
<td>methanol</td>
<td>0,0</td>
<td>0,0</td>
</tr>
<tr>
<td>ethanol</td>
<td>5,0</td>
<td>1,4</td>
</tr>
<tr>
<td>acetone + propanal</td>
<td>2,6</td>
<td>0,4</td>
</tr>
<tr>
<td>iso-propanol</td>
<td>0,3</td>
<td>1,0</td>
</tr>
<tr>
<td>n-propanol</td>
<td>2,0</td>
<td>1,8</td>
</tr>
<tr>
<td>ethylene glycol</td>
<td>0,0</td>
<td>0,0</td>
</tr>
<tr>
<td>1,2-propanediol</td>
<td>65,6</td>
<td>91,3</td>
</tr>
<tr>
<td>conversion (%)</td>
<td>77,9</td>
<td>98,7</td>
</tr>
</tbody>
</table>

100 ml batch reactor, 230 °C, 1 h, 40 ml 20 wt% hydroxy acetone in $\text{H}_2\text{O}$, 4 wt% catalyst
### New bifunctional catalyst: Effect of gaseous products

<table>
<thead>
<tr>
<th>Product</th>
<th>Carbon Selectivity (%)</th>
<th>Carbon Mass Balance of Liquid Products (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>no H₂ 24 h</td>
<td>5 bar CO₂ 24 h</td>
</tr>
<tr>
<td>methanol</td>
<td>0,9</td>
<td>0,8</td>
</tr>
<tr>
<td>ethanol</td>
<td>10,6</td>
<td>12,2</td>
</tr>
<tr>
<td>acetone + propanal</td>
<td>0,9</td>
<td>1,0</td>
</tr>
<tr>
<td>iso-propanol</td>
<td>1,9</td>
<td>1,9</td>
</tr>
<tr>
<td>n-propanol</td>
<td>8,9</td>
<td>8,2</td>
</tr>
<tr>
<td>ethylene glycol</td>
<td>1,0</td>
<td>0,8</td>
</tr>
<tr>
<td>hydroxy-acetone</td>
<td>2,0</td>
<td>2,4</td>
</tr>
<tr>
<td>1,2-propanediol</td>
<td>45,8</td>
<td>43,7</td>
</tr>
<tr>
<td>conversion (%)</td>
<td>100,0</td>
<td>99,7</td>
</tr>
<tr>
<td>carbon mass balance of liquid products (%)</td>
<td>72,0</td>
<td>71,0</td>
</tr>
</tbody>
</table>

100 ml batch reactor, 230 °C, 24 or 72 h, 40 ml 20 wt% glycerol in H₂O, 4 wt% catalyst
### New bifunctional catalyst: Effect of gaseous products

<table>
<thead>
<tr>
<th>Product</th>
<th>Carbon Selectivity (%)</th>
<th>Conversion (%)</th>
<th>Carbon mass balance of liquid products (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>no H₂ 24 h</td>
<td>5 bar CO₂ 24 h</td>
<td>20 bar CO₂ 24 h</td>
</tr>
<tr>
<td>methanol</td>
<td>0,9 0,9</td>
<td>0,8 0,8</td>
<td>0,7 0,7</td>
</tr>
<tr>
<td>ethanol</td>
<td>10,6 10,6</td>
<td>12,2 12,2</td>
<td>12,3 9,6</td>
</tr>
<tr>
<td>acetone + propanal</td>
<td>0,9 0,9</td>
<td>1,0 1,0</td>
<td>2,2 9,6</td>
</tr>
<tr>
<td>iso-propanol</td>
<td>1,9 1,9</td>
<td>1,9 1,9</td>
<td>0,0 1,3</td>
</tr>
<tr>
<td>n-propanol</td>
<td>8,9 8,2</td>
<td>8,2 10,5</td>
<td>7,1 8,0</td>
</tr>
<tr>
<td>ethylene glycol</td>
<td>1,0 0,8</td>
<td>0,8 0,4</td>
<td>2,0 2,0</td>
</tr>
<tr>
<td>hydroxy-acetone</td>
<td>2,0 2,4</td>
<td>2,4 2,4</td>
<td>2,0 1,0</td>
</tr>
<tr>
<td>1,2-propanediol</td>
<td>45,8 43,7</td>
<td>34,4 50,7</td>
<td></td>
</tr>
<tr>
<td>conversion (%)</td>
<td>100,0 99,7</td>
<td>99,4 99,2</td>
<td>96,3 97,4</td>
</tr>
<tr>
<td>carbon mass balance of liquid products (%)</td>
<td>72,0 71,0</td>
<td>62,9 74,0</td>
<td>97,4</td>
</tr>
</tbody>
</table>

- Equimolar amount of H₂ and glycerol
  - Decreased activity
  - 72 h for full conversion

Inhibition reforming

- Increased S for 1,2-propanediol 77 %
- Increased MB for liquid C 97 %

100 ml batch reactor, 230 °C, 72 h, 40 ml 20 wt% glycerol in H₂O, 4 wt% catalyst, S = selectivity, MB = carbon mass balance of liquid products
New bifunctional catalyst: Effect of gaseous products

<table>
<thead>
<tr>
<th>Product</th>
<th>no H₂</th>
<th>5 bar CO₂</th>
<th>20 bar CO₂</th>
<th>5 bar H₂</th>
<th>42 bar H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>0,9</td>
<td>0,8</td>
<td>0,7</td>
<td>0,9</td>
<td>1,2</td>
</tr>
<tr>
<td>ethanol</td>
<td>10,6</td>
<td>12,2</td>
<td>12,3</td>
<td>9,6</td>
<td>6,7</td>
</tr>
<tr>
<td>acetone + propanal</td>
<td>0,9</td>
<td>1,0</td>
<td>2,2</td>
<td>0,5</td>
<td>0,2</td>
</tr>
<tr>
<td>iso-propanol</td>
<td>1,9</td>
<td>1,9</td>
<td>0,0</td>
<td>1,3</td>
<td>1,4</td>
</tr>
<tr>
<td>n-propanol</td>
<td>8,9</td>
<td>8,2</td>
<td>10,5</td>
<td>7,1</td>
<td>8,0</td>
</tr>
<tr>
<td>ethylene glycol</td>
<td>1,0</td>
<td>0,8</td>
<td>0,4</td>
<td>2,0</td>
<td>2,0</td>
</tr>
<tr>
<td>hydroxy-acetone</td>
<td>2,0</td>
<td>2,4</td>
<td>2,4</td>
<td>2,0</td>
<td>1,0</td>
</tr>
<tr>
<td>1,2-propanediol</td>
<td>45,8</td>
<td>43,7</td>
<td>34,4</td>
<td>50,7</td>
<td>76,8</td>
</tr>
<tr>
<td>conversion (%)</td>
<td>100,0</td>
<td>99,7</td>
<td>99,2</td>
<td>96,3</td>
<td>100,0</td>
</tr>
<tr>
<td>carbon mass balance of liquid products (%)</td>
<td>72,0</td>
<td>71,0</td>
<td>62,9</td>
<td>74,0</td>
<td>97,4</td>
</tr>
</tbody>
</table>

- 5 bar CO₂: No effect
- 20 bar CO₂: Increased activity
  - Decreased 1,2-propanediol selectivity
  - Decreased carbon mass balance liquid products

Consecutive reactions:

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3
\]

100 ml batch reactor, 230 °C, 24 h, 40 ml 20 wt% glycerol in H₂O, 4 wt% catalyst
Origin of acidity in bifunctional mechanism

- **20 bar CO\(_2\) as acid catalyst, no catalyst**
  - Hydroxy acetone is formed in presence of 20 bar CO\(_2\)
  - Versus thermostability of glycerol \((X = 0 \%)\) without catalyst

- **Only the metal as catalyst, no carrier**
  - Low conversion
  - Higher S\(_{\text{side products}}\)
  - High MB\(_{\text{liquids}}\)

**CO\(_2\) as acid catalyst**

100 ml batch reactor, 230 °C, 7 h, 40 ml 20 wt% glycerol in H\(_2\)O, 20 bars CO\(_2\), \(X = \text{conversion}, S = \text{selectivity}\)

100 ml batch reactor, 230 °C, 24 h, 40 ml 20 wt% glycerol in H\(_2\)O, 0.26 mmol metal (…) or patented catalyst (―), \(X = \text{conversion}, S = \text{selectivity}, Y = \text{yield}, \text{mb} = \text{carbon mass balance of liquid products}, \text{PDO} = 1,2\text{-propanediol}, \text{n-propOL} = \text{n-propanol}, \text{OH-AcON} = \text{hydroxy acetone}\)
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• **Conclusions**
Bifunctional mechanism:
Extended scheme

1. Glycerol (hydrolysis) → Hydroxy acetone (dehydration) → 2-Hydroxy propanal
2. 1,2-Propanediol (dehydration) → Propanal (hydrogenation) → Acetone
3. Propane (hydrogenation) → Ethane
4. N-Propanol (dehydration) → Iso-propanol
5. Ethanol (dehydration) + CO → Ethene

Chemical reactions:
- Acid hydrolysis
- Dehydration
- Isomerisation
- Hydrogenation
- C-CO cracking
- Hydrogenation
Suggested reforming mechanism: Based on experimental data

Equilibrated via water gas shift reaction:
\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]
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Conclusions

- **Characteristics of the process**
  - *in situ* $\text{H}_2$ production: reforming + water gas shift reaction
  - $\rightarrow$ Inhibition reforming by biogenic $\text{H}_2$ pressure

\[
8 \text{C}_3\text{H}_8\text{O}_3 + 3 \text{H}_2\text{O} \rightarrow 7 \text{C}_3\text{H}_8\text{O}_2 + 3 \text{CO}_2
\]

- $X_{\text{glycerol}} = 85\%$
- $S_{1,2\text{-propanediol}} = 64\%$
- $MB_{\text{liquid C}} = 89\%$

\[
\begin{align*}
3 \text{CO} + 3 \text{H}_2\text{O} & \rightarrow 3 \text{CO}_2 + 3 \text{H}_2 \\
7 \text{C}_3\text{H}_8\text{O}_3 + 7 \text{H}_2 & \rightarrow 7 \text{C}_3\text{H}_8\text{O}_2
\end{align*}
\]

- **Specific carrier**
  - Good stability of 1,2-propanediol $\rightarrow$ Affinity glycerol > affinity 1,2-propanediol
  - Fine tuned acidity $\rightarrow$ Minor consecutive reactions
  - Quenching carbon acid acidity
  - Isomerisation $\rightarrow$ Provides more substrates for reforming
Thank you for your attention!