NOVEL WATER GAS SHIFT CATALYSTS

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Commercial Water Gas Shift (WGS)

\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H = -9.7 \text{ kcal/mol}
\]

HTS Catalysts:
Fe-Cr$_2$O$_3$

LTS Catalysts:
Cu-ZnO-Al$_2$O$_3$

Graph showing the reaction temperature and exit CO content.
Candidate Catalysts

<table>
<thead>
<tr>
<th>Material</th>
<th>Price* ($ per lb.)</th>
<th>Relative Price</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>1,116</td>
<td>159</td>
</tr>
<tr>
<td>Rh</td>
<td>14,050</td>
<td>2,007</td>
</tr>
<tr>
<td>Pd</td>
<td>5,515</td>
<td>788</td>
</tr>
<tr>
<td>Ag</td>
<td>66</td>
<td>9.4</td>
</tr>
<tr>
<td>Ir</td>
<td>5,468</td>
<td>781</td>
</tr>
<tr>
<td>Pt</td>
<td>6,827</td>
<td>975</td>
</tr>
<tr>
<td>Au</td>
<td>4,350</td>
<td>621</td>
</tr>
<tr>
<td>MoO₃</td>
<td>3.86</td>
<td>0.6</td>
</tr>
<tr>
<td>Cu/Zn/Al Catalyst</td>
<td>7.00</td>
<td>1.0</td>
</tr>
</tbody>
</table>

* Prices in February, 2002.

WGS Micro-Reactor

38%
17%
9%
6%

30%
Effect of Pretreatment

CO Consumption Rate (µmol/g•s) vs. Reduction Temperature (°C)

- **340 °C**
- **H₂ Reduction**
- **CH₄/H₂ Reduction**
- **In-situ**

Correlations?

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Rate (µmol/gr/s)</th>
<th>Rate/Peak Area (1/s)</th>
<th>CO Uptake (ml/gr)</th>
<th>TOF (1/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Passivated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂/Ar-500 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄/H₂/Ar-500 °C</td>
<td>34</td>
<td>2.2</td>
<td>6.0</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Michigan Engineering
Mo$_2$C Catalysts

\[ \frac{H_2}{CO} = 3.33 \]

Dry gas = 12% CO in H$_2$

GHSV $\approx 300,000$ hr$^{-1}$

240 °C

CO Consumption Rate (µmol/g•sec)

\[
\begin{align*}
1000/T (K^{-1}) & \\
11 \text{ kcal/mol} \quad & \\
10 \text{ kcal/mol} \quad & \\
240 ^\circ C \quad & \\
17 \text{ kcal/mol} \quad & \\
21 \text{ kcal/mol} \quad & \\
22 \text{ kcal/mol} \quad & \\
\end{align*}
\]

H$_2$O:CO = 3.33

H$_2$ gas = 12% CO in H$_2$

GHSV = 300,000 hr$^{-1}$

Catalyst Options

- Multimetallic Carbide
- Carbide Supported Catalyst
η-Carbides

Mo-M η-Carbides

Intensity (Arbitrary Units)

CO Consumption Rate (nmol/m²•sec)
Mo₂C-Supported Catalysts

Carbide Supported Catalyst

Oxycarbide or Oxide Supported Catalyst

Mo₂C-Supported Catalysts: Modified Method

H₂O:CO=3.33
Dry gas=12% CO in H₂
GHSV=300,000 hr⁻¹
Ultra-Low Temperature Shift

H₂O:CO=3.33

Dry gas=12% CO in H₂

GHSV ≈ 300,000 hr⁻¹

Conclusions/Challenges

• Bulk carbides are highly active for WGS
• Reaction of CO and oxygen or hydroxyl appears to be RDS
• Carbide-supported catalysts hold promise for use in LTS and perhaps ULTS
• Reducible oxide supported Au catalysts can be highly active for WGS but they deactivate
• Introduction of textural promoters can help reduce deactivation
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