Ni/Al₂O₃ xerogel catalysts for biogas cleaning

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Introduction
The thermo-chemical conversion method that is biomass gasification is generating emphatic interest for the production of biogas (CO + H₂). However, this process presents two major drawbacks: (i) the tar formation and (ii) the presence of sulphur compounds in gaseous effluents. In order to counter these effects, two solutions are commonly used: physical cleaning (washing, cyclone, filter…) and chemical destruction. The chemical way, which consists in catalytic removal of tars by a catalyst composed of a metallic element dispersed on a refractory oxide matrix, appears to be a very interesting solution. In this way, Ni/Al₂O₃ xerogel catalysts were synthesized by the sol-gel process by using aluminium precursors, 3-(2-aminoethy lamino)propyltrimethoxysilane (EDAS) to complex Ni²⁺ ions, and stearic acid in water and ethanol used as solvents.

Synthesis of Ni/Al₂O₃ xerogel catalysts

EDAS + Ethanol + Ni(NO₃)₃

Surfactant

Al(NO₃)₃ + H₂O

NH₃

Sol

Gel

Sample

Stirring: 85°C, 24h
Aging: 85°C, 24h
Drying: 85°C, 24h
Washing: H₂O/ethanol
Calcination: 500°C, 8h, air

Suggested mechanism:
The complexation of Ni²⁺ ions by EDAS allows to disperse homogeneously, after calcination and reduction steps, Ni nanoparticles into the alumina network.

EDAS

H₂O

Stearic acid

Note: Ni loading = 2%wt.

Conclusions and perspectives
- EDAS and surfactants increase the specific surface area of Ni/Al₂O₃ xerogel catalysts and the dispersion of Ni particles.
- Further experiments using other surfactants (P123®, TMAH) will be investigated.
- Catalytical tars reforming will be done with the two best catalyst synthesized.

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Nitrogen adsorption isotherms on samples of Ni/Al₂O₃ catalysts

<table>
<thead>
<tr>
<th>Composition</th>
<th>Standard</th>
<th>EDAS</th>
<th>EDAS+ S1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(NO₃)₃</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>H₂O</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Ethanol</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Ni(NO₃)₃</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>EDAS</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

Crystallinity
XRD measurements were realized on samples after H₂ reduction (750°C, 1h, 5°C/min)
- γ-Al₂O₃ in all samples
- Ni₃(0) presence with EDAS
- NiAl₂O₄ presence without EDAS
- Higher alumina crystallites size without EDAS

Sintering resistance
TEM observations after Temperature Programmed Reduction (25-1000°C, 2°C/min, H₂)
- Stearic acid affords a very effective influence against nanoparticles sintering

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