In situ characterization of Pd2Ga catalysts for methanol synthesis by Electron Microscopy and X-ray Diffraction

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**In situ** characterization of Pd\textsubscript{2}Ga intermetallic compounds for methanol synthesis

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**Introduction**

Methanol (\text{CH}_3\text{OH}) is a chemical produced in 40 million tons per year\textsuperscript{1} and amongst many applications, it can be used as a fuel or energy carrier. The synthesis is generally carried out from \text{H}_2 and \text{CO} at pressures up to 100 bar using a Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalyst. New materials able to synthesize methanol from \text{H}_2 and \text{CO} at low pressure, such as Ni-Ga and Pd-Ga intermetallic compounds, have been predicted by DFT calculations and tested in a reactor\textsuperscript{2,3}. In this study Pd\textsubscript{2}Ga nanoparticles are investigated by complementary techniques such as XRD, TEM and ETEM, providing information on catalytic properties, size, morphology and crystal phase as summarized in the table.

**Catalytic path and test of Pd\textsubscript{2}Ga/SiO\textsubscript{2} (1 bar)**

A high surface area (HSA) silica is impregnated with a solution of Pd and Ga nitrates in nitric acid. The catalyst is dried and calcined in air then reduced at 550°C in H\textsubscript{2}. Methanol synthesis from H\textsubscript{2} and CO\textsubscript{2} is carried out in the range 160-250°C and the products are measured by gas chromatography. The yield from Pd\textsubscript{2}Ga/SiO\textsubscript{2} catalyst is found to be higher than the one given by the commercial Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalyst.

**Investigation by in-situ XRD (1 bar)**

XRD patterns using synchrotron radiation are acquired at the 711 beam line of the Max II Laboratory (Lund, Sweden) during each step of the catalytic path to study the crystal phase and the alloy formation. During drying and calcination a PdO phase is observed (GaO\textsubscript{2} amorphous) and the active phase for the methanol synthesis is formed upon reduction.

**Sample preparation for TEM**

1. **Model catalyst**

\[ \text{Pd(NO}_3\text{)}\textsubscript{2} + \text{Ga(NO}_3\text{)}\textsubscript{2} + \text{HNO}_3 + \text{H}_2 \text{O} \]

<table>
<thead>
<tr>
<th>Reactor</th>
<th>XRD</th>
<th>TEM</th>
<th>ETEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Calculated</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Reduction</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Activity</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Pressure</td>
<td>1 - 10 bar</td>
<td>10\textsuperscript{+} - 1 bar</td>
<td>HV</td>
</tr>
<tr>
<td>Flow</td>
<td>5 Nl/min</td>
<td>100 Nl/min</td>
<td>-</td>
</tr>
</tbody>
</table>

**Sample preparation for ETEM**

1. **Real system (3-D)**

\[ \text{Pd(NO}_3\text{)}\textsubscript{2} + \text{Ga(NO}_3\text{)}\textsubscript{2} + \text{H}_2 \text{O} \]

**TEM of identical location (HV)**

The catalytic path is carried out at 1 bar in a furnace (Anton Paar XRK 900) connected to a gas system and containing a ceramic holder for 6 TEM grids. After each step of the path (see arrows in the figure) the grids are transferred to the TEM (HV), where images of identical locations are acquired in order to follow the evolution of the catalysts through the path.

**Conclusion**

- Pd\textsubscript{2}Ga intermetallic compounds have been investigated by complementary techniques (Reactor measurement, XRD, TEM and ETEM).
- The test of the catalyst in the reactor shows that the methanol yield from Pd\textsubscript{2}Ga/SiO\textsubscript{2} is higher to the one given by Cu/ZnO/Al\textsubscript{2}O\textsubscript{3}.
- XRD shows that the Pd\textsubscript{2}Ga phase is formed upon reduction.
- Morphological changes and nanoparticle formation are observed by TEM imaging of identical locations and by ETEM experiments.
- Further investigation is required in order to further optimize the Pd\textsubscript{2}Ga alloys for the methanol synthesis reaction from CO\textsubscript{2}.

**References**

2. F. Studt et al. in preparation.

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