Hydrogen production by Oxidative Steam Reforming of Methanol over Cu/CeO2-ZrO2 catalysts.

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Introduction
The PEM (proton-exchange membrane) fuel cell generally requires H2 as fuel; there are various strategies for on board storage of H2 in the vehicle: gas compressed, liquid, H2 storage materials such as metal hydrides and carbon nanotubes. However, all these options require a dedicated filling station infrastructure and raise issues concerning safety and cost. Olah [1] puts forth a convincing case for why the chemical storage of hydrogen in the form of methanol offers distinct advantages over alternate means. The main advantage of liquid fuels is their high energy density and ease of handling, and the fact that they can be used for the on-demand production of hydrogen for fuel cells, with applications in mobile and stationary grid-independent power systems. Methanol is readily available and can be catalytically converted into a H2-rich gas at moderated temperature (200-300°C). Methanol has high H/C ratio and no C-C bonds, hence minimizing the risk for coke formation. Moreover, as methanol can be produced from renewable sources, its reforming does not contribute to a net addition of CO2 to the atmosphere.

Materials and Methods
CeO2-ZrO2 was prepared using the sol-gel method with basic catalyst and calcined at 600 °C for 5h. The combustion method was used for the synthesis of CeO2. Cerium nitrate (Ce(NO3)3•6H2O) was calcined at 700°C for 5h. Copper (3 wt.%) was incorporated by classical impregnation technique to the calcined supports. Characterization by several techniques, such as adsorption-desorption of N2, X-ray Diffraction, Scanning Electron Microscopy in order to determine surface area (BET), crystalline structures and morphology of catalytic materials was performed. The catalytic activity of the catalysts was evaluated in Oxidative Steam reforming of methanol (OSRM) reaction, from 250°C to 360°C, the partial pressure of CH3OH, H2O y O2 was 75, 12.75 y 22.4 Torr respectively, and molar ratio CH3OH:H2O:O2=0.1357:0.5:0.31.

Results and Discussion
Table 1 summarizes the BET specific surface area of the supports and the catalysts after different thermal treatments. CeO2 support exhibited a higher value of specific surface area (ca. 60 m²/g) than the mixed oxides and ZrO2. When the ceria content goes up to 50 and 50 wt.% on the mixed oxide the surface area values are close to 16 m²/g. Cu impregnation on the supports causes a decrease in the surface area, this behavior could be attributed to the blockade of the pores of the support by the Cu, as well as to the thermal treatments, but the tendency in the surface area was maintained. Mixtures of T and M phases of ZrO2 were observed for the high Zr/Ce ratio catalyst. However, for Zr/Ce=0.5 ratio the Zr0.84Ce0.16O2 and Zr0.4Ce0.6O2 were observed. Low Zr/Ce ratio showed a cubic phase of CeO2. Diffraction peak of Cu was observed only on Cu/ZrO2 and Cu/CZ50. This is due to the low surface area of the samples that promoted the low dispersion of copper.

Table 1. Surface area of Cu/CeO2-ZrO2 catalysts.

<table>
<thead>
<tr>
<th>Support</th>
<th>S (m²/g)</th>
<th>Catalyst</th>
<th>S (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO2</td>
<td>60</td>
<td>Cu/CeO2</td>
<td>56</td>
</tr>
<tr>
<td>ZC90</td>
<td>57</td>
<td>Cu/ZC90</td>
<td>52</td>
</tr>
<tr>
<td>ZC50</td>
<td>16</td>
<td>Cu/ZC50</td>
<td>14</td>
</tr>
<tr>
<td>ZC10</td>
<td>29</td>
<td>Cu/ZC10</td>
<td>27</td>
</tr>
<tr>
<td>ZrO2</td>
<td>7</td>
<td>Cu/ZrO2</td>
<td>5</td>
</tr>
</tbody>
</table>

Significance
Ceria-rich catalysts were the most active in the methanol conversion, the most selective towards H2 and had the allowed selectivity towards CO.

Figure 1. Effect of temperature on the catalytic performance in the oxidative steam reforming of methanol over Cu/ZrO2-CeO2 catalysts.

The ceria loaded to circinia promotes the reducibility of the copper oxide at lower temperatures, which indicates the presence of highly dispersed Cu. The ceria-rich catalysts also showed high activity in the transformation of the methanol and high selectivity towards H2. The presence of highly dispersed Cu is therefore likely to be an important factor in determining the efficiency of the CeO2 rich catalysts in the OSRM reaction, that there are not present in the circinia-rich catalysts.

References