

## Hydrogen production by Oxidative Steam Reforming of Methanol over Cu/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts.

Ma. Magdalena Aguila, Raúl Pérez-Hernández\*.

Instituto Nacional de Investigaciones Nucleares Carr. México-Toluca S/N La Marquesa,  
Ocoyoacac, Edo. de México C. P. 52750, México.  
[pehr@nuclear.inin.mx](mailto:pehr@nuclear.inin.mx)

### Introduction

The PEM (proton-exchange membrane) fuel cell generally requires H<sub>2</sub> as fuel; there are various strategies for on board storage of H<sub>2</sub> in the vehicle: gas compressed, liquid, H<sub>2</sub> 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 H<sub>2</sub>-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 CO<sub>2</sub> to the atmosphere.

### Materials and Methods

CeO<sub>2</sub>-ZrO<sub>2</sub> 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 CeO<sub>2</sub>. Cerium nitrate (Ce(NO<sub>3</sub>)<sub>3</sub>•6H<sub>2</sub>O) 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 N<sub>2</sub>, 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 CH<sub>3</sub>OH, H<sub>2</sub>O y O<sub>2</sub> was 75, 12.75 y 22.4 Torr respectively, and molar ratio CH<sub>3</sub>OH:H<sub>2</sub>O:O<sub>2</sub>=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. CeO<sub>2</sub> support exhibited a higher value of specific surface area (ca. 60 m<sup>2</sup>/g) than the mixed oxides and ZrO<sub>2</sub>. When the ceria content goes up to 50 and 50 wt.% on the mixed oxide the surface area values are close to 16 m<sup>2</sup>/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 ZrO<sub>2</sub> were observed for the high Zr/Ce ratio catalyst. However, for Zr/Ce=0.5 ratio the Zr<sub>0.84</sub>Ce<sub>0.16</sub>O<sub>2</sub> and Zr<sub>0.4</sub>Ce<sub>0.6</sub>O<sub>2</sub> were observed. Low Zr/Ce ratio showed a cubic phase of CeO<sub>2</sub>. Diffraction peak

of Cu was observed only on Cu/ZrO<sub>2</sub> 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/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts.

Support	S (m <sup>2</sup> /g)	Catalyst	S (m <sup>2</sup> /g)
CeO <sub>2</sub>	60	Cu/CeO <sub>2</sub>	56
ZC90	57	Cu/ZC90	52
ZC50	16	Cu/ZC50	14
ZC10	29	Cu/ZC	27
ZrO <sub>2</sub>	7	Cu/ZrO <sub>2</sub>	5

### Significance

Ceria-rich catalysts were the most active in the methanol conversion, the most selective towards H<sub>2</sub> and had the allowed selectivity towards CO.

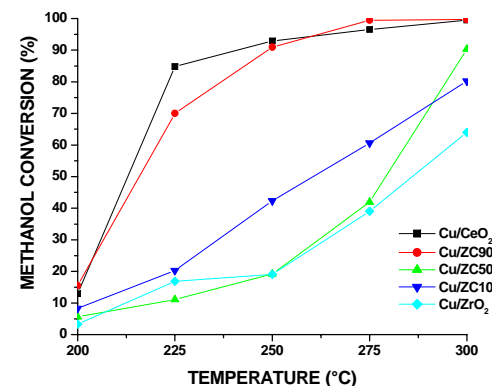


Figure 1. Effect of temperature on the catalytic performance in the oxidative steam reforming of methanol over Cu/ZrO<sub>2</sub>-CeO<sub>2</sub> catalysts.

The ceria loaded to cerionia 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 H<sub>2</sub>. The presence of highly dispersed Cu is therefore likely to be an important factor in determining the efficiency of the CeO<sub>2</sub> rich catalysts in the OSRM reaction, that there are not present in the cerionia-rich catalysts.

### References

1. Olah G.A. Catal. Lett. 26, 93 (2001).