# One-step synthesized CuO-CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system as catalyst for OSRM process

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A structurally organized mesoporous CuO/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst (8.3 % CuO, 17.0 % CeO<sub>2</sub>) was prepared by a new single-step template sol-gel synthesis, characterized by TGA, XRD, N<sub>2</sub> adsorption and TPR, and tested for oxidative steam reforming of methanol (OSRM) at T = 200–400°C, H<sub>2</sub>O/CH<sub>3</sub>OH/O<sub>2</sub> molar ratios = 1.1/1/0.12, CH<sub>3</sub>OH concentration = 17.8%, GHSV =  $6 \times 10^4 h^{-1}$ . The catalyst contained Cu<sup>2+</sup> species strongly interacting with CeO<sub>2</sub>, besides a CuO phase highly dispersed in alumina. After reduction in H<sub>2</sub> the catalyst, compared with more conventional CuO/CeO<sub>2</sub> systems, showed good activity and H<sub>2</sub> yield in the OSRM process.

## **1. Introduction**

The application of hydrogen PEM fuel cells technology to car traction needs solving the problem of  $H_2$  supply. To overcome problems related to  $H_2$  distribution and storage, now it is preferred to produce  $H_2$  on board starting from a liquid fuel, such as methanol (Lattner and Harold, 2007). Steam reforming (SRM, reaction (1)) and partial oxidation (POM, reaction (2)) are the two catalytic processes most often used to obtain hydrogen from methanol (Palo et al., 2007, Navarro et al., 2007). The combination of the endothermic (1) and the exothermic (2) reactions gives rise to oxidative steam reforming (OSRM), that is potentially an autothermal process and can give some advantages such as a smaller reactor volume and a simpler reactor design (Lattner and Harold, 2005).

$CH_3OH_{(g)} + H_2O_{(g)} = CO_2 + 3 H_2$	$\Delta H^{\circ} = 49.5 \text{ kJ mol}^{-1}$	(1)
$CH_3OH_{(g)} + \frac{1}{2}O_2 = CO_2 + 2H_2$	$\Delta H^{\circ} = -192.3 \text{ kJ mol}^{-1}$	(2)

Unfortunately, some parasitic reactions also occurs in this processes, the most harmful by-product being CO, that also at low concentration (>20 ppm) is a poison for the platinum anodes of PEMFCs and must be eliminated by suitable purification devices. Therefore there is great interest in developing highly selective catalysts. The catalysts employed for SRM and OSRM are generally based on metallic Cu or Pd. Palladium catalysts have higher thermal stability (Liu et al., 2005, Iwasa et al., 2004, Cubeiro and Fierro, 1998) but lower selectivity, because they also activate methanol decomposition, producing noticeable amounts of CO (Iwasa et al., 2004, Lenarda et al., 2007, Lenarda et al., 2006, Karim et al., 2006, Liu et al., 2006). For this reason, Cu catalysts still

maintain a leading position. Metallic Cu is mostly dispersed in metal oxides such as ZnO (Fukahori et al., 2006, Raimondi et al., 2003, Reitz et al., 2001) and ZnO/Al<sub>2</sub>O<sub>3</sub> (Horny et al., 2004, Lee et al., 2004, Catillon et al., 2004, Murcia-Mascarós et al., 2001, Velu et al., 2000). Moreover in recent years great attention is paid to Cu/CeO<sub>2</sub> systems (Patel and Pant, 2006, Men et al., 2004, Liu et al., 2003, Liu et al., 2002). These systems, taking advantage of the high oxygen mobility and oxygen storage capacity of ceria, are suitable for several oxidation processes such as CO preferential oxidation (PROX) (Moretti et al., 2007a) and water gas shift (WGS) ([Li et al., 2000). The presence of  $CeO_2$  as support or promoter in Cu based catalysts had several favourable effects for the SRM and OSRM processes. The addition of ceria to Cu/Zn/Al oxide catalysts led to a significant inhibition of CO production and improved the long term stability, probably due to the oxygen storage capacity of  $CeO_2$  that favoured coke gasification under the reducing conditions of reforming (Patel and Pant, 2006). Moreover the presence of ceria hindered Cu sintering in Cu/Al<sub>2</sub>O<sub>3</sub> catalysts, thus increasing the thermal stability (Zhang and Shi, 2003). These effects were attributed to the high dispersion of metallic Cu and to a strong metal/support interaction (Shiau et al., 2006, Men et al., 2004, Liu et al., 2003) that can give rise also to formation of solid solutions Ce<sub>1-x</sub>Cu<sub>x</sub>O<sub>2-x</sub> (Liu et al., 2002). Cu/CeO<sub>2</sub> catalysts were prepared by different methods, such as impregnation, co-precipitation, sol-gel synthesis, hydrothermal synthesis, decomposition or combustion of suitable precursor compounds, and the performances of the catalysts depended strongly on the preparation methodology (Liu et al., 2007, Shiau et al., 2006, Avgouropoulos et al., 2005, Pintar et al., 2005, Liu et al., 2002). In previous works Cu/Ce catalysts supported on an ordered mesoporous alumina were prepared by a new single-step template sol-gel synthesis (Moretti et al., 2007a). These systems, characterized by a structurally organized mesoporosity, with high surface area and good thermal stability, exhibited interesting catalytic activity in the PROX reaction (Moretti et al., 2007a). In this paper a CuO/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst prepared by this new approach is studied for the SRM and OSRM processes.

# 2. Experimental

## 2.1 Catalyst preparation

All chemicals used in this paper were purchased from Aldrich and used as received, without further purification. Cu and Ce stearates were prepared according to the procedure described previously (Moretti et al., 2007b). The following molar ratio was used: 1 Al(sec-BuO)\_3 : 0.053 ( $C_{17}H_{35}COO$ )\_3Ce : 0.072 ( $C_{17}H_{35}COO$ )\_2Cu : 24 n-C<sub>3</sub>H<sub>7</sub>OH : 3 H<sub>2</sub>O. Ce and Cu stearates were dissolved in n-propanol/water by sonication, then aluminum tri-sec-butoxide was added. The resulting suspension was aged for 50 h in a Teflon-lined autoclave at 100°C and autogenous pressure. The product was washed with ethanol, dried at 50°C overnight and treated at 410°C in nitrogen flow for 6 h and at 550°C in air flow for 5 h. The catalyst composition was 17.0 wt% CeO<sub>2</sub> and 8.3 wt% CuO (Al<sub>2</sub>O<sub>3</sub> balance). The catalyst was identified as EMCe<sub>17</sub>Cu<sub>8</sub>.

#### 2.2 Catalyst characterization

Thermogravimetric analysis was carried out at rate of 10°Cmin<sup>-1</sup> in air flow with a Netzsch STA 409 instrument.

 $N_2$  adsorption-desorption measurements were performed using an ASAP 2010 Micromeritics apparatus. Specific surface areas (S.A.) was measured by BET method. The pore size distribution was calculated following the BJH method.

X-ray diffraction patterns were obtained with a Bragg-Brentano powder diffractometer using CuK $\alpha$  radiation. The average dimension of the crystallites was determined by Scherrer's equation.

Copper dispersion was measured by N<sub>2</sub>O passivation method (Moretti et al., 2008) using a laboratory apparatus. Cu surface areas and Cu particle sizes were calculated assuming a surface Cu concentration of  $1.47 \cdot 10^{19}$  atoms m<sup>-2</sup>.

TPR measurements were carried out in a laboratory apparatus using a 5%  $H_2$ /Ar mixture and a heating rate of 10°C min<sup>-1</sup> on samples treated in air flow at 500°C.

#### 2.3 Catalytic activity measurements

Catalytic activity measurements were carried out in a laboratory flow apparatus with a fixed bed reactor operating at atmospheric pressure. Liquid feed (H<sub>2</sub>O/CH<sub>3</sub>OH) was regulated by a metering pump and gaseous feeds (O<sub>2</sub>, He) by electronic mass flow controllers. The products H<sub>2</sub>, CO (detection limit=0.01%), CO<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, CH<sub>3</sub>OH, H<sub>2</sub>O were analyzed by gas chromatography. The OSRM tests were carried out at T=200–400°C, H<sub>2</sub>O/CH<sub>3</sub>OH/O<sub>2</sub> molar ratios=1.1/1/0.12, CH<sub>3</sub>OH concentration=17.8%, GHSV=6×10<sup>4</sup>h<sup>-1</sup>. SRM tests were carried out under similar conditions, but excluding O<sub>2</sub> feed. Each test lasted 1.5–2h, and during this time the products were sampled and analyzed two or three times to verify that constant conversion was attained. In preliminary tests it was ascertained that diffusive resistances were negligible.

# 3. Results and discussion

Thermogravimetric analysis (Fig.1) was performed in order to determine the calcination temperature necessary to completely remove the organic phase of surfactant.



Fig.1. TG/DTG profiles of the as-synthesized sample EMCe<sub>17</sub>Cu<sub>8</sub>.

The weight loss up to ca.  $250^{\circ}$ C can be attributed to the removal of residual organic solvent and physisorbed and bulk water, while that starting at  $250^{\circ}$ C and ending at  $550^{\circ}$ C can be assigned to the elimination of the structure-directing agent (in the form of stearates). Based on these data, the calcination temperature of  $550^{\circ}$ C was selected. Adsorption-desorption isotherms are shown Fig. 2. The sample possesses a Type IV isotherm with a hysteresis loop typical of mesoporous materials, with a BET surface area of  $360 \text{ m}^2\text{g}^{-1}$ . The BJH pore size distribution (in the inset) is narrow and centred at around 3.9 nm and the total pore volume Vs, calculated at p/p°=0.98, is 0.48 cm<sup>3</sup>g<sup>-1</sup>.



Fig. 2.  $N_2$  adsorption-desorption isotherm at 77K (• adsorption branch;  $\circ$  desorption branch) and BJH pore size distribution (in the inset).

The diffractogram of EMCe<sub>17</sub>Cu<sub>8</sub> (Fig. 3) exhibits broad reflections due to  $\gamma$ -alumina, with a poorly microcrystalline structure, and peaks attributable to the presence of CeO<sub>2</sub> with a fluorite lattice structure. The average dimension of the ceria crystallites, calculated from the main peak at  $2\theta = 28.6^{\circ}$ , according to the Scherrer's equation,



Fig. 3. X-ray diffraction pattern of the catalyst  $EMCe_{17}Cu_8$ , after thermal treatment at 550°C.

resulted about 3.0 nm. CuO appeared in the X-ray pattern as tenorite phase only with a broad and very weak peak, at  $2\theta = 35.54^{\circ}$ . This is an indication of particles with dimension below the XRD detection limit, suggesting a good copper dispersion on the ceria and alumina surface. Copper dispersion measured by N<sub>2</sub>O passivation was 69%, confirming the effectiveness of the preparation method in obtaining highly dispersed Cu(0) phases.

The TPR profile of the EMCe<sub>17</sub>Cu<sub>8</sub> sample previously oxidized in air at 500°C, is shown in Fig. 4 together with those of the reference materials CuO and CeO<sub>2</sub>. The total amount of H<sub>2</sub> consumed by the sample EMCe<sub>17</sub>Cu<sub>8</sub> is 1.10 mmol per g of catalyst, comparable to the Cu content (1.05 mmol g<sup>-1</sup>), thus indicating complete reduction of  $Cu^{2+}$  to  $Cu^{0}$ . On account of the very limited reduction of the phase  $CeO_2$ , it is supposed that the contribution of this component to the TPR profile is negligible. The TPR profile of the oxidized catalyst is very different from that of CuO: in fact, two peaks are observed at 202 and 301°C, followed by a long tail, while CuO shows one peak at 400°C. This suggests that most of Cu is not present in the catalyst as the pure oxide. Taking into account the results of previous TPR measurements on a similar material (Moretti et al., 2008), the appearance of two low temperature peaks is likely related to the presence of : i)  $Cu^{2+}$  species interacting with  $CeO_2$ , that are the most easily reducible and ii) a CuO phase highly dispersed in alumina. The TPR signal around 400°C can be attributed to reduction of larger CuO particles. The tailing at high temperatures is probably related to less reducible Cu<sup>+</sup> species, that are strongly stabilized in the  $CeO_2$  phase, as indicated by previous studies (Liu et al., 2002, Martinez-Arias et al., 1998).



Fig. 4. TPR spectra of the catalyst  $EMCe_{17}Cu_8$  and the reference materials CuO and CeO<sub>2</sub>. All the spectra are normalized to the amounts of oxides contained in 1g of  $EMCe_{17}Cu_8$ .

The results of methanol steam reforming tests under oxidizing (OSRM) and nonoxidizing (SRM) conditions are reported in Fig. 5. Methanol conversion increases with the temperature according to typical S-shaped curves, reaching about 100%, with  $H_2$ yield up to 2.5 mol per mol CH<sub>3</sub>OH at 350-400°C under OSRM conditions. It can be noted that the conversion values and  $H_2$  yields are noticeably lower under SRM conditions. The large increase of activity under oxidizing conditions can be explained by the role of CeO<sub>2</sub> in activating O<sub>2</sub> (Patel and Pant, 2006). Conversion to CO<sub>2</sub> (Fig. 6) parallels CH<sub>3</sub>OH conversion, while CO production is very low up to 300°C (0.15%) and increases at higher temperature, up to 6-7% at 400°C. Other by-products are not observed in appreciable amounts under any conditions.

It could be interesting to compare the present results with those obtained on  $Cu/CeO_2/(Al_2O_3)$  catalysts prepared by different routes, to understand the effect of the synthesis procedure. Few works can be selected to this purpose, because the literature dealing with methanol (oxidative) reforming on this type of catalysts is not very extended. Moreover the comparison is not always easy due to different catalyst composition and operating conditions.



Fig. 5. CH<sub>3</sub>OH conversion and H<sub>2</sub> yield as a function of temperature in OSRM and SRM tests. Reaction conditions: see text. Full symbols: OSRM; empty symbols: SRM.



Fig. 6. CH<sub>3</sub>OH conversion to CO<sub>2</sub> and CO as a function of temperature in OSRM and SRM tests. Reaction conditions: see text. Full symbols: OSRM; empty symbols: SRM.

Patel and Pant (2007) studied Cu/Ce/Al systems prepared by co-precipitation for OSRM: the most active of these systems (Cu/Ce/Al =30/20/50, SA = 102 m<sup>2</sup> g<sup>-1</sup>, Cu dispersion =14.8%) tested at contact time of 9 kg<sub>cat</sub> s mol<sub>CH30H</sub><sup>-1</sup> (GHSV of the present tests corresponds to a contact time of 8 kg<sub>cat</sub> s mol<sub>CH30H</sub><sup>-1</sup>) gave methanol conversion of 35% at 200°C and 80% at 300°C. These values, considering the higher Cu content of the catalyst, appears comparable with those reported in the present work. Moreover the CO concentration, 0.15% at 300°C, is also comparable with the above data. A Cu/CeO<sub>2</sub> catalysts prepared by impregnation (10 wt% Cu) tested under OSRM conditions at GHSV = 30000 h<sup>-1</sup>, gave CH<sub>3</sub>OH conversion of 10-80% between 210-260°C (Pérez-Hernández et al., 2007).

## 4. Conclusions

A new one-pot method for the preparation of Cu-CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts has allowed to obtain a structurally organized material with a narrow pore distribution, a very high surface area and dispersion of the Cu metal phase. The catalyst has shown high activity and good hydrogen selectivity in the oxidative steam reforming of methanol. The good activity values shown by this type of catalysts also in the preferential CO oxidation (CO-PROX) allows to forecast its practical applications in OSRM processes of high selectivity.

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