

## CO Preferential Oxidation activity of a Ce-Zr-Cu oxide system with layered morphology

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Production of H<sub>2</sub> for polymer fuel cells (PEMFCs) is usually accomplished by a multi-step process that includes catalytic reforming of liquid fuels (such as MeOH or EtOH) and subsequently preferential oxidation of CO (CO-PROX), since the gas stream reformatted in most cases presents a relatively high CO concentration, that even at ppm levels is a poison for the Pt anodes of PEMFCs. Among different types of catalysts for the purification of CO in H<sub>2</sub>-rich stream, those based on Cu-Ce oxides have shown promising properties in terms of activity, selectivity and resistance to CO<sub>2</sub> and H<sub>2</sub>O.

In this work, a series of Ce-Zr-Cu oxide catalysts prepared by a slow co-precipitation method and heat-treated at different temperatures were examined with the aim to determine the effect of the thermal treatment on the active species.

The materials were characterized by DRIFT-IR spectroscopy, X-ray Powder Diffraction (XRPD), N<sub>2</sub>-physisorption at -196°C, Electron Microscopies (SEM and TEM), Temperature-Programmed Reduction (H<sub>2</sub>-TPR) and X-ray Photoelectron Spectroscopy (XPS).

The as-prepared material showed a desert rose-like structure, made up of long (> 10 μm) and thin (about 2 nm) petals with quite homogeneous size and morphology and maintained its morphology composed by micro-sheets even after prolonged thermal treatment at 650°C.

H<sub>2</sub>-TPR investigation suggested the presence of different copper species and a shift toward lower reduction temperature in the samples while increasing the calcination temperature. This significant difference among the reduction temperatures of the more reactive Cu species could be ascribed to the mobility of the Cu ions, present as interstitial/substitutional defects in the ceria lattice, that at high temperature, can migrate outside the ceria oxide network becoming highly scattered Cu ions

easily reducible for the intimate contact with CeO<sub>2</sub>. Furthermore, from XPS data, the ratio Cu<sub>rid</sub>/Cu<sup>2+</sup> increased while increasing the calcination temperature.

The catalytic activity of the samples was evaluated in the CO-PROX reaction test in the 40-190°C temperature range, using a synthetic reformat gas (1.25% CO, 1.25% O<sub>2</sub>, 50.0% H<sub>2</sub>, 0-10% H<sub>2</sub>O, 0-15% CO<sub>2</sub>, He balance).

The different thermal treatment showed a significant influence on the catalytic performance of the Ce-Zr-Cu oxide system. Even if the samples have the same chemical composition (with 5.6 wt.% Cu), they exhibited a different catalytic behavior and the sample calcined at the highest temperature displayed the highest activity for the presence of the highest amount of easily reducible Cu species.