

NANOSTRUCTURED CUO-CEO₂ CATALYSTS FOR PREFERENTIAL OXIDATION OF CO IN H₂-RICH STREAMS

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Hydrocarbons are considered as efficient sources of hydrogen for its use as a fuel of proton exchange membrane fuel cells (PEMFC). However, the gas produced after reforming of hydrocarbon fuels followed by water gas-shift processes employed for this purpose still presents in most cases (typical composition: 45-75 vol.% H₂, 15-25 vol.% CO₂, 0.5-2 vol.% CO, a few vol.% H₂O and traces of unconverted fuel [1]) a relatively high CO concentration that disallows efficient handling of the fuel by the Pt alloy anode usually employed in the PEMFC. Preferential oxidation of CO (CO-PROX) has been recognized as one of the most straightforward and cost-effective methods to achieve acceptable CO concentrations (below ca. 100 ppm) [1,2]. Among different catalysts tested for the process, formulations based on closely interacting CuO-CeO₂ have shown promising properties in terms of activity, selectivity and resistance to CO₂ and H₂O, while being most interesting from an economical point of view [1,3]. The particular ability of this class of catalysts has been essentially attributed to the exceptional redox properties achieved by interfacial sites upon strong interaction of both catalyst components [1-5]. The present work aims to get, in the context of the mentioned process, deeper insights into such properties by analysing a series of CuO-CeO₂ catalysts differing in the copper loading and/or in the preparation method employed. Nanostructured configurations of the oxide catalysts are chosen on the basis of their higher potentialities when redox catalytic processes like those examined here are involved [6,7].

Nanostructured catalysts involving combinations between copper oxide and ceria were prepared by two different methods: i) incipient wetness impregnation of a nanosized CeO₂ support (prepared by a microemulsion method and displaying primary nanoparticles of a rounded shape with ca 7 nm average size after calcination at 773 K [4]) with copper nitrate solutions (copper loads of 0.5-5.0 wt.%); and ii) copper and cerium coprecipitation (Ce_{0.8-0.95}Cu_{0.2-0.05}O_{2-ξ} atomic composition ranges) within reverse microemulsions [5]. In all cases, the catalysts were dried and calcined under air at 773 K (and further *in-situ* treated under pure O₂ or O₂ diluted in Ar at 773 K) prior to its characterization or catalytic testing. S_{BET} specific areas around 100 m²g⁻¹ were observed for the catalysts prepared by impregnation while values between 100 and 150 m²g⁻¹, increasing with the amount of copper, were observed for the coprecipitated systems. Catalytic activity results performed under an atmospheric pressure flow of 1 % CO, 1.25 % O₂ and 50 % H₂ (Ar balance) are shown in Figure 1. Additional catalytic tests have been focussed to explore the deactivation of the catalytically most interesting system (1% CuO/CeO₂) in the presence of 15 % CO₂ and/or 10 % H₂O. The results show that although a certain deactivation of CO oxidation properties is produced, the catalyst is still able to maintain 100 % CO conversion (at a selectivity level over ca. 70 %) in a short temperature range (ca. 400-430 K) in the presence of both CO₂ and H₂O. In turn, an aging test for this system (during ca. 30 h) has shown a slow deactivation of the catalyst involving a decrease in CO oxidation selectivity, although 100 % CO conversion could still be maintained. The catalytic activity results are explained on the basis of characterization

results done by XRD, Raman, XAFS, XPS and EPR while *operando*-DRIFTS has been employed to analyse changes taking place in the catalysts during the course of the catalytic reactions. On the basis of these results, the main catalytic properties of these systems for CO-PROX are correlated with the CuO-CeO₂ interfacial redox characteristics present in each case [4,5]. These are shown to depend strongly on the type of CuO entities present (from CuO oligonuclear clusters to well formed CuO nanoparticles as well as isolated copper cations) and the degree of copper incorporation into the fluorite structure (through mainly isomorphic substitution and very favoured for the coprecipitated catalysts). These aspects basically determine the degree of copper interaction with the support and the respective stabilization of determinate redox states of copper. This latter is shown to be of relevancy for the differential activation of CO/H₂, which allows rationalizing the selectivity behaviour of the catalysts. In turn, interfacial properties are shown to be strongly modified by deactivating agents like CO₂ and H₂O.

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Figures:

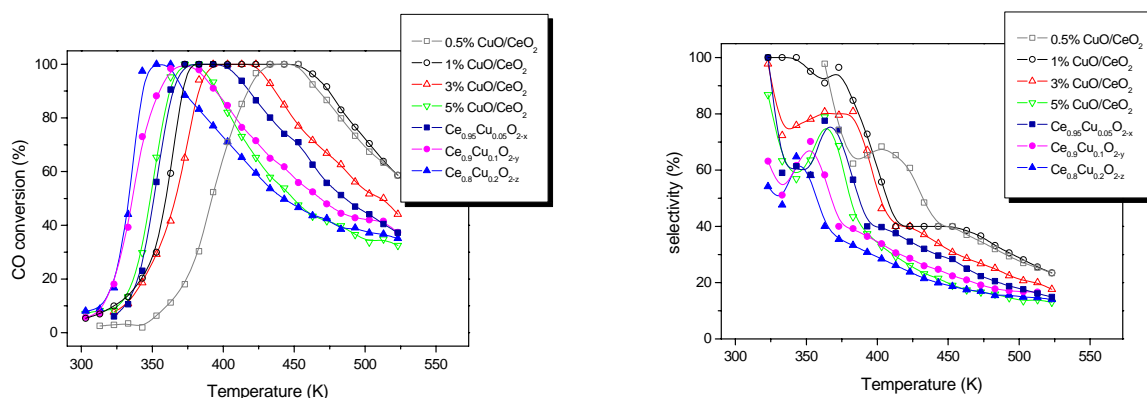


Figure 1. CO conversion and selectivity for the CO oxidation process obtained during catalytic tests under CO-H₂-O₂ over the indicated catalysts