



Preferential oxidation of CO in excess H₂ over CuO/CeO₂ catalysts: Characterization and performance as a function of the exposed face present in the CeO₂ support

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ABSTRACT

A series of oxidised copper-cerium nanostructured catalysts prepared by impregnation of copper over ceria supports synthesized by different methods (hydrothermal with varying preparation parameters, microemulsion/precipitation), in order to achieve different specific morphologies (nanocubes, nanorods and nanospheres), have been examined with respect to their catalytic properties for preferential oxidation of CO in excess H₂ (CO-PROX). The catalysts have been characterized in detail by XRD, Raman, S_{BET} measurement, HREM, XPS, TPR and EPR, which allows establishing a model of structural characteristics of the catalysts. The characterization results have been correlated with analysis of CO-PROX catalytic properties by means of catalytic activity measurements complemented by *operando*-DRIFTS. Structural dependence of the CO oxidation reaction on the dispersed copper oxide entities as a function of the exposed face present at the surface of the different ceria supports is revealed. An important overall enhancement of the CO-PROX performance is detected for the sample supported on ceria nanocubes which is proposed to be a consequence of the interaction between copper oxide and (100) faces of the ceria support.

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1. Introduction

Hydrogen production from hydrocarbons for its use as fuel of proton exchange membrane fuel cells requires a final purification step in order to decrease the CO concentration resulting after reforming and water-gas shift (WGS) steps. Among different possible alternatives, preferential or selective catalytic oxidation of CO upon introduction of a small amount of O₂ in the H₂-rich stream (CO-PROX) is considered as most interesting from practical and economical points of view, most particularly for mobile applications [1]. Among different possible alternatives, catalysts combining copper and cerium oxides have demonstrated promising characteristics for CO-PROX, being able to compete with less economically interesting noble metal catalysts [1,2].

Main properties of CuO–CeO₂ systems for this process appear related to synergetic interactions between the two constituent oxides which determine interfacial characteristics [3]. This is based on the fact that active sites for the CO oxidation reaction, whose relative activity with respect to that of competing H₂ oxidation reaction basically determines overall performance for the process [4–6], are proposed to be located at such interface between both oxides [4,5,7,8], being formed by Cu⁺ entities which result from ceria-promoted reduction of dispersed CuO upon interaction with the reactant mixture [4,5,9–14]. In turn, active sites for the H₂ oxidation reaction are apparently formed over the dispersed copper oxide particles upon extension of their reduction from the interface [5]. The fact that different active sites could be responsible for the two competing reactions is in agreement with kinetic measurements showing the absence of dependence of CO and H₂ oxidation rates with respect to H₂ and CO partial pressures, respectively, thus suggesting no important competency between the two reactants for the active sites [6,15]. However, it cannot be discarded that some degree of competency arises at high reaction temperature, in the non-selective region, when CO desorption from active reduced

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copper sites becomes favoured, even though, to the best of our knowledge, no direct evidence for this is available yet [16]. Indeed, kinetic models are available in which such competency appears also reflected [17]; certainly, the origin of the discrepancy in macroscopic kinetic results can be related to the continuous changes in surface chemical characteristics upon interaction with the reactant mixture as a function of reaction temperature, nature of reactant mixture and type of sample examined [4,5,18,19]. Notwithstanding such controversy, there is general agreement that the mentioned copper oxide reduction process (related to an induction step taking place upon interaction of the catalyst with the reactant mixture [4,12]) leading to generation of active sites for the two reactions, as well as the catalytic activity over these sites, must in principle depend strongly on interfacial properties, which should be taken into account in order to explain observed ceria promoting effects [5,7,8,10,20].

In this respect, a possible way to tune interfacial interactions between the two oxide components could consist in changing the geometric type of interacting surfaces. In this sense, Skårman et al. reported a study on systems of copper oxide deposited on CeO₂ thin films prepared by rf magnetron sputtering showing the higher magnitude of synergetic effects between copper oxide and ceria (001) surfaces, compared to thermodynamically most stable (111) ones, for CO oxidation [21]. In a similar sense, Zhou et al. reported a higher CO oxidation activity of copper oxide dispersed on high-energy, more reactive (001) and (110) planes of CeO₂ nanorods prepared by a hydrothermal method in comparison with an analogous sample in which the ceria support was prepared by simple precipitation and which is assumed to expose mainly (111) surfaces [22]; in the same sense, NO reduction by CO was shown to be most favoured for CuO entities in contact with ceria nanorods compared with nanocubes or nanopolyhedra [23]. Concerning the CO-PROX application, only one very recent work following this type of approach seems to be available [24]. In contrast to the two mentioned works [21,22], in this latter report CO oxidation was found to be most favoured over copper oxide deposited on ceria nanooctahedra (exposing (111) faces), which in turn apparently displayed higher surface copper content according to XPS measurement than on ceria nanorods ((110) and (100) faces) or nanocubes ((100) faces) [24].

Considering these apparent discrepancies and in order to shed some more light in this respect, the present work analyses CO-PROX performance of catalysts of copper oxide (1 wt.% in all cases) deposited on different nanocrystalline ceria supports prepared by hydrothermal or microemulsion/precipitation methods, which display specific morphologies exposing different crystal planes of the CeO₂ lattice. For this purpose, a multitechnique approach (XRD, Raman spectroscopy, S_{BET}, HREM, XPS, EPR, TPR) has been followed for catalysts characterization while catalytic properties have been examined by conventional catalytic testing as well as *operando*-DRIFTS. The results show an important enhancement of CO-PROX characteristics for a sample supported on ceria nanocubes exposing (100) faces; this is attributed to the particular capability of such surface structure for a favourable interaction with active copper oxide entities which allows achieving for them a high dispersion degree (or, in other words, avoiding segregation of non-interacting entities).

2. Experimental

2.1. Sample preparation

Procedures available in the literature have been employed to prepare CeO₂ supports in the form of nanorods and nanocubes [25]. For this, Ce(NO₃)₃·6H₂O (Aldrich) used as the cerium

precursor was dissolved along with NaOH in deionized water. Then, the mixture was introduced in Teflon flasks of 125 mL filled at 75% of the total volume and, after stirring, was held in a stainless steel autoclave and subjected to hydrothermal treatment during 24 h at 100 °C or 180 °C for the synthesis of ceria nanorods or nanocubes, respectively. After the hydrothermal treatment, the precipitates were separated by centrifugation, washed with deionized water and ethanol several times, followed by drying at 60 °C under air overnight. A third CeO₂ support (with final shape close to nanospheres, as will be shown below) was prepared by microemulsion method, using methods as reported elsewhere [26]. Briefly, cerium(III) nitrate was introduced in a reverse microemulsion (water in oil) using *n*-heptane as the organic phase, Triton X-100 (Aldrich) as surfactant, and hexanol as cosurfactant. Then, this suspension was mixed with another similar suspension containing as aqueous phase an alkali solution (TMAH, Aldrich) in order to precipitate the cerium. The resulting mixture was stirred for 24 h, centrifuged, decanted, and rinsed with methanol. Finally, the solid portion was dried overnight at 100 °C. Following drying, the three supports were calcined under air for 2 h at 500 °C. Basic physicochemical characteristics of these CeO₂ supports along with the nomenclature employed for them (where NC, NR and NS hold for nanocubes, nanorods and nanospheres, respectively, in accordance with shapes observed, see below) are summarized in Table 1.

Samples of copper supported on the three CeO₂ supports (Cu wt % of 1.0) were prepared by incipient wetness impregnation of the supports with copper nitrate aqueous solutions. Following impregnation, the samples were dried overnight at 100 °C and finally calcined under air at 500 °C for 2 h. Their characteristics are summarized as well in Table 1.

2.2. Techniques

Powder XRD patterns of the samples were recorded on a Seifert XRD 3000P diffractometer using nickel-filtered Cu K_α radiation operating at 40 kV and 40 mA, using a 0.02° step size and 2 s counting time per point. Analysis of the diffraction peaks was done with the computer program ANALYZE Rayflex Version 2.293.

Raman spectra were obtained at room temperature (RT) with a Bruker RFS-100 FT-Raman spectrometer provided with a diode-pumped germanium solid-state detector, which operates at liquid nitrogen temperature. A NdYAG laser (1064 nm) was used as excitation source at a power of 100 mW. Powdered samples were pressed in a holder and analyzed (100 scans, 4 cm⁻¹ resolution) without further treatment. It must be noted that we have selected infrared excitation for these experiments because the use of visible excitation (results not shown) requires a careful control of exciting power (while keeping reasonable signal/noise ratio) in order to avoid a blue shift in the main triply degenerate F_{2g} mode of fluorite CeO₂ (only occurring for Cu-containing samples, results not shown) [27], which is likely a consequence of sample heating (and consequent lattice expansion) after electronic relaxation (considering that light absorption by Cu²⁺ entities extends to the visible region according to UV-vis analysis [28]); similar sample heating problems as a consequence of interaction with the visible Raman laser beam have been pointed out elsewhere [29,30].

High resolution electron microscopy (HREM) data, including high angle annular dark field (HAADF) images and X-ray energy dispersive spectra (XEDS), were recorded on a JEOL 2010 field emission gun transmission electron microscope operated at 200 kV equipped with an EELS spectrometer GIF2000 (Gatan Imaging Filter) and an EDS spectrometer Oxford INCA Energy 2000 system. XEDS and EELS analysis were performed in STEM mode, with a probe size of ca. 1 nm and 0.5 nm, respectively. Specimens were prepared by depositing small portions of the samples to be investigated onto a molybdenum grid supporting a perforated carbon film. Deposition

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