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CO oxidation and COPrOx over preformed Au nanoparticles supported over nanoshaped CeO$_2$

Lluís Soler[a], Albert Casanovas[a], Aitor Urrich[a], Inmaculada Angurell[b], Jordi Llorca[a,*]

[a] Institute of Energy Technologies and Centre for Research in Nanoengineering, Universitat Politècnica de Catalunya, Diagonal 647, ed. ETSEIB, 08028 Barcelona, Spain
[b] Department of Inorganic Chemistry, Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain

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ABSTRACT

Au/CeO$_2$ (0.25% wt. Au) catalysts were prepared by anchoring preformed Au nanoparticles over ceria polycrystals, cubes and rods and tested in the oxidation of CO and COPrOx. The use of preformed Au nanoparticles assured a constant Au particle size (ca. 5 nm by HRTEM) for all samples, which allowed to a precise assessment of the effect of the morphology of nanoshaped ceria on catalytic activity. The catalytic performance of the Au/CeO$_2$-rods was much better than that of the Au/CeO$_2$-polycrystals and Au/CeO$_2$-cubes both in the oxidation of CO and COPrOx reactions. The Au/CeO$_2$-rods exhibited the highest amount of oxidized Au and Ce(III) species by XPS, whereas in the Au/CeO$_2$-cubes gold was totally metallic and the amount of Ce(III) was minimum. An intermediate situation was encountered in the Au/CeO$_2$-polycrystals. Considering the differences in the oxidation states of Au and Ce and the fact that all samples were prepared with preformed metallic Au nanoparticles of the same size, the results indicate that the intrinsic nature of the different ceria surfaces exerts a prominent role in the gold-ceria interaction and in the electron density transfer from Au to Ce, which in turn has a strong effect on catalytic activity. Gold nanoparticles strongly interact with CeO$_2$-{1 1 0} surfaces with respect to CeO$_2$-{1 1 1} and CeO$_2$-{1 0 0}, even when Au nanoparticles are prepared separately and simply deposited by impregnation.

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1. Introduction

The oxidation of carbon monoxide (CO) and, in particular, its preferential oxidation in the presence of large quantities of hydrogen (H$_2$) represents a very important aspect of fuel cell technology and the development of processes devoted to obtain CO-free hydrogen streams is a critical issue and an essential requirement for feeding proton exchange membrane fuel cells (PEMFC) [1]. Carbon monoxide preferential oxidation (COPrOx) is particularly appealing when applied to low-scale or portable reformer-PEMFC systems due to its fairly simple implementation, low operation costs and minimal loss of hydrogen [2–4]. In the COPrOx, two oxidation reactions compete for the oxygen consumption and, as a consequence, COPrOx catalysts have to exhibit high CO oxidation activity, while H$_2$ oxidation has to be maintained low in order to avoid fuel losses, at temperatures ranging from 80 to 200 °C. A profuse number of studies on the design of suitable catalysts for the competitive oxi-

dation of CO in the presence of H$_2$ have been published. Among them, supported Au catalysts exhibit exceptionally high CO oxidation activity in the low-temperature range when gold is dispersed as particles with diameters smaller than 5 nm [5–11].

Ceria is a key component for many oxidation catalysts and its catalytic activity shows a strong dependence on morphology [12,13]. The shape-dependent activity of ceria has been recognized not only in the catalytic oxidation of CO [14–21], but also on NO reduction [22], water-gas shift reaction [23–25], reforming reactions [26–29] and soot combustion [30]. Polycrystalline ceria nanoparticles usually consist of octahedra or truncated octahedron shapes, which mainly expose the most stable {1 1 1} facets in order to minimize surface energy, whereas nanorods are terminated by {1 1 0} and {1 0 0} planes and nanocubes expose {1 0 0} surfaces. The energy required to form oxygen vacancies on the {1 1 1} surface of CeO$_2$ is higher than those on {1 1 0} and {1 0 0} surfaces, so there are more oxygen vacancies on {1 1 0} and {1 0 0} planes [31]. As the number of vacancies increases, the movement of oxygen atoms in the lattice becomes easier, and the increased diffusion rate of oxygen in the lattice results in increased catalytic activity [32]. Accordingly, the reactivity of nanoshaped ceria rods and cubes

for the oxidation of CO is higher than that of the ceria polycrystals [33–35].

When considering Au/CeO$_2$ catalysts, the emergence of various ceria nanoshapes should enable the study of the CeO$_2$ morphology on the metal-oxide interaction and catalytic activity, but in spite of numerous studies in this field [36–38], the nature of the Au-oxide interface remains a controversial issue. The main problem is the formation of different Au ensembles and structures over the different ceria nanoshapes arising from the preparation methods and/or pretreatments, which exhibit different intrinsic reactivity per se. Data clearly show that the morphology of ceria strongly affects the structure of gold nanoparticles prepared from Au salts [39]. Very often, CeO$_2$ rods stabilize Au atoms and clusters whereas Au nanoparticles are found in Au/CeO$_2$ cubes [40,41]. In this way, the discussion about the influence of ceria nanoshapes on catalytic activity is masked by different gold particle sizes and structures, which are critical factors for catalytic activity. To overcome this difficulty, in this work we study the CO oxidation and COPrOx reaction over preformed Au metal nanoparticles supported on ceria nanocubes, nanorods and nanopolyhedra in an effort to elucidate the precise role of the nanoshape of the ceria support. The use of preformed Au nanoparticles guarantees the same Au particle size and a similar architecture of the Au-support interaction for all the samples tested, so the effects of the ceria nanoshape on catalytic performance can be properly investigated [42,43].

2. Experimental

2.1. Catalyst preparation

Conventional CeO$_2$ polycrystals (CeO$_2$-p) were prepared by precipitation adding 35 ml of an aqueous solution of 0.4 M Ce(NO$_3$)$_3$·6H$_2$O using an electrospray (Digital Ultrasonic Atomizer, Sonaer Inc.) to create a fine aerosol of liquid droplets into 245 ml of a 0.2 M NaOH solution under vigorous stirring. The resultant suspension was kept under agitation for 30 min. Then, the suspension was transferred into a PTFE-lined cylinder and sealed in a stainless steel autoclave and heated at 423 K for 24 h. After cooling, the resulting mixture was centrifuged and washed three times with deionized water and three times with ethanol for separation and purification of the powder, which was dried at 333 K overnight. Ceria nanocubes (CeO$_2$-c), and nanorods (CeO$_2$-r) were prepared as reported elsewhere in detail [44]. Briefly, they were synthesized adding 35 ml of an aqueous solution of 0.4 M Ce(NO$_3$)$_3$·6H$_2$O by means of an electrospray into 245 ml of a 6.9 M NaOH solution for CeO$_2$-c and 9.0 M NaOH solution for CeO$_2$-r, under vigorous stirring for 30 min. The suspension of CeO$_2$-c was heated at 453 K for 24 h, and the suspension of CeO$_2$-r was heated at 373 K for 24 h. After cooling, the resulting mixtures were processed as described above for CeO$_2$-p.

The preparation of the model Au nanoparticles was reported in detail in Ref. [45]. They were synthesized following the two-phase method described for the synthesis of dodecanethiol-capped monometallic Au nanoparticles [46], which involved the transfer of AuCl$_4^-$ to a toluene solution using tetraoctylammonium bromide followed by a single reduction step with NaBH$_4$ in the presence of dodecanethiol. The Au/CeO$_2$ catalysts were prepared by incipient wetness impregnation from a toluene solution (the solution was homogenized and divided in three parts) containing the model Au nanoparticles (40 mM) over CeO$_2$ polycrystals, nanocubes and nanorods (Au/CeO$_2$-p, Au/CeO$_2$-c and Au/CeO$_2$-r, respectively). Samples were calcined at 673 K for 4 h to remove the protecting shell. The Au loading over nanoshaped ceria samples was determined by ICP-OES to be 0.25 ± 0.02% wt.
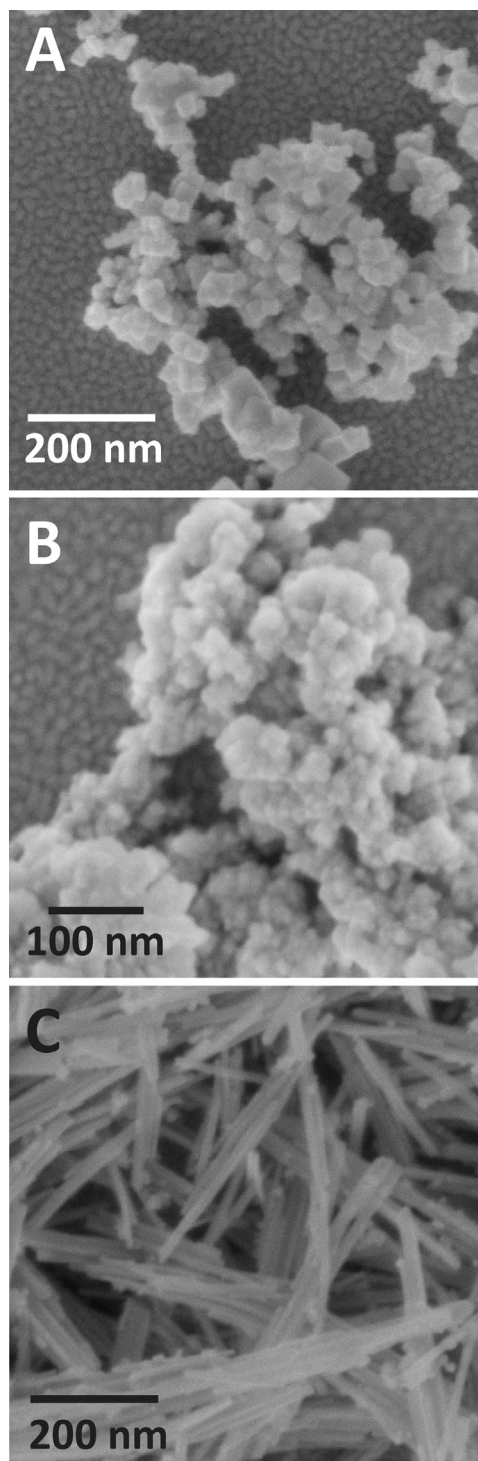

Fig. 1. SEM images of nanoshaped ceria supports. A: CeO$_2$-cubes. B: CeO$_2$-polycrystals. C: CeO$_2$-rods.

2.2. Catalyst characterization

Scanning electron microscopy (SEM) images were recorded at 5 kV using a Zeiss Neon40Crossbeam Station instrument equipped with a field emission source. The free software Fiji was used to measure the particle size of the samples. About two hundred particles were considered for particle size distribution estimation. High resolution transmission electron microscopy (HRTEM) was carried out using a JEOL 2010F electron microscope equipped with a field emission source at an accelerating voltage of 200 kV. Samples