



Au deposited on CeO₂ prepared by a nanocasting route: A high activity catalyst for CO oxidation



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ABSTRACT

A set of catalysts comprised of gold on different CeO₂ supports has been prepared by a nanocasting route and characterized by several physicochemical techniques. These catalysts have been tested for CO oxidation and show outstanding catalytic activity. Higher calcination temperatures of the hard template, producing a poorly ordered silica template, have led to a higher amount of oxygen vacancies on the surface of CeO₂. The presence of surface oxygen defects in the support combined with the deposition of Au nanoparticles (ca. 3 nm) homogeneously dispersed on the CeO₂ support may explain the excellent behaviour for low temperature CO oxidation. Surprisingly, it has been observed that the degree of inverse replication of the template is not relevant in the catalytic performance, as in all cases neither the characteristics of the ceria surface nor the dispersion and oxidation state of gold are greatly modified by the formation of inter-particle bridges.

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1. Introduction

Cerium oxide has been shown as one of the most efficient supports for gold nanoparticles in an increasing number of catalytic reactions, especially for low temperature CO oxidation and water gas shift [1–3]. The precise nature of the active gold sites for these reactions is not completely understood, but it is known that small gold particles in the range of a few nanometres are required to achieve high CO conversion [4]. The influence of the oxidation state of gold has also been studied and it seems that the coexistence of cationic and metallic gold leads to the best catalytic performance, although there is still some controversy [5,6]. In contrast, there seems to be less doubt about the paramount importance of the perimeter between gold particles and the metal oxide support [7]. This interface is highly influenced by the characteristics of the metal oxide support, such as support particle size [8], redox properties [9,10] and concentration of surface oxygen defects [11,12]. Thus, it has been reported that ceria with low particle size and both high surface area and oxygen storage capacity can effec-

tively disperse gold leading to efficient catalysts. Recently, the nature of exposed surface planes of a CeO₂ support has been linked to the catalytic activity of gold/ceria, as this modifies the redox properties, which are determinant for anchoring gold on the surface [12–14]. Thus, gold supported on ceria nanorods with {110} exposed planes are more active than gold on ceria nanoparticles or nanocubes with {100} planes exposed [15].

Ceria has also been demonstrated to be an efficient support for gold when it presents a high surface area. Thus a nanocrystalline CeO₂ of 3–4 nm size and a surface area of 180 m² g^{−1}, with a large number of surface oxygen vacancies, increases the CO oxidation activity of gold nanoparticles by 2 orders of magnitude compared to a non-nanocrystalline ceria [16]. One way to produce high surface area ceria supports can be through the use of siliceous hard templates [17]. Accordingly, a three-dimensional 1a-3d cubic arrangement of pores channellike structure, KIT-6, can yield ordered mesoporous cerium oxide with highly crystalline walls and good thermal stability, after the silica template is removed [18].

On the other hand, using KIT-6 as a hard template it has also been shown that ceria with different mesostructural order can be obtained by slight modifications in the preparation procedure [19]. Highly ordered mesoporous metal oxides with large particle

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sizes were obtained when they were calcined in glass vials covered with a glass slide. In contrast, products synthesized in open Petri dishes gave small nanoparticles with poor mesostructural order. It seems that the release of water and other gas phase by-products in the calcination process is a controlling variable in order to tune the nanocrystal growth of the materials inside the mesopore space of the template. Following this procedure, we have synthesized ceria from KIT-6 templates, both with covered and open vessels, expecting to obtain CeO_2 supports with differing degrees of template inverse replication.

On ceria supports prepared by a nanocasting route, we have incorporated gold through a deposition–precipitation method. To date, the role of ordered CeO_2 structures in the final catalytic behaviour of gold/ceria catalysts has not been studied in the scientific literature. In the present article, high surface area ceria has been synthesized using mesoporous silica KIT-6 as a hard template. KIT-6 silica templates have been prepared by modifying the calcination temperature (450 and 650 °C) leading to materials with different physico-chemical properties.

2. Materials and methods

2.1. Synthesis of the mesoporous silica (KIT-6 silica)

KIT-6 was synthesized in acidic conditions using a mixture of Pluronic P123 triblock copolymer ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, Sigma–Aldrich) as structure agent and butanol (99.9%, Sigma–Aldrich). Thus, 6 g of P123 was added to a solution of 220 g of distilled water and 12 g of concentrated HCl (37 wt.%, Scharlau). The mixture was stirred for 6 h at 35 °C and then 6 g of butanol was added under stirring for another hour. Finally, 12.48 g of tetraethyl orthosilicate (TEOS, 98%, Aldrich) was added and stirred for 24 h at the same temperature. The mixture was aged for 24 h at 80 °C, under static conditions for hydrothermal treatment. Lastly, the white solids were recovered by filtration, washed with deionized water and dried for 24 h at 100 °C. Thereafter, the products were calcined in flowing air at either 450 or 650 °C (denoted as –450 or –650) for 6 h at a heating rate of 2 °C min^{−1} [18] obtaining a final mass of silica ca. 3.4 g in each batch.

2.2. Preparation of mesoporous cerium oxide

In order to study the influence of the synthesis method on the growth of the crystallites of CeO_2 and its final structure, each sample of the mesoporous silica KIT-6 calcined at different temperatures was separated into two portions [19]. One portion was used to synthesize cerium oxide in a covered vessel (denoted as C in sample names); and with the second portion, the preparation was conducted in an open vessel (denoted as O in sample name). The cerium oxide supports were prepared as follows: 0.45 g of KIT-6 was suspended in 15 ml of ethanol (HPLC grade, Scharlau) containing 1.2 g of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99%, Sigma–Aldrich). After 30 min stirring, the solid obtained was dried at room temperature and calcined at 350 °C for 4 h to completely decompose the nitrate species. The mixture of silica–ceria was re-suspended in 15 ml of ethanol containing 0.6 g of cerium precursor in order to achieve higher metal loadings, dried at room temperature and then calcined at 550 °C for 6 h. Finally, the silica template was removed from the silica–ceria mixture with 10 ml of 2 M NaOH ($\geq 98\%$, Sigma–Aldrich) at 70 °C until evaporation was completed. This etching process was repeated twice. However, before evaporation, the solid was collected by vacuum filtration and rinsed with distilled water until washings with a neutral pH were observed. Finally, samples were dried for 24 h at 100 °C [18] obtaining a final mass of ceria ca. 0.69 g in each batch.

2.3. Au deposition and catalyst preparation

The conventional deposition–precipitation technique was employed for gold deposition onto the mesoporous CeO_2 matrix. In a typical synthesis, 50 ml of an aqueous solution (ca. 0.077 g, of 7 wt.% gold with respect to support) of $\text{KAuCl}_4 \cdot 3\text{H}_2\text{O}$ (98% Aldrich) was heated to 70 °C in a water bath whilst wrapped in an aluminium foil to exclude light. The initial pH was around 2.4, which was slowly adjusted to pH 9 by dropwise addition of a 0.2-M NaOH solution to initiate hydrolysis of the Au–Cl bonds. After the pH had been constant for 30 min, 0.5 g of dried CeO_2 was dispersed into the solution. pH variations into the acidic region (pH 5–6) were reverted by adding 0.2 M NaOH up to pH 9. After the pH had been constant for 15 min, the suspension was stirred for another hour at the same temperature. Finally, the suspension was cooled, filtered and washed with distilled water until no chloride ions were detected by the AgNO_3 test. The resulting yellow cake was dried at 100 °C for 12 h, followed by calcination at 400 °C for 4 h in static air. Upon reduction, the colour of the samples changed to black–deep violet. All the samples were stored at room temperature under vacuum in a desiccator, away from light.

2.4. Characterization techniques

KIT-6 templates, CeO_2 supports and catalysts samples were characterized by N_2 adsorption at −196 °C, using a Micromeritics ASAP 2020 apparatus. Samples were degassed at 150 °C prior to analysis. From these data, the following textural parameters were calculated: multipoint Brunauer–Emmet–Teller (BET) surface area (S_{BET}) was estimated from the relative pressure range from 0.05 to 0.25. Total pore volume (V_T) was calculated using the adsorbed volume at a relative pressure of 0.95. The pore size distribution and mean pore size (d_0) of the mesoporous materials was analysed using the Barrett–Joyner–Halenda (BJH) method applied to the desorption branch of the isotherm.

Elemental analysis was performed by inductively coupled plasma/optical emission spectroscopy (ICP/OES) using a JY2000 Ultrace Horiba spectrometer. Concentration (wt.%) of Au and possible synthesis residues like Si and K were determined for each catalyst.

Powder X-ray Diffraction (XRD) was used to identify the crystalline phases present in the samples. A Bruker D8 Advance diffractometer with monochromatic Cu K α source operated at 40 kV and 40 mA was used. The experimental patterns were calibrated against a silicon standard, and the crystalline phases were identified by matching the experimental patterns to the JCPDS powder diffraction file database.

Unpolarized Raman spectra were obtained using a Renishaw system-1000 dispersive laser Raman microscope. The excitation source used was an argon ion laser (514.5 nm) operated at a power of 20 mW and at room temperature. The laser was focused on powdered samples placed on a microscope slide to produce a spot size ca. 3 μm in diameter. A backscattering geometry with an angle of 180° between illuminating and collected radiation was used for recording data. The acquisition time was 60 s for each spectrum with a spectral resolution of 1 cm^{−1}. It is important also to note that no damage to the samples has been noticed (shifts or changes in intensity of the bands).

Temperature programmed reduction (TPR) studies were performed using a TPDRO 1100 Thermo instrument with a thermal conductivity detector. In all the experiments, 10 vol.% H_2 in Ar, at a constant flow rate of 50 ml min^{−1}, was used as reducing gas. A temperature range of 30–750 °C and a constant heating rate of 10 °C min^{−1} were used.

X-ray photoelectron spectroscopy (XPS) measurements were made on a Kratos Axis ultra DLD photoelectron spectrometer using

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