



Stabilized gold on cerium-modified cryptomelane: Highly active in low-temperature CO oxidation



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ABSTRACT

Cerium-doped cryptomelane stabilizes polyhedron Au nano-particles smaller than 3 nm. The obtained Au/Ce/cryptomelane catalyst is highly active for CO oxidation. Cationic, neutral, and anionic gold species were found on Ce/cryptomelane. The modification of cryptomelane by the addition of cerium is twofold: (i) cerium is incorporated in the tunnels of cryptomelane, increasing the number of defects which function as nucleation sites for gold and (ii) ceria nano-particles at the surface induce charge transfer between gold and cryptomelane. TOF for Au/Ce–K–OMS–2 is about twice that of Au/CeO₂ prepared by the same procedure.

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1. Introduction

In the bulk form, gold (Au) is considered the most noble of all metals, due to low adsorption energy of gases and high energy barriers for their dissociation, which are crucial aspects in catalytic reactions [1]. In contrast, nanometer-sized Au particles exhibit exceptional catalytic activity for several reactions, such as CO oxidation at low temperatures [2–8].

Extensive experimental [8–12] and theoretical work [13–17] has been carried out in recent years, aiming to understand the origin of this exceptional reactivity, as well as the influence of many variables such as particle size, support, and method of preparation on the overall catalytic activity. Some important conclusions have been reached, the most relevant being the high structure-sensitivity of Au catalysis. The influence of particle size on activity can be explained in two ways: (1) the high concentration of low-coordinated sites on the surface of small nano-particles is responsible for the activation of CO and possibly oxygen [13,14,16,17]; and (2) quantum size effects [9].

In addition to the particle size, the support also has a large influence on the catalytic performance; Au catalysts are generally more active when supported on reducible oxides. The support supplies activated oxygen at the metal/oxide boundary [18,19] and helps to disperse and stabilize Au species due to metal–support interactions [3,20], charge transfer [21–23], and support-induced strains [9]. The combination of these effects might also occur, i.e., Au–support interaction can influence the morphology of the Au particles and thus influence the number of low-coordinated atoms or the strain [24]. For example, more rounded nano-particles were present on TiO₂, while highly faceted nano-particles were present on ZnO [25]; the morphology of Au has a strong effect on the activation of oxygen [26].

Among the different reducible oxides, nano-structured manganese oxides are interesting materials due to their high mobility and storage capacity of oxygen [27,28]. In particular, cryptomelane-type manganese oxide octahedral molecular sieves (OMS–2) are of special interest due to their tunnel structures and related properties and applications [29,30]. Cryptomelane is an octahedral molecular sieve (OMS–2), composed of 2 × 2 edge-shared MnO₆ octahedral chains, which are corner-connected to form a one-dimensional tunnel structure with a pore size of 4.6 Å. The tunnels are partially filled with potassium cations exhibiting a high mobility due to their weak interaction with MnO₂. The octahedral sites are occupied by a combination of Mn(III) and Mn(IV) that compensate

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the positive charge of the K ions [27,28]. Martínez et al. studied the catalytic properties of this material doped with highly dispersed Au (~2.5 nm) and obtained high catalytic activities for CO oxidation [31]. It was found that besides particle size, Au–support interactions play a crucial role in the final catalytic performance; however, no insight on the nature of these interactions was presented.

Several studies on oxide-supported metal clusters show that surface defects (point defects, F centers, oxygen vacancies) on the support could serve as anchoring sites for metal clusters or even single atoms [24,32–35]. The surface defects alter the electronic configuration of Au species enabling catalytic reactions such as CO oxidation at low temperatures [35]. The amount of these defects can be increased by introducing dopants. Based on this approach, we present the synthesis, characterization, and catalytic performance in the low-temperature oxidation of CO by using catalysts with low Au loadings (0.5 wt%) supported on cerium (Ce)-doped cryptomelane (Ce–K–OMS-2).

2. Experimental

2.1. Synthesis and characterization

Cryptomelane-type manganese oxide (K-OMS-2) was synthesized by the reflux method developed by Luo et al. [36]. Ce was incorporated on K-OMS-2 using the following procedure: 1.5 g of K-OMS-2 was stirred in 200 mL aqueous solution of 0.5 M of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ for 24 h (resultant sample, Ce–K–OMS-2). The solid obtained was filtered and washed with distilled water, followed by drying at 100 °C and calcination in air at 450 °C for 4.5 h, using a ramp of 2.5 °C/min.

0.5wt% of Au was supported on K-OMS-2 and Ce–K–OMS-2 by double incipient wetness impregnation (DIWI). DIWI consists of a first impregnation step using a solution of HAuCl_4 (using sonication), followed by addition of an aqueous solution of Na_2CO_3 (1 M), under constant ultrasonic stirring [37]. The resulting solid was washed repeatedly with distilled water for chloride removal and dried in the oven at ~110 °C for 12 h. Table 1 summarizes all the materials synthesized in this work, as well as the nomenclature used.

The crystalline structure and chemical composition of the materials were obtained by X-ray diffraction (XRD, PANalytical X'Pert PRO diffractometer with $\text{Cu K}\alpha$ radiation source) and inductively coupled plasma/optical emission spectroscopy (ICP-OES, PerkinElmer Optima3000dv), respectively. The morphology of the samples was investigated by transmission electron microscopy (TEM, Leo 906 E apparatus) and higher angular annular dark field imaging (HAADF, JEOL2010F instrument) equipped with an energy-dispersive X-ray (EDX) spectrometer.

The oxidation state of Ce on the surface was determined by X-ray photoelectron spectroscopy (XPS). XPS analysis was performed using an ESCALAB 200A, VG Scientific (UK) with PISCES software for data acquisition and analysis. Al ($\text{K}\alpha$) or Mg ($\text{K}\alpha$) X-ray source (1486.6 eV or 1253.6 eV, respectively) operating at 15 kV (300 W)

was used, and the spectrometer, calibrated with reference to $\text{Ag } 3d_{5/2}$ (368.27 eV), was operated in CAE mode with a pass energy of 20 eV (ROI) and 50 eV (survey). Data acquisition was performed with a pressure lower than 1×10^{-6} Pa. The effect of the electric charge was corrected by reference to the carbon peak (285 eV). Deconvolution of spectra was performed with the XPSPEAK4.1 program, using peak fitting with Gaussian–Lorentzian peak shape and Shirley-type background subtraction.

The reduction profile of the samples was studied by temperature-programmed reduction (TPR) using a fixed-bed reactor, connected to a TCD or MS detector. About 20 mg of sample was loaded in the reactor and pre-treated with a mixture of 10 vol.% O_2 /Ar for 1 h at 200 °C. After that, the system was cooled down to room temperature and flushed with argon until removal of all oxygen. The reducing gas was a mixture of 10 vol.% H_2 /Ar (H_2 -TPR) or 5 vol.% CO /Ar (CO -TPR) at a flow rate of 30 cm^3 (STP)/min. The temperature was increased from room temperature to 600 °C with a ramp of 10 °C/min. The average oxidation state of manganese (AOS) was determined from the integral hydrogen consumption and assuming MnO as the final oxide phase.

The dispersion and morphology of Au was characterized by electron microscopy. The following expression was used to calculate the dispersion from the average particle size:

$$D = \frac{6Mn_s}{\rho N d} \approx \frac{1.17}{d(\text{nm})} \quad (1)$$

where M represents the molar mass of Au (197 g/mol), n_s the number of atoms of Au per unit area ($1.15 \times 10^{19} \text{ m}^{-2}$), ρ the density of Au (19.3 g/cm^3), N is Avogadro's number, and d (nm) the average particle size.

The electronic structure and coordination of Au were studied by infrared spectroscopy, using CO as a probe molecule. Spectra were recorded at room temperature on a Nicolet model 8700 spectrometer equipped with a high-temperature DRIFTS cell and a MCT/A detector with a spectral resolution of 4 cm^{-1} . Prior to CO adsorption, the sample was pre-treated *in situ* in helium at 100 °C for 1 h and then cooled to room temperature. 5 vol.% CO /He was introduced in the cell for 30 min at room temperature. Subsequently, the system was flushed with He at the same temperature, to remove physisorbed CO. Each reported spectrum is an average of 128 scans.

2.2. Catalytic Performance tests

Catalytic activity measurements for CO oxidation were performed using a continuous-flow fixed-bed reactor. The catalyst sample weight was 200 mg and the feed gas (5 vol.% CO and 10 vol.% O_2 in He) was passed through the catalytic bed at a total flow rate of 50 cm^3 (STP) min^{-1} . The reaction temperature was raised from room temperature by steps of 25 °C until 100% conversion was obtained. The reactor was maintained at each temperature for 20 min in order to obtain experimental values at steady state. The composition of the outgoing gas stream was determined by gas chromatography. Further details of the experimental setup can be found elsewhere [38].

Table 1

Chemical composition (obtained by ICP), average oxidation state of manganese (AOS) (obtained by H_2 -TPR), percentage of Ce(III) on the surface and oxygen vacancies (obtained by studying $\text{Ce}3d$ and $\text{O}1s$ spectra, respectively, Fig. 4 and Table S2).

Sample	K/Mn ^b	Ce/wt% ^b	Au/wt% ^b	AOS ± 0.03 ^b	Ce(III), %	O _{II} , %
K-OMS-2	0.14	–	–	3.70	–	14
Ce–K–OMS-2	0.17	6.0	–	3.80	9	16
Au/K-OMS-2	0.14	–	0.5	3.70	–	–
Au/Ce–K–OMS-2	0.16	6.0	0.5	3.90	40	18

^b Bulk.

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