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CO oxidation over gold supported on Cs, Li and Ti-doped cryptomelane materials

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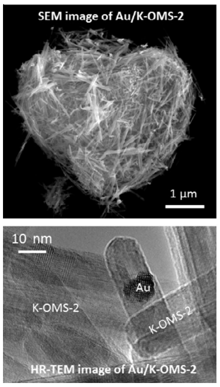
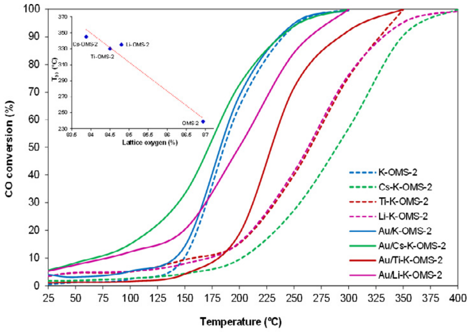
GRAPHICAL ABSTRACT





Addition of Au to cryptomelane (K-OMS-2) materials doped with Cs, Ti and Li improves the catalytic activity for CO oxidation. That is due to the effect of gold on samples reducibility, gold particle size and lattice oxygen donating ability of samples.

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ABSTRACT

Cryptomelane-type manganese oxides were synthesized by redox reaction under acid and reflux conditions. Different metals (cesium, lithium and titanium) were incorporated into the tunnel structure by the ion-exchange technique. Gold was loaded onto these materials (1 wt%) by a double impregnation method. The obtained catalysts were characterized by high-resolution transmission electron microscopy, energy-dispersive X-ray spectrometry, scanning electron microscopy, X-ray diffraction and temperature-programmed reduction. The catalytic activity of these materials was evaluated in the oxidation of carbon monoxide. The incorporation of Cs, Li or Ti into cryptomelane was detrimental in terms of catalytic activity. Further addition of gold to cryptomelane doped materials significantly improved the catalytic performance, especially for Cs-K-OMS-2 and Li–K-OMS-2 (to a smaller extent). Addition of gold to the Ti containing material did not show a significant improvement. The observed trends are related to the effect of gold on samples reducibility and to the gold particle size. The lattice oxygen can also be considered accountable for the activity of the materials, since the most active cryptomelane catalysts are those with higher lattice oxygen donating ability for the oxidation of the CO molecule.

1. Introduction

Octahedral molecular sieves (OMS) have received considerable attention, due to their amazing catalytic properties and shape-selective character [1–5]. The open frameworks of these materials

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consist in edge and corner shared MnO_6 octahedra, the internal pores being occupied by cations and water molecules. Cryptomelane-type manganese oxides (K-OMS-2) are one particular group of the OMS family called hollandite, and have tunnel structures that consist of 2 × 2 arrays of MnO_6 octahedra [2,5]. Inside the tunnels, potassium cations and small amounts of water stabilize the structure, and can be partially ion-exchanged with other cations with appropriate sizes. The average manganese oxidation state is around 3.8, which corresponds to a larger proportion of Mn (IV) and lower amounts of Mn (III) [1–6]. The open tunnel structure and mixed valences of OMS-2 make this material very attractive for oxidation catalysis and, therefore, the synthesis of cryptomelane materials with high purity, small particle size, high surface area, and high yield has been a challenge in recent years [5].

In order to further improve the electronic and catalytic properties, other metal cations can be introduced inside the tunnels or into the framework, by subsequent ion-exchange [5,7–9] or by substitution during synthesis [10,11]. It was observed that the introduction of alkali metals into the tunnel can significantly modify the physical and chemical properties of cryptomelane, specially the surface acid-base properties [12]. OMS materials modified with Ce [13,14], Co [7,13,15,16], Cu [7,13,17–19], Mg [7], Mo [20], Ni [7], Zn [7], Ag [21–24], Pd [15,25] and Au [26], have been reported. These materials have been used as catalysts for the oxidation of carbon monoxide [14,15,18–31] and volatile organic compounds (VOCs) [5,32–46]. The high activity of OMS materials has been attributed to the presence of the redox couple Mn(III)/Mn(IV), high mobility of lattice oxygen, open structure and high hydrophobicity [5,46].

In previous works, we used cryptomelane catalysts for the oxidation of VOCs (ethyl acetate, toluene and ethanol) [5,33,36,37,42] and studied the effect of adding different amounts of Cs and Li to cryptomelane on the oxidation of ethyl acetate [34,43]. The effect of addition of gold to un-doped and Ce doped cryptomelane was also reported for the oxidation of CO [14], as well as the effect of Au on several manganese oxides for CO [47] and VOCs [44] oxidation. In this work, cryptomelane materials modified with Ce, Cs and Li, alone and loaded with gold were used for CO oxidation, a reaction that is often used as a model for testing Au catalysts [14,29,47–63]. There are other test reactions combining both heterogeneous and homogeneous gold catalysis [64–66], but CO oxidation is still the most widespread test reaction.

2. Experimental

2.1. Catalyst preparation

2.1.1. Cryptomelane materials

Cryptomelane-type manganese oxides (K-OMS-2) were synthesized using the reflux approach in acidic medium developed by Luo et al. [67]. Cesium, lithium and titanium were incorporated into the tunnel structure by ion-exchange (samples Cs-K-OMS-2, Li-K-OMS-2 and Ti-K-OMS-2, respectively): 1 g of cryptomelane was stirred with 30 mL of 0.5 M solution of the respective nitrate precursors (Aldrich) for 7 days. The solid obtained was filtered and washed with distilled water, followed by drying at 100 °C and calcination at 450 °C in air for 4.5 h.

2.1.2. Gold loaded cryptomelane materials

Gold was loaded onto the supports by a double impregnation method [44,47,57,68], which consists in impregnation with a solution of $HAuCl_4$ (using sonication), followed by addition of an aqueous solution of Na_2CO_3 (1 M), under constant ultrasonic stirring. The resulting solid was washed repeatedly with distilled water for chloride removal (which is well known to cause sinterisation of Au particles, thus turning them inactive [29,60,69,70]), and dried in the oven at ~110 °C overnight.

2.2. Characterization techniques

Supports were characterized by N_2 adsorption at −196 °C and temperature-programmed reduction (TPR). Selected samples were also analysed by scanning electron microscopy and X-ray diffraction (XRD). Au-loaded samples were characterized by TPR and by transmission electron microscopy (TEM). Chemical composition was determined with energy-dispersive X-ray spectroscopy (EDS).

BET surface areas were calculated from the N_2 adsorption isotherms obtained in a Quantachrome Instruments Nova 4200e. All samples were previously degassed before analysis at 160 °C, for 5 h.

TPR experiments were carried out in a fully automated AMI-200 Catalyst Characterization Instrument (Altamira Instruments) under H_2 atmosphere, to acquire information on the reducibility of the samples.

Surface analysis for morphological characterization was carried out by SEM, using a FEI Quanta 400 FEG ESEM (15 keV) electron microscope. The sample powders were mounted on a double-sided adhesive tape and observed at different magnifications under two different detection modes: secondary and back-scattered electrons. EDS confirmed the nature of the components.

The surface composition of the samples was determined by X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS Ultra HSA, with VISION software for data acquisition and CASAXPS software for data analysis. The effect of the electric charge was corrected by reference to the carbon peak (284.6 eV). The Mn 3s multiplet splitting was used to calculate the average oxidation state (AOS) of manganese, according to the relationship [71]: $AOS = 8.95 - 1.13\ \Delta E$ (eV), where ΔE is the energy difference between the main peak and its satellite (multiplet splitting).

XRD analysis was carried out in a PAN'alytical X'Pert MPD equipped with an X'Celerator detector and secondary monochromator (Cu Kα = 0.154 nm, 50 kV, 40 mA). The collected spectra were analysed by Rietveld refinement using the PowderCell software, allowing the determination of the crystallite sizes.

The structural characterization of the samples was performed using a JEOL 2010F Field Emission Gun Transmission Electron Microscope (FEG-TEM), working in both High Resolution TEM (HR-TEM) and Scanning TEM (STEM) modes at 200 kV accelerating voltage. Further details for the other techniques can be found elsewhere [14,29,44,47,57,60,72–77].

2.3. Catalytic tests

Catalytic activity measurements for CO oxidation were performed using a continuous-flow reactor. The catalyst sample weight was 200 mg and the feed gas (5% CO, 10% O_2 in He) was passed through the catalytic bed at a total flow rate of 50 cm^3/min. The composition of the outgoing gas stream was determined by gas chromatography. Further details can be found elsewhere [29,47,57–63].

3. Results and discussion

3.1. Textural characterization of supports

Table 1 shows the BET surface areas obtained for the different cryptomelane catalysts. The values were around 55 m^2/g and did not change much upon incorporation of Cs, Li or Ti. Addition of gold also did not change the textural properties of cryptomelane.