Applied Catalysis B: Environmental 123–124 (2012) 27–35

Contents lists available at SciVerse ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Cu-modified cryptomelane oxide as active catalyst for CO oxidation reactions

Willinton Y. Hernández [a,*], Miguel A. Centeno [a], Svetlana Ivanova [a], Pierre Eloy [b], Eric M. Gaigneaux [b], José A. Odriozola [a]

[a] Departamento de Química Inorgánica e Instituto de Ciencia de Materiales de Sevilla, Centro Mixto Universidad de Sevilla-CSIC, Avda. Américo Vespuccio 49, 41092 Seville, Spain
[b] Université catholique de Louvain, Institute of Condensed Matter and Nanosciences, Division Molecules, Solids and Reactivity, Croix du Sud 2/17, B-1348 Louvain-la-Neuve, Belgium

ARTICLE INFO

Article history:
Received 1 March 2012
Received in revised form 17 April 2012
Accepted 19 April 2012
Available online 25 April 2012

Keywords:
CO oxidation
Manganese oxides
Octahedral molecular sieve (OMS)
Cu-modified cryptomelane

ABSTRACT

Manganese oxide octahedral molecular sieves (cryptomelane structure) were synthesized by a solvent-free method and tested in the total oxidation of CO (TOX), and preferential oxidation of CO in presence of hydrogen (PROX). The influence of Cu in the cryptomelane structure was evaluated by several characterization techniques such as: X-ray fluorescence (XRF), thermogravimetric analysis (TGA), hydrogen temperature programmed reduction (TPR-H_2) and X-ray photoelectron spectroscopy (XPS). The Cu-modified manganese oxide material (OMS-Cu) showed very high catalytic activity for CO oxidation in comparison to the bare manganese oxide octahedral molecular sieve (OMS). The improved catalytic activity observed in OMS-Cu catalyst was associated to a high lattice oxygen mobility and availability due to the formation of Cu—Mn—O bridges. In addition, under PROX reaction conditions the catalytic activity considerably decreases in the presence of 10% (v/v) CO_2 in the feed while the same amount of water provokes an improvement in the CO conversion and O_2 selectivity.

1. Introduction

Catalytic carbon monoxide oxidation is an important process in a number of applications including respiratory protection, CO gas sensors, CO_2 lasers, and automotive exhaust treatment [1,2]. In addition, due to the actual interest in proton exchange membrane fuel cell (PEMFC) technology, the preferential oxidation of CO in presence of hydrogen (PROX) has become a relevant technological and environmental application of this catalytic reaction [3,4]. The PROX process constitutes a key step in the H_2 fuel clean-up process for feeds coming from reforming reactions aiming at ensuring a high purity of hydrogen (CO concentration below 10 ppm). Catalysts based on noble metals nanoparticles (e.g. Pt, Ru and Au) supported on reducible metal oxides present high catalytic activity for CO oxidation [1,5]. Nevertheless, the high cost of precious metals has addressed the research on this topic to look for alternative catalysts. Considerable efforts have been directed toward the design of CO oxidation catalysts based on transition metal oxides or composite transition metal oxides.

Cryptomelane-type manganese dioxide materials have been found as effective catalysts for different oxidation reactions [6–10]. Cryptomelane, an octahedral molecular sieve, is an allotropic form of manganese oxide having a well-defined 2 × 2 tunnel structure (OMS-2) consisting in double chains of edge-shared MnO_6 octahedra and corner-sharing of the double chains (general formula $K_xMn_8O_{16}$). The pore size of the tunnel is 0.46 nm [11]. The average manganese oxidation state in cryptomelane is around 3.8 resulting from the presence of mainly Mn^{4+} and only small amounts of Mn^{3+} and Mn^{2+}. Potassium aqua-complex ions are situated inside the tunnels to provide charge balance and to stabilize the structure. The enhanced catalytic properties of this kind of materials have been associated with their porosity, tunnel structures, degree of crystallinity, reducibility and average oxidation state of the manganese atoms [6,8]. OMS-2 materials doped by metal cations such as Cu [7,12,13], Co [7,12], Ag [12,14,15], Ti [16], Ce [17], Zr [18], V [19] and Pb [20] have been also successfully applied to the oxidation of CO [12,14,15,20]. The improved catalytic properties observed in these materials were correlated with an enhanced lattice oxygen mobility and reactivity due to the interaction of the dopant cation with the manganese oxide structure [7,14,15]. However, the nature of the modification induced by the presence of the dopant cation in the crytomelane structure and the determination of the active sites still remains an unresolved subject.

In our previous work [7], the synthesis and characterization of a series of metal transition-doped OMS-2 structures (Cu^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}) dedicated as active catalysts in the preferential oxidation of CO in the presence of hydrogen was reported. The material modified with copper was shown to be the most active. This tendency was correlated with the reducibility and the lattice oxygen availability promoted by the presence of the dopant cation in the oxide

---

* Corresponding author. Present address: Université de Lyon, Institut de Recherches sur la Catalyse et l'Environnement de Lyon, UMR 5256, CNRS, Université Claude Bernard Lyon 1, 2 Avenue A. Einstein, F-69626 Villeurbanne, France.
E-mail address: yesid.hernandez@ircelyon.univ-lyon1.fr (W.Y. Hernández).

0926-3373/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcatb.2012.04.024

structure. In addition, the remarkable catalytic activity shown by Cu-doped cryptomelane catalyst was also related to the presence of finely dispersed CuO species as a very active phase for CO oxidation [21].

In the present work, we have focused on the physicochemical characterization of the Cu-modified OMS-2 materials synthesized by milling method, and their catalytic activity in the total oxidation of carbon monoxide reaction. In addition, considering the promising results already reported for this material in the PROX reaction [7] and the actual relevance of this catalytic process from environmental and technological point of view, the activity and selectivity of Cu-modified OMS-2 catalysts were here evaluated using more "realistic" PROX reaction conditions. The influence of the presence of 10% (v/v) CO_2 and/or 10% (v/v) H_2O in the reactive stream on the catalytic efficiency was therefore investigated.

2. Experimental

2.1. Synthesis

Cryptomelane oxides were prepared by solid-state reaction between Mn^{7+} and Mn^{2+} species in a high-energy ball milling with stainless steel balls and jar, as described elsewhere [6,7,22]. In a typical experiment, $KMnO_4$ (Panreac 99.0%) and $Mn(CH_3COO)_2{\cdot}4H_2O$ (Panreac 99.0%) (stoichiometric ratio 2:3) were mixed homogeneously and then milled for 1 h at 300 rpm. The resulting black solid was kept 4 h in a capped bottle at 80 °C. The obtained product was thoroughly washed with water until neutrality, dried at 80 °C overnight and finally calcined at 450 °C for 2 h (OMS). Cu-modified cryptomelane (OMS-Cu) was obtained by adding the corresponding metal acetate ($Cu(CH_3COO)_2{\cdot}H_2O$ Sigma–Aldrich > 98.0%) to the $KMnO_4$ and $Mn(CH_3COO)_2{\cdot}4H_2O$ mixture during the milling. The $Cu^{2+}/(Cu^{2+} + Mn^{2+})$ molar ratio employed was 0.1.

2.2. Characterization

The chemical analysis of the samples was performed by X-ray fluorescence spectrometry (XRF) in a Panalytical AXIOS PW4400 sequential spectrophotometer with a rhodium tube as the source of radiation.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were employed to study the thermal behavior of the samples. The experiments were performed with a TA Instrument model SDT Q600. The samples were heated from room temperature to 900 °C (10 °C/min^{-1}) in a nitrogen atmosphere (100 mL/min^{-1}). The heat flow data were dynamically normalized using the instantaneous weight of the sample at the respective temperature.

A homemade apparatus was used for obtaining the TPR profiles of the catalysts. In a typical experiment, about 50 mg of solid was loaded in a U-shaped quartz reactor and submitted to a gas mixture flow constituted by 5% hydrogen in Ar at 50 mL/min^{-1}, and then heated from room temperature to 900 °C at 10 °C/min^{-1}. A molecular sieve 13× was used to retain the reduction products, mostly H_2O and CO_2. The effluent gases were analyzed by means of a TCD detector. Hydrogen consumption was determined upon calibration of the system with CuO (Strem Chemicals, 99.999% Cu).

X-ray photoelectron spectroscopy (XPS) analyses were performed on a SSX 100/206 photoelectron spectrometer from Surface Science Instruments (USA) equipped with a monochromatized microfocused Al X-ray source (powered at 20 mA and 10 kV). The samples powders pressed in small stainless steel troughs of 4 mm diameter were placed on a ceramic carousel. The pressure in the analysis chamber was around 5×10^{-9} Torr. The analyzed area was approximately 1.4 mm^2 and the pass energy was set at 150 eV. In these conditions, the resolution determined by the full width at half maximum (FWHM) of the Au $4f_{7/2}$ peak was around 1.6 eV. A flood gun set at 10 eV and a Ni grid placed 3 mm above the sample surface were used for charge stabilization. The following sequence of spectra was recorded: survey spectrum, C 1s, O 1s together with Mn 3s, Mn 2p, Fe 2p, Cu 2p, K 2p and C 1s again to check the stability of charge compensation in function of time and the absence of degradation of the sample during the analyses. The binding energies were calculated with respect to the C—(C,H) component of the C 1s peak fixed at 284.8 eV. Data treatment was performed with the CasaXPS program (Casa Software Ltd, UK). The spectra were decomposed with the least squares fitting routine provided by the software with a Gaussian/Lorentzian (85/15) product function and after subtraction of a non-linear baseline (Shirley type). Molar fractions were calculated using peak areas normalized on the basis of acquisition parameters and sensitivity factors provided by the manufacturer.

2.3. Catalytic activity

For the TOX reaction, the catalysts were pretreated in a 30 mL/min activation flow of 21% O_2 balanced in He. The light-off curves (from room temperature to 450 °C, 5 °C/min) were obtained with a 42 mL/min reactive stream of 3.4% CO (Air Liquide, 99.997%) and 21% O_2 (Air Liquide, 99.999%) in He (Abelló Linde, 99.999%). The reaction was carried out in a conventional continuous flow U-shaped glass reactor working at atmospheric pressure where 80 mg of sample was placed between glass wool. The reaction was followed by mass spectrometry (Balzers® Thermostar).

Preferential oxidation of CO in the presence of hydrogen reactions were carried out at atmospheric pressure in a stainless steel fixed bed reactor (inner diameter of 0.9 cm) with 100 mL/min of a reaction feed, composed by 2% CO (Air Liquide, 99.997%), 1% O_2 (Air Liquide, 99.999%), 50% H_2 (Abelló Linde, 99.999%) and N_2 (Abelló Linde, 99.999%) as balance. The catalyst (100 mg, $100 < \phi < 200$ μm) was diluted in crushed glass of the same particle size, enough to obtain a bed height of 0.5 cm. Prior to all catalytic measurements, the samples were treated in a 21 vol.% O_2/N_2 mixture at 300 °C for 1 h. Products and reactants were separated and quantified by on-line gas chromatography (Agilent 7890A), employing Haysep Q®, Porapak Q® and molecular sieve columns.

The influence of CO_2 and H_2O on the catalytic activity was investigated by co-introducing 10% CO_2 and/or 10% H_2O in the reaction mixture.

The CO conversion, O_2 conversion and O_2 selectivity were calculated using the following formulas:

$$\text{CO conversion}\,(\%) = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100. \quad (1)$$

$$\text{O}_2\text{ conversion}\,(\%) = \frac{[\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}}{[\text{O}_2]_{\text{in}}} \times 100. \quad (2)$$

$$\text{O}_2\text{ selectivity}\,(\%) = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{2([\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}})} \times 100. \quad (3)$$

According to the statistics treatment applied to all the data points presented (error of twice the standard error of several analyses), the catalytic curves obtained represent roughly a 95% of confidence interval.

3. Results and discussions

3.1. Chemical analysis

The XRF results obtained for the synthesized solids are presented in Table 1. The presence of iron, coming from the balls and jar used in the milling, was detected in both materials with and without added copper. Nevertheless, it is very interesting to