



# Storage capacity and oxygen mobility in mixed oxides from transition metals promoted by cerium



Camilo Perdomo<sup>a</sup>, Alejandro Pérez<sup>b</sup>, Rafael Molina<sup>a</sup>, Sonia Moreno<sup>a,\*</sup>

<sup>a</sup> Estado Sólido y Catálisis Ambiental (ESCA), Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, Carrera 30 45-03, Bogotá, Colombia

<sup>b</sup> Grupo de Investigación Fitoquímica (GIFUJ), Departamento de Química, Facultad de Ciencias, Pontificia Universidad Javeriana, Carrera 7 No. 43-82, Bogotá D.C, Colombia

## ARTICLE INFO

### Article history:

Received 5 March 2016

Received in revised form 19 April 2016

Accepted 21 April 2016

Available online 25 April 2016

### Keywords:

Mixed oxides

Cooperative effect

Oxygen vacancies

OSC

Isotopic exchange

## ABSTRACT

The oxygen mobility and storage capacity of Ce–Co/Cu–MgAl or Ce–MgAl mixed oxides, obtained by hydrotalcite precursors, were evaluated using Toluene-temperature-programmed-reaction, <sup>18</sup>O<sub>2</sub> isotopic exchange and O<sub>2</sub>–H<sub>2</sub> titration. The presence of oxygen vacancies-related species was evaluated by means of Electron Paramagnetic Resonance. A correlation was found between the studied properties and the catalytic activity of the oxides in total oxidation processes. It was evidenced that catalytic activity depends on two related processes: the facility with which the solid can be reduced and its ability to regenerate itself in the presence of molecular oxygen in the gas phase. These processes are enhanced by Cu–Co cooperative effect in the mixed oxides. Additionally, the incorporation of Ce in the Co–Cu catalysts improved their oxygen transport properties.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

The presence of oxygen vacancies in the structure of mixed oxides of transition metals is decisive in the redox reactions in which they participate, aside from being fundamental in the reaction mechanism in catalytic oxidation processes [1].

The use of rare earths as catalysts or as promoters in mixed oxides, especially Ce, has been widely documented due to the stability of the corresponding redox pair which confers interesting properties of oxygen transport to the crystalline network of the oxide [2]. Among the most relevant applications of the solids made up of these elements is the oxidation of Volatile Organic Compounds (VOC's) [3]. It has been established that these oxidation reactions can occur without the presence of oxygen during a short time period and at high temperatures [4]. Additionally, it has been reported that the activity of the catalysts is influenced by the presence of certain oxygen species on the surface, which are consumed during the course of the reaction and can be regenerated in the presence of an atmosphere which is rich in this gas [5]. These aspects are related to the oxygen mobility in the material which basically depends on the oxygen content in the network, the temperature,

the composition of the oxide and obviously, is intimately related to the presence non-stoichiometric defects in the oxide [6–9]. The use of Co and Cu mixed oxides based on the calcination of hydrotalcite type solids in oxidation reactions of VOCs has been reported, highlighting the increase in catalytic activity due to the cooperative effect produced between these two metals when they are both present in the same solid. [10]. Likewise, it has been reported that the incorporation of rare earths especially Ce, produce a positive effect with regard to the activity of the solids and this is attributed mainly to the improvement of the oxygen transport properties in the catalysts [6,10].

In this work, the results by X-ray Diffraction and X-ray Fluorescence regarding the structural properties and chemical composition, as well as the properties related to oxygen mobility in Co/Cu–MgAl mixed oxides are analyzed, as well as the effect of the incorporation of Ce, through characterizations by means of temperature programmed reaction (TPR) with toluene [4], the determination of the oxygen storage capacity (OSC) using H<sub>2</sub> and O<sub>2</sub> titration techniques, and isotopic exchange using <sup>18</sup>O<sub>2</sub>. Additionally, the results obtained by means of electronic paramagnetic resonance for the detection of species associated to the presence of oxygen vacancies in the solids under study are presented.

Using the temperature of maximum CO<sub>2</sub> production and its relative production as comparing criteria of the solids by Toluene-TPRS,

\* Corresponding author.

E-mail address: [smorenog@unal.edu.co](mailto:smorenog@unal.edu.co) (S. Moreno).

it can be evaluated the catalytic activity of the solids under extreme reaction conditions (absence of oxygen in the reactor feed) [4].

The OSC of the solids is related to the most reactive oxygen species in the solid in order to carry out the reaction process with a reducing agent (i.e. H<sub>2</sub>). Additionally, OSC measures are also related to the easiness with which these oxygen-reactive species are regenerated with O<sub>2</sub> in the gas phase [6–8,11].

Isotopic exchange with <sup>18</sup>O<sub>2</sub> gives information about oxygen incorporation in the catalyst (i.e. oxygen mobility). The results obtained by this technique are usually expressed in terms of the concentration of homo-nuclear (<sup>16</sup>O<sub>2</sub>, <sup>18</sup>O<sub>2</sub>) and hetero-nuclear (<sup>16</sup>O<sup>18</sup>O) oxygen species in the fluent gas, which depends on the easiness of the <sup>18</sup>O<sub>2</sub> uptake by the solid and the ability to dissociate the oxygen molecule over its surface [6–8].

The findings provide more knowledge about oxygen transport and redox properties in transition and rare earth metal mixed oxides, highlighting the essential effect of the chemical composition of the materials on these properties. Also, the results bring to light the close relationship that exists between the oxygen mobility and OSC of these solids and their catalytic behavior in total oxidation reactions of VOCs (toluene).

## 2. Experimental

Mixed oxides (MO) were obtained by the calcination at 500 °C for 16 h from hydrotalcite type precursors (HT) ([M<sup>2+</sup> + Mg<sup>2+</sup>]/Al<sup>3+</sup> = 3; M<sup>2+</sup>: Co<sup>2+</sup> or Cu<sup>2+</sup>). Solids were composed of Mg, Al (HT/MO-MgAl) and 20% mol of Co or Cu (HT/MO-Co and HT/MO-Cu), as well as with a Co:Cu equimolar mixture (1:1)(HT/MO-CoCu). The effect of the incorporation of Ce through a reconstruction process of the hydrotalcites from MO-MgAl and MO-CoCu mixed oxides with 5% mol Ce (MO-CoCuCe) was also studied. These solids were used in previous works as catalysts for the total oxidation of VOCs, revealing considerable differences in catalytic activity [10,12,13].

X-ray diffraction patterns (XRD) of hydrotalcite precursors and final mixed oxides were obtained using a Panalytical X Pert PRO MPD device, equipped with a Cu K $\alpha$  anode.

Chemical composition of the mixed oxides was evaluated by X-ray Fluorescence (XRF) with Philips MagiX Pro PW2440 equipment.

For the Toluene-temperature-programmed-reaction (TPRS) the sample (100 mg) was pretreated with an air stream at 400 °C for 2 h. Then, it was subjected to a stream of 600 ppm of toluene in He (flow rate 200 mL/min) with a heating rate of 10 °C/min to 400 °C [4]. The production of CO<sub>2</sub> was monitored using a Bacharach Model 3150CO<sub>2</sub> analyzer equipped with an IR detector.

The catalytic activity tests were achieved using the same conditions mentioned above for the TPRS, changing the mixture of 600 ppm of toluene in He for a mixture of 600 ppm of toluene in air with the same flow rate.

In the evaluation of the Oxygen Storage Capacity, the samples (30 mg) were pretreated at 400 °C with an air flow of 30 mL/min for 1 h. The cleaning of the solid was carried out using an Ar flow of 30 mL/min for 0.5 h and then pulses of 20  $\mu$ L of H<sub>2</sub> and O<sub>2</sub> were injected alternately, at intervals of 2 min at 400 °C. The consumption of H<sub>2</sub> and O<sub>2</sub> was analyzed as well as the production of H<sub>2</sub>O, by means of an OmniStar™ ThermoStar™ GSD 320 mass spectrometer [7].

For the isotopic interchange with <sup>18</sup>O<sub>2</sub>, the sample (30 mg) must be treated at 400 °C for 1 h in the presence of a 30 mL air flow. The excess O<sub>2</sub> is removed using a 30 mL/min flow of Ar. The <sup>18</sup>O<sub>2</sub> is injected by pulses (1 pulse for each temperature), while an Ar flow is used as a carrier gas and the products of the reaction are monitored at different temperatures (200 °C, 260 °C, 340 °C and 400 °C) with an OmniStar™ ThermoStar™ GSD 320 mass spectrometer [14,15].

**Table 1**  
Chemical composition analysis of the catalysts by X-ray Fluorescence.

Solid	Molar proportions					Cell parameters	
	Co	Cu	Mg	Al	M <sup>2+</sup> /M <sup>3+</sup>	a (nm)	c (nm)
MO-MgAl			1.18	0.39	3.02	3.06	2.33
MO-Co	0.46	–	0.74	0.40	3.00	3.07	2.36
MO-Cu	–	0.39	0.73	0.37	3.03	3.07	2.31
MO-CoCu	0.19	0.26	0.60	0.34	3.09	3.07	2.33

**Table 2**  
Chemical composition of Ce-promoted solids by X-ray Fluorescence.

Solid	Co/Al	Cu/Al	Mg/Al	M <sup>2+</sup> /M <sup>3+</sup>	%Ce
MO-Ce	–	–	3.02	3.02	3.77
MO-CeCoCu	0.38	0.55	1.75	2.7	3.33

In this manner, the oxygen mobility in the different catalysts can be evidenced by means of the determination of the concentrations of the desorption products <sup>16</sup>O<sup>18</sup>O ( $m/z = 34$ ) <sup>18</sup>O<sup>18</sup>O ( $m/z = 36$ ) and <sup>16</sup>O<sup>16</sup>O ( $m/z = 32$ ).

The EPR spectrums of the samples (8 mg) were taken with Bruker ESP 300E equipment in a quartz cell, at a temperature of 293 K with a microwave frequency of 9,44 GHz (X Band).

## 3. Results and discussion

The initial characterization of the catalysts by XRD and XRF showed the successful achievement of the hydrotalcite precursors (Fig. 1a) and the incorporation of the metallic active phases into the solids (Table 1).

The elemental analysis by XRF (Tables 1 and 2) verifies the successful introduction of the metals (cobalt and copper) into the modified solids with respect to the original hydrotalcite (MO-MgAl). The values of the ratio M<sup>2+</sup>/M<sup>3+</sup> are very close to those established in the synthesis of these materials (M<sup>2+</sup>/M<sup>3+</sup> = 3) which reflects the effectiveness of the preparation method. Likewise the presence of cerium is verified, evidencing that the reconstruction method allows the Ce incorporation in the hydrotalcite structure.

In Table 2 is appreciable that the incorporation of cerium does not correspond to the expected nominal amount (5%). This lesser introduction of the transition metal could be the result of a partial metal extraction possibly due to the formation of metallic chelates during the synthesis (Ce-EDTA) and removed in step washes.

In all diffraction patterns hydrotalcites strong signals can be observed ( $2^\circ\theta = 11.3^\circ, 22.7^\circ$  and  $34.6^\circ$ ), values reported in literature for hydrotalcite-like solids (JCPDS 14-191). These signals are lost after the calcination process of the solids (Fig. 1b) due to the formation of periclase phase in all solids (MgO JCPDS 45-0946) and the corresponding oxides of copper and cobalt: tenorite (CuO JCPDS 48-1548) and Co<sub>3</sub>O<sub>4</sub> oxides (JCPDS 42-1467). In the MO-Co solid can be observed segregated phases with probably low crystalline structure (broad peaks) which can be observed in Fig. 1b, where the presence of Co<sub>3</sub>O<sub>4</sub> segregated as a free oxide is appreciable. The presence of a mixture of two spinel phases very difficult to differentiate by XRD as CoAl<sub>2</sub>O<sub>4</sub> (JCPDS 440160) and Co<sub>2</sub>AlO<sub>4</sub> (JCPDS 380814) they may be the cause of the breadth of diffraction peaks, whereas for the solid MO-Cu the diffraction patterns prevail the signs of periclase (MgO) and tenorite (CuO).

The absence or decrease in intensity of the CuO and Co<sub>3</sub>O<sub>4</sub> signals in the solid MO-CoCu show a total miscibility of these metals in the brucite-like structure. Pérez et al. [12] establish the absence of signals in the XRD patterns of the Co-Cu solid to the stabilization and incorporation of Co<sup>2+</sup> in the interlayer of the magnesium precisely because of the presence of copper in the structure of the mixed oxide.

Download English Version:

<https://daneshyari.com/en/article/5347421>

Download Persian Version:

<https://daneshyari.com/article/5347421>

[Daneshyari.com](https://daneshyari.com)