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Effect of Mg and Al on manganese oxides as catalysts for VOC oxidation



María Haidy Castaño, Rafael Molina, Sonia Moreno*

Estado Sólido y Catálisis Ambiental (ESCA), Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, Cra 30 N° 45-03, Bogotá, Colombia

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ABSTRACT

Manganese mixed oxides with the compositions Mn-Mg-Al-O and Mn-O were synthesized by the self-combustion method. The effects of Mg and Al incorporation on the structural, textural, redox and catalytic properties of the manganese oxides were evaluated. The catalysts were characterized by X-ray diffraction (XRD), N₂ adsorption, temperature-programmed desorption of oxygen (O₂-TPD), temperature-programmed reduction (H₂-TPR), oxygen storage capacity (OSC), ¹⁸O/¹⁶O oxygen isotope exchange, and their catalytic performance was evaluated in the oxidation of toluene, ethyl acetate and 2-propanol. The analyses showed that the use of a glycine/nitrate ratio equal to 0.56 in the self-combustion favors the formation of the Mn₃O₄ phase and the incorporation of Mg and Al into the structure stabilizes this phase after a thermal process. In addition, the surface area increases, the particle size decreases, and the presence of electrophilic oxygens is favored, which increases the adsorption sites, exposes the active centers and facilitates the occurrence of redox cycles, leading to a better catalytic performance in the total conversion of the oxygenated compounds on the Mn-Mg-Al-O mixed oxide. In the oxide that only contains manganese, the presence of nucleophilic oxygens with great mobility was observed, leading to its good activity in the oxidation of the VOCs.

The catalytic tests showed that a high oxygen exchange capacity leads to lower temperatures of conversion of toluene, which suggests that, for the oxidation of aromatic compounds, the lattice oxygen plays a fundamental role in the catalytic activity. In contrast, in the oxidation of oxygenated compounds that require lower temperatures of conversion, the existence of surface oxygens such as O₂⁻ and O⁻ favors the catalytic process and therefore ensures superior activity in the transformation of ethyl acetate and 2-propanol on the Mn-Mg-Al-O mixed oxide.

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1. Introduction

Manganese oxides are among the most active catalysts in the oxidation of VOCs and show high efficiency in the oxidation of ethyl acetate, toluene, ethanol and other catalytic oxidation processes [1–3]. Their catalytic properties are attributed to the ability of the metal to form oxides with different oxidation states, Mn²⁺/Mn³⁺ or Mn³⁺/Mn⁴⁺ and to the participation of the lattice oxygens in the catalytic process through a Mars Van Krevelen mechanism [4].

Generally, the oxide mixture presents better physico-chemical and catalytic properties than the individual oxides due to cooperative effects between the elements and changes in the structural or redox properties. Thus, the mixed oxides from hydrotalcite-type

precursors consisting of Mg-Al-M (M: Mn, Co, Cu, Fe) are active catalysts in the oxidation of different volatile organic compounds (VOCs) thanks to the unique properties of these oxides, such as high surface area, good thermal stability, good redox properties, homogeneous dispersion of the elements and basic properties, among others [5–8].

Hydrotalcites present a laminar structure formed by Mg²⁺ and Al³⁺ ions that can be substituted by divalent or trivalent cations, producing materials with different compositions [9]. Generally, the formation of hydrotalcites as oxide precursors proceeds through co-precipitation which usually requires prolonged times and the need to separate the product after the precipitation. Thus, self-combustion is an interesting, versatile and accessible method for obtaining mixed oxides because is possible to directly generate the oxides in much shorter synthesis times without the need to form precursors.

* Corresponding author.

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

Self-combustion is an oxidation–reduction reaction between a fuel and an oxidizer. It generates mixed oxides with great potential in reactions of catalytic interest, since the intimate mixture between the constituents of the reaction and the rapid evolution of gaseous products during the combustion dissipate heat, limit the temperature increase and inhibit particle size growth, allowing the formation of final materials rich in defects with well-dispersed active phases and highly porous structures [10].

In this work, manganese oxides were synthesized using self-combustion as the synthesis method. One of the oxides was prepared maintaining a composition similar to that obtained when using hydrotalcite-type precursors (Mg + Mn/Al), while the other solid corresponds to an oxide of manganese alone. The characteristics of these catalysts were compared to evaluate the effect of the presence and absence of Mg and Al on the structural, textural and redox properties, as well as the oxygen species and their mobility in the catalysts. In addition, the catalytic potential of the solids in the total oxidation of three VOCs of different nature was studied. The interest in the transformation of these organic compounds is because these substances come from industrial processes, mobile sources or household products and are considered to be among the most polluting substances in the atmosphere due to their high vapor pressure and easy evaporation at room temperature [11].

In addition, to determine whether the self-combustion method allows for the obtaining of materials with characteristics that are appropriate to obtain catalysts for the oxidation of VOCs, a manganese oxide was synthesized and characterized by thermal decomposition, and its properties were compared with those of the oxides synthesized by self-combustion.

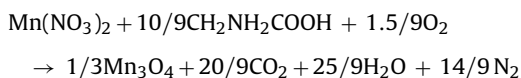
2. Experimental

2.1. Catalyst synthesis

For the synthesis of the oxides, nitrate solutions of $\text{Mg}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$ and $\text{Mn}(\text{NO}_3)_2$ were used as oxidizing agents and a solution of glycine [$\text{CH}_2\text{NH}_2\text{COOH}$] as fuel. A fuel/oxidant stoichiometric ratio of 0.56 was used in all cases, which is the ratio that leads the best redox and catalytic properties on manganese oxides [12]. For the mixed oxides containing Mg–Al and Mg–Al–Mn, molar ratios of $\text{M}^{2+}/\text{M}^{3+} = 3$ and $\text{Mn}^{2+}/\text{Mg}^{2+} = 1$ were maintained.

The oxides were obtained by the addition of the respective nitrates to glycine, maintaining constant agitation. The resulting solution was evaporated slowly until a gel was obtained, which was heated to approximately 100 °C (~10 min). Once the ignition reaction was reached (~3 min), a powder was obtained and calcined at 500 °C for 4 h to remove remaining carbonaceous residues and finally obtain the oxides; **OMn**, corresponds to the manganese oxide that contains only manganese; **OMgAl**, consists of Mg–Al; and **OMnMgAl**, contains Mn–Mg–Al.

The general reaction between manganese nitrate and glycine, assuming only the generation of CO_2 , H_2O , N_2 and the respective manganese oxide, can be described as follows:



In comparison a manganese oxide **MnOx** was synthesized by means of the decomposition of $\text{Mn}(\text{NO}_3)_2$ at 500 °C for 4 h.

2.2. Characterization

The X-ray patterns were collected in a *Panalytical X'Pert PRO MPD* diffractometer equipped with a copper anode ($\lambda = 1.5406 \text{ \AA}$), using a

speed of 1° min^{-1} and a step size of 0.02° . The diffraction patterns were identified by comparison with the JCPDS (Joint Committee of Powder Diffraction Standards) database.

To determine the specific area, the Brunauer–Emmett–Teller (BET) model and a Micromeritics ASAP 2020 instrument were used. The samples were degassed at 350 °C for 4 h, and the N_2 adsorption–desorption isotherms at -196°C were then obtained.

The temperature-programmed characterizations (H_2 -TPR and O_2 -TPD) were conducted in a CHEMBET 3000 QUANTACHROME device equipped with a thermal conductivity detector. For O_2 -TPD, the mixed oxides (0.100 g) were degassed at 400 °C for 1 h in the presence of He. The adsorption of O_2 (9.99% O_2 in He) was performed at 400 °C and at room temperature, under the same atmosphere for 1 h for each temperature. A He flow of 50 mL min^{-1} was used to remove the excess O_2 , and finally, the O_2 desorption was carried out by increasing the temperature at a heating rate of 10°C/min up to 900 °C.

For the H_2 -TPR, the mixed oxides (100 mg) were degassed at 400 °C under a flow of 50 mL min^{-1} of N_2 and reduced under a flow of 30 mL min^{-1} of H_2/Ar (10% v/v) with a heating ramp-up of 10°C/min .

In the determination of the oxygen storage capacity (OSC) of mixed oxides, 0.015 g of catalyst in 0.100 g of SiC was pre-oxidized under an air flow of 10 mL min^{-1} (21% O_2) at 400 °C for 1 h and subsequently purged with argon until $^{32}\text{O}_2$ was not detected. For the analyses, the temperature was maintained at 400 °C and the Ar flow at 10 mL min^{-1} , and successive pulses of 50 μL of H_2 (99.99%) were injected until the samples were saturated, followed by successive pulses of 50 μL of O_2 (15.2% in He) to re-oxidize the solid until no O_2 consumption was observed. The concentrations of the output gases H_2 , O_2 , H_2O , Ar and He were monitored by mass spectrometry (OmniStar mass spectrometer) following the signals $m/z = 2, 32, 18, 40$ and 4, respectively.

The OSC was calculated based on the amount of oxygen consumed during the re-oxidation stage after the H_2 pulses and expressed in terms of $\mu\text{mol O}_2 \text{ g}^{-1}$ of catalysts. The OriginPro 8.5 software was used to quantify the areas of each of the pulses associated with the O_2 signal.

In the $^{18}\text{O}/^{16}\text{O}$ isotope exchange analyses, the samples (0.015 g with 0.100 g of SiC) were treated under a flow of air (10 mL min^{-1}) at 400 °C for 1 h. After pretreatment, the sample was left to cool to 200 °C under a flow of argon. Pulses of 20 μL of $^{18}\text{O}_2$ were injected into the samples at 200, 260, 350 and 400 °C (one pulse at each temperature) in the presence of an argon flow of 10 mL min^{-1} . The composition of the output gas was monitored by mass spectrometry (OmniStar mass spectrometer) following the signals $m/z = 36, 34$ and 32, corresponding to $^{18}\text{O}_2$, $^{18}\text{O}^{16}\text{O}$ and $^{16}\text{O}_2$, respectively. The OriginPro 8.5 software was used to quantify the areas under the signals of the mentioned species.

In the catalytic evaluation, a fixed-bed reactor that operates at atmospheric pressure and in the temperature range from 400 to 100 °C was used. The samples (0.200 g sieved $< 250 \mu\text{m}$) were pre-treated in an air flow (21% O_2) at 400 °C for 1 h. The conversion curves were obtained by cooling at 1.5°C/min from 400 to 100 °C while maintaining a total flow of 280 mL min^{-1} of air with the VOC to be treated (600 ppm of toluene, 1000 ppm of ethyl acetate or 1000 ppm of 2-propanol). The reactants and products of the oxidation of toluene and ethyl acetate were analyzed in line using a Shimadzu GC-17A gas chromatograph, and the production of CO_2 was analyzed using a Bacharach Model 3150 CO_2 analyzer equipped with an IR detector. The oxidation reaction of 2-propanol was monitored by mass spectrometry (Balzers OmniStar mass spectrometer) following the signals $m/z = 45, 43, 41, 18$ and 44, assigned to 2-propanol, acetone, propene, water and carbon dioxide, respectively.

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