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Cooperative effect of the Co–Mn mixed oxides for the catalytic oxidation of VOCs: Influence of the synthesis method

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ABSTRACT

Mixed oxides of manganese, cobalt and their mixture were synthesized by auto-combustion and co-precipitation methodology maintaining a constant M^{2+}/Al^{3+} ratio of 3.0, which is characteristic of the oxides obtained from the thermal decomposition of hydrotalcite-type precursors (in manganese oxides $M^{2+} = Mg + Mn$, in cobalt oxides $M^{2+} = Mg + Co$ and in manganese-cobalt oxides $M^{2+} = Mg + Mn + Co$). The catalysts were characterized by the following techniques: X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM), N_2 adsorption, temperature-programmed reduction (H_2-TPR), temperature programmed desorption of oxygen (O_2-TPD) and ^{18}O isotope exchange. All of the materials were evaluated for the catalytic oxidation of two organic compounds of different reactivities: toluene and 2-propanol. It was observed that the joint participation of the absorbed oxygen species on the surface and the lattice oxygen atoms are responsible for the catalytic activity of the materials. However, the redox properties and the oxygen mobility play a determining role in the oxidation of the two volatile organic compounds (VOCs), with the oxygen mobility playing a more significant role in the cobalt oxides, whereas the redox properties are fundamental in the manganese oxides and in the Co and Mn mixture. The existence of a cooperative effect between the Co and Mn oxides is demonstrated when the co-precipitation method is used for the synthesis of the mixed oxide. This effect is not observed when auto-combustion is used for the synthesis; therefore, the autocombustion manganese oxide is the most active catalyst in the oxidation of the two VOCs by this methodology.

1. Introduction

Volatile organic compounds (VOCs) are an important type of atmospheric pollutant emitted from diverse industrial and domestic sources. Because these compounds generate negative effects on human health and on the environment, the implementation of control technologies is required to eliminate or transform them. Catalytic oxidation appears to be the optimum technology to reduce the VOC emissions because a lower oxidation temperature is required (typically <400 °C) and it generates a smaller amount of NO_x [1]. However, the catalytic formulation is not elementary due to the great variety of VOC molecules and their different reactivity; therefore, there is continued interest in the search for new catalytic materials that can achieve a greater efficiency in the removal of these contaminants.

Numerous synthesis methods have been used for the preparation of metal oxides [2–4], with the co-precipitation method being one of the most commonly used for the production of hydrotalcite compounds as precursors of mixed oxides [5,6].

The hydrotalcite structure is derived from the brucite $Mg(OH)_2$ where part of Mg^{2+} is substituted by a trivalent metal like Al^{3+}. Also, it is possible to substitute Mg^{2+} and Al^{3+} ions by divalent cations ($M^{2+} = Zn, Mn, Co\ldots$) and trivalent cations ($M^{3+} = Fe, Cr\ldots$), respectively, and the excess of positive charge generated is compensated by anions within the interlayer spacing [7].

Thermal decomposition of hydrotalcite compounds induces the formation of oxides with elevated surface areas (100–300 m^2/g), homogeneous inter-dispersion of the elements, dispersion of the active phase, synergistic effects and a basic character, which are some of the most interesting properties of the mixed oxides achieved using the hydrotalcite-type precursor [6,8–10]. The interest in these materials have increased because they are used in different reactions of industrial importance such as ethanol reforming [11], removal of SO_2 and NO_x [12] and VOC oxidation [7,13].

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Recently, the auto-combustion process has gained significant interest as a synthesis method due to its good textural properties and the excellent dispersion and distribution of the active phase obtained in the final oxides in short synthesis times. The characteristics that contribute to the unique properties of the synthesized product can be summarized as follows: (i) the initial reaction medium (aqueous solution) enables mixing of the reactants at a molecular level, allowing a precise and uniform formulation of the desired composition; (ii) the high reaction temperatures ensure products with a high purity and crystallinity; and (iii) the short duration of the process and the formation of several gases inhibit the growth of the particle size and favor the synthesis of solids with high surface areas [14,15]. Additionally, the auto-combustion process is based on systems in which the reactants react exothermally when they reach ignition and sustain the combustion wave. The combustion temperatures can be high (~5000 K) and the velocity of the combustion wave is high (~25 cm/s). The extreme temperature gradients and the rapid cooling rate associated with the reaction allow the generation of very stable products with a significant concentration of defects [16]. This synthesis method allows the formation of mixed oxides with good redox properties, good distribution, excellent dispersion of the active phases and similar characteristics to those oxides generated by using hydrotalcite, without the necessity of passing through the initial formation of a precursor.

Systems based on manganese and cobalt oxides are considered efficient catalysts in the oxidation of VOCs [17,18]. Generally, the mixture of these oxides presents better characteristics than the individual oxides due to the cooperative effects between the elements, the changes in the redox properties or the structural changes of the material. Kovanda et al. [19] have reported a series of Co–(Mg)–Mn–(Al) oxides prepared from hydrotalcite-type precursors used in the oxidation reaction of ethanol in which the catalytic activity increases with the increasing (Co + Mn) content, resulting in a higher content of reducible species in the structure. For the oxidation of toluene, ethanol and butanol on the mixed oxides of Co, Mn and CoMn, Aguilera et al. [20] have reported that the oxide presenting the best catalytic performance is the mixed oxide containing Co and Mn in which the generation of amorphous phases and redox cycles are responsible for this behavior. However, to our knowledge, there is limited information on the possible cooperative effects that can exist between the oxides of Co and Mn synthesized by routes different from the traditional co-precipitation method.

In this study, our attention was focused on the synthesis of the mixed oxides of manganese, cobalt and their mixtures M–Mg–Al (M = Mn and/or Co) using auto-combustion and co-precipitation to evaluate the influence of the synthesis method on the catalytic, redox, structural and textural properties and the possible cooperative effect between the phases present in the material. Furthermore, when considering the importance of the oxygen mobility in the catalytic performance of the metal oxides [21,22], in the present study, we evaluated the influence of this property on the catalytic oxidation of the two VOCs.

2. Experimental

2.1. *Synthesis of the catalysts*

2.1.1. *Auto-combustion*

For the synthesis of the Mg–Al–M mixed oxides (M= Mn and/or Co) by the auto-combustion method, solutions of the following nitrates were used: $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Mn(NO_3)_2{\cdot}6H_2O$ and/or $Co(NO_3)_2{\cdot}6H_2O$ acting as oxidizers. A solution of glycine [CH_2NH_2COOH] was used that acts as a fuel, maintaining the following constant molar ratios: [Mg^{2+} + (Mn^{2+} and/or Co^{2+})/Al^{3+} = 3.0], [(Mn^{2+} and/or Co^{2+})/Mg^{2+} = 1.0], [Co^{2+}/Mn^{2+} = 0.5] and with a fuel/oxidizer stoichiometric ratio equal to 0.56 in all of the cases.

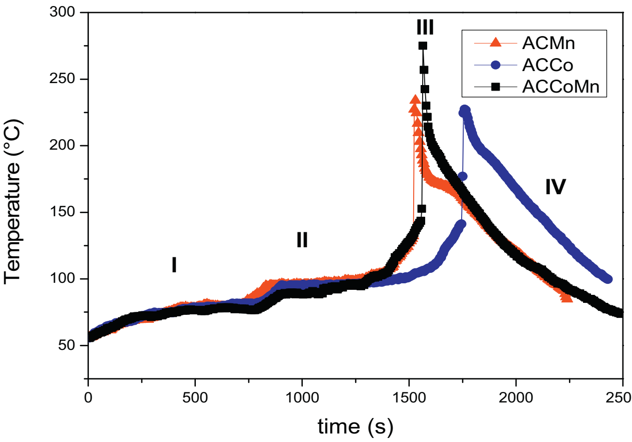

Fig. 1. Profile of the temperature *vs* time for the oxides prepared by auto-combustion.

The Mg–Al–Mn, Mg–Al–Co and Mg–Al–Co–Mn mixed oxides were obtained by the addition of the respective nitrates to glycine while maintaining constant agitation. The resulting solution was slowly evaporated until a gel was obtained, which was heated to approximately 100 °C, providing the impetus to perform the ignition process. Once the ignition reaction was achieved a powder was obtained, which was calcined at 500 °C for 4 h to eliminate the remaining carbonaceous residues and finally, obtaining the corresponding oxides, referred as ACMn, ACCo and ACCoMn according to the active phase (AC represents auto-combustion).

In summary, the auto-combustion proceeds in four stages corresponding to the process of water evaporation (**I**), gel formation (**II**), ignition with the generation of the oxides (**III**) and the cooling of the solid system (**IV**) [14,23], respectively.

Fig. 1 shows the profile of the temperature *vs* time for the mixed oxides obtained by auto-combustion. The maximum temperatures registered by the thermocouple do not correspond to the temperature values reported, which are approximately 1500 °C [14,24,25], because the data collection rate is lower than the combustion rate.

2.2. *Co-precipitation*

The mixed oxides of Mn, Co and the Co–Mn mixture were obtained by the thermal decomposition of the hydrotalcite-type precursors, which were obtained by the simultaneous co-precipitation method maintaining constant ratios: M^{2+}/Al^{3+} = 3.0, (M^{2+} = Mg, Mn and/or Co), (Mn^{2+} and/or Co^{2+})/Mg^{2+} = 1.0 and Co^{2+}/Mn^{2+} = 0.5.

For the synthesis, the nitrates of Mg^{2+}, Al^{3+}, Mn^{2+} and/or Co^{2+} were mixed and added dropwise to a 0.2 M K_2CO_3 solution with constant agitation, maintaining the pH between 9.5 and 10.5 (*via* the addition of a 1 M NaOH solution). The obtained precipitate was aged for 24 h without agitation. Subsequently, the solid was washed and dried in air at 60 °C for 18 h (obtaining the hydrotalcite) and calcined at 500 °C for 16 h to obtain the respective oxides: CPMn, CPCo and CPCoMn (CP indicates co-precipitation).

2.3. *Characterization*

The temperature–time profile of the oxide synthesis process by auto-combustion was collected through a K-type thermocouple