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Full Length Article

Insights on the combustion mechanism of ethanol and *n*-hexane in honeycomb monolithic type catalysts: Influence of the amount and nature of Mn-Cu mixed oxide

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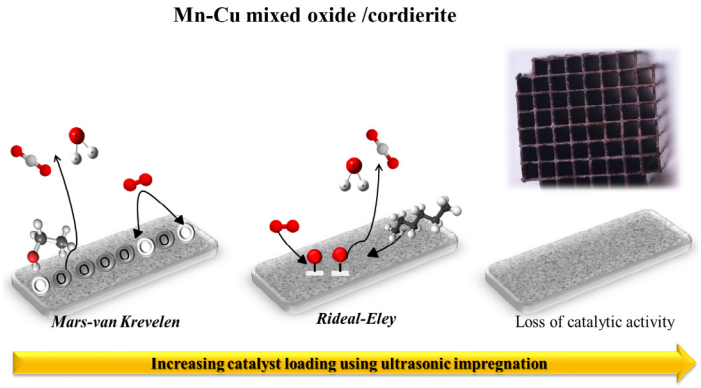
HIGHLIGHTS

- Mn-Cu catalysts deposited on ceramic monoliths using ultrasonic impregnation.
- Mn-Cu catalysts evaluated in the total oxidation of volatile organic compounds of different chemical nature.
- Effect of alumina and active phase loads in the catalytic activity and mechanisms of oxygen supply.

GRAPHICAL ABSTRACT



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ABSTRACT

Mn-Cu mixed oxides were deposited by ultrasonic impregnation on ceramic honeycomb monoliths. Its catalytic performance was evaluated in the combustion of ethanol and *n*-hexane, VOC molecules of different chemical nature. The catalysts were characterized by N_2 physisorption, SEM-EDS, XRD, X-ray fluorescence, XPS, TPR, TPD-O_2 and OSC measurements. It was observed that the catalyst with the lowest content of Mn-Cu phase was the most active in the combustion of ethanol. This was attributed to the higher content of Mn^{4+} and the increase of lattice oxygen mobility, which would favor a Mars-van Krevelen type mechanism. The catalyst with a medium content of Mn-Cu, proved to be the most active in the combustion of *n*-hexane. This was associated with a high content of oxygen vacancies and easy availability of oxygen adsorbed on the surface, promoting the combustion of *n*-hexane, possibly through a Rideal-Eley type mechanism. The catalyst with the highest content of the Mn-Cu phase showed low activity in combustion of ethanol and *n*-hexane, which was attributed to a higher crystallinity of the Mn-Cu phases generated.

1. Introduction

As a result of the continuous advance in the development of catalytic systems for the organic volatile compounds (VOCs) combustion, the current efforts lead to find new catalysts of transition

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metals or the optimization of the ones already studied, due to their low cost and especially their high activity and selectivity [1,2]. Although these catalytic systems present some disadvantages, such as those related with the chemical properties, distribution and dispersion of the active phase, which decrease their stability and activity, some systems have shown a similar catalytic performance to those based on noble metals [3]. In this context, it has been demonstrated that the mixture of metal species can induce cooperative effects. This leads to an increase in mobility of oxygens (optimization of the selectivity to the total oxidation), as well as stabilization of the more active catalyst species (activity improvement), so allowing successive reactivation treatments of the catalyst [4].

The Mn-Cu mixed oxides have been successfully employed in catalytic combustion of several VOC molecules and even mixtures of them. They have been used as bulk catalysts as well as supported on monolithic structures by our working group [5–8]. The excellent performance of the Mn-Cu system has been attributed to the formation of low crystallinity oxides and to the presence of $Mn_{1.5}Cu_{1.5}O_4$ incomplete spinel, where manganese in its highest oxidation state (Mn^{4+}) can be found and forms a redox couple with the copper [5].

The catalytic performance of the Mn-Cu system can be optimized by increasing the content of this phase on monolithic supports; but this does not ensure reproduction of the system of phases or the type of interaction that can occur between them. Thus, the complexity of the surface architecture achieved for different catalyst contents can promote different types of adsorption, which also makes possible multiple oxygen supply with different mechanisms involved.

Generally, on metal oxide catalysts, especially in mixed systems, besides the Langmuir-Hinshelwood and Rideal-Eley mechanisms, the Mars-van Krevelen type mechanism (with formation of surface oxygen vacancies as a key step and their subsequent replacement by oxygen of the gas phase) is dominant [3]. It has been reported that the combustion of oxygenated VOC molecules (alcohols, aldehydes, ketones, etc.) proceeds by a Mars-van Krevelen type mechanism, while combustion of saturated and unsaturated hydrocarbons (*n*-hexane, propane, toluene, etc.) is carried out by a Riedeal-Eley mechanism or a combination of both mechanisms [9].

In the above context, the aim of this work is to study the effect of increasing the Mn-Cu content over the surface of the monoliths on the type of phases generated. In addition, the relationship between these phases and their catalytic behaviour in the combustion of VOC molecules of different chemical nature has been studied. For this purpose, catalysts with different loading of active phase were tested in the combustion of two representative molecules of each group, an oxygenated molecule as ethanol and a hydrocarbon one as *n*-hexane.

2. Experimental

2.1. Synthesis of catalysts

Cordierite monoliths were provided by Corning (400 cpsi and 6.5 mil wall thickness) and samples of 10mmx10mmx10mm in laboratory scale were used. The samples were blown with air in order to eliminate particles or dust from the packaging. Then, monoliths were dipped in a colloidal alumina slurry (Nyacol ®), for 10 s and withdrawn to constant speed of 3 cm min^{-1}. The suspension excess was eliminated by blowing air during 45 s. Monoliths were then dried at 120 °C for 1 h. One or two soaks were made and finally the samples were calcined at 500 °C for 2 h. The monoliths previously coated with alumina were impregnated with aqueous solutions of $(CH_3COO)_2Mn{\cdot}4H_2O$ and $(CH_3COO)_2Cu{\cdot}4H_2O$ in a 9:1 M ratio with a total precursor concentration of 0.4 g ml^{-1}. Monoliths were immersed in the solution and shaken by ultrasound for 1 h. The solution excess was removed by blowing air for 45 s. Finally, they were dried at 80 °C for 24 h and calcined at 250 °C for 2 h and 500 °C for 3 h [6,10]. One or two impregnations were made with a calcination treatment in between. The monoliths were called AxCy where A = Alumina, x = 1 or 2 depending on the number of loads performed, C = Catalyst (Mn-Cu phase), and y = 1 or 2 depending on the number of impregnations performed. The monoliths only coated with alumina were named A1 and A2 corresponding to one or two washcoat loading cycles, respectively. In order to study the reproducibility of the synthesis five specimens were prepared for each catalyst.

2.2. Characterization techniques

The adherence of the coatings was evaluated in terms of the weight loss after exposure of the monoliths to ultrasounds. Monoliths were immersed in 25 ml petroleum ether, inside a sealed beaker, and then treated in an ultrasound bath for 30 min. After that, they were dried at 120 °C for 2 h. The weight loss was gravimetrically determined measuring the weight of the samples both before and after the ultrasonic treatment.

The chemical composition of the catalyst was analyzed by X-ray fluorescence spectroscopy (XRF). A Bruker M4 tornado apparatus, with a voltage of 50 kV, intensity of 200 μA and a multipoint analysis was employed.

SEM images and EDS spectra were obtained using a Quanta 200 scanning electron microscope (Philips) equipped with a Phoenix microanalysis system using a nominal resolution of 3 nm.

The specific surface area of catalysts was calculated by the BET method from the nitrogen physisorption isotherms obtained at −196 °C on samples out gassed at 150 °C using a Micromeritics Accusorb 2100E apparatus.

XRD patterns were obtained by using a Rigaku diffractometer operated at 30 kV and 25 mA by employing V-filtered Cr Kα radiation (λ = 0.2291 nm).

XPS data were obtained with a Multitecnic UniSpecs equipment with a dual X-ray source of Mg/Al and a hemispheric analyser PHOIBOS 150. Pass energy of 30 eV and an Al anode operated at 100 W was used. The pressure was kept under 29.10^{-8} mbar.

The TPR experiments were performed in a quartz U-type tubular reactor using a TCD as detector. The measurements were made with milled monoliths. Sample amounts were adjusted so as to have 26 mg of Mn-Cu phase in each case. Before each run, the sample was oxidized in a 50 ml min^{-1} flow of 20 vol.% O_2 in He at 300 °C for 30 min. After that, He was admitted to remove oxygen and finally, the system was cooled at 25 °C. The reducing gas was a mixture of 5 vol% H_2 in N_2, at a total flow rate of 30 ml min^{-1}. The temperature was increased at a rate of 10 °C min^{-1} from room temperature to 700 °C; then it was kept constant at 700 °C until the signal of hydrogen consumption returned to its initial values.

O_2-TPD experiments were performed in a quartz reactor using a TCD as detector. The measurements were made with milled monoliths. Sample amounts were adjusted as above commented, and were pre-treated with helium gas increasing the temperature from room temperature up to 700 °C at 10 °C min^{-1}. The samples were oxidized with a 20% O_2/He mixture at a total flow rate of 30 ml min^{-1} at 700 °C for 30 min. Then, they were cooled down to room temperature in the oxidizing mixture and flushed by a stream of purified He for 30 min. The desorption was carried out in the same conditions as the pre-treatment, maintaining the temperature at 700 °C until the TCD signal returned to baseline.

Oxygen Storage Capacity (OSC) of the catalysts was estimated by means of volumetric oxygen adsorption. Previously the