Applied Catalysis A: General 408 (2011) 96–104

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

# Cooperative effect of Ce and Pr in the catalytic combustion of ethanol in mixed Cu/CoMgAl oxides obtained from hydrotalcites

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ARTICLE INFO

*Article history:*
Received 16 June 2011
Received in revised form 6 September 2011
Accepted 11 September 2011
Available online 16 September 2011

*Keywords:*
Cooperative effect
Hydrotalcite
Mixed oxide
Ethanol oxidation
VOCs

ABSTRACT

The cooperative effect of Ce and Pr in the modification of mixed copper and cobalt oxide catalysts which were synthesized starting from the co-precipitation method of a hydrotalcite structure was evaluated in the catalytic combustion of ethanol. The solids were characterized by XRD, XRF, $H_2$–TPR, $O_2$–TPD and $N_2$ adsorption. The greatest catalytic performance was associated with the increase in the oxygen storage capacity and reducibility in the solids that contain rare earth elements (Ce–Pr) and with the improvement in the specific surface area. Additionally, the high selectivity towards $CO_2$, which is the principal product in total oxidation, demonstrates that the solids modified with Cu and/or Co and promoted with rare earth elements, are excellent catalysts in the total oxidation of ethanol, evidencing a cooperative effect among the metals.

## 1. Introduction

The rapid economic development in present day society has led to an increase in the demand for energy and the deterioration in the quality of the ecosystems. Among all the contaminants of the environment, the contamination which is generated by volatile organic compounds (VOCs) is the most preoccupying.

The term VOCs encompasses all the volatile organic compounds capable of producing photochemical oxidants by means of reactions provoked by solar light, in the presence of nitrogen oxides [1,2].

Nowadays, the majority of the industrialized countries have incorporated control measures through legislation, which would tend to limit the environmental impact and the risks that these compounds might occasion on human health [2,3]. In order to reduce the VOCs, several series of technologies are proposed that could be applied in accordance with the diverse concentrations, categories and sources of the contaminants [4,5].

Thermal combustion and reversible physical processes are beneficial when the concentration of the contaminant is relatively high. On the contrary, catalytic oxidation is the best option to eliminate the organic compounds present in the gaseous phase in very low concentrations. The presence of a catalyst permits working at lower temperatures (between 350 and 400 °C) than those employed in thermal oxidation, which represents an important economic benefit [2].

Numerous works evaluate the behaviour of some catalysts, among others those based in noble metals (Au, Pt, Pd) [6–8] and transition metals, particularly Cu [1,9,10], Co [11,12], Fe, Mn [1,11,13–15]; these latter ones have the additional advantage of having a lower cost and a greater thermal resistance. However, their limited activity at low temperatures does not make them competitive in comparison with noble metal catalysts.

In order to overcome this inconvenience it is necessary to design catalysts in which the formation of highly dispersed metallic species is favoured, which improve the catalytic properties and prolong the useful life of the catalysts. Hydrotalcites are presented as precursors of mixed oxides, with an enormous potential for the generation of well dispersed, active and very stable catalysts.

These materials have motivated a great interest in catalysis as anion interchangers [16,17], catalytic supports; and because of their basic properties, they have been employed in aldol condensation reactions [18,19], methanol synthesis [20,21], dehydrogenation of isopropanol [22], dehydrogenation of alkenes [23], among others.

Also, the interest in the application of calcined hydrotalcites (oxides) as catalysts in the environmental field is very important. For example, the materials resulting from the calcination of hydrotalcites based on copper and/or cobalt are very active and selective in the decomposition reaction of nitrogen oxides [24,25] as well as

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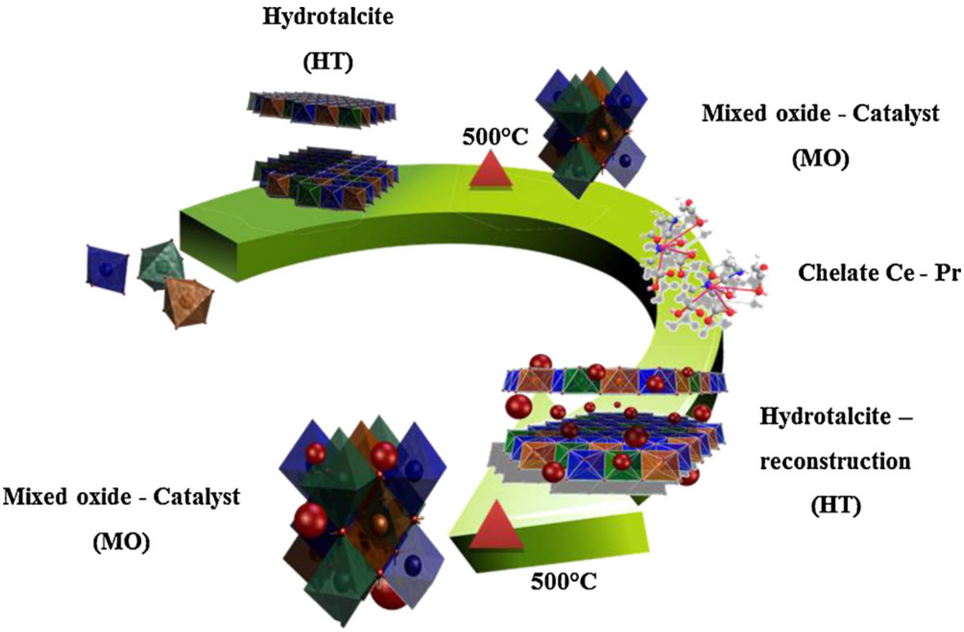
doi:10.1016/j.apcata.2011.09.013



**Scheme 1.** Synthesis methodology of the catalysts.

in the decomposition of sulphur oxides [26,27]. When transition metals are incorporated within the hydrotalcite structure, materials are obtained which are used equally as catalysts or as catalytic supports in redox reactions such as the selective oxidation of hydrocarbons [28] and in the total oxidation reactions of volatile organic compounds [1,11,29].

The catalytic activity of the hydrotalcites depends essentially on the $M^{2+}/M^{3+}$ ratio, on the different cations that make up the network, on the nature of the compensation anions, and among other factors on the activation temperature [17,30].

It is important to point out that the joint use of diverse metallic phases can lead to a synergistic or cooperative effect tending towards an improvement in the catalytic properties [31,32]. The use of metallic mixtures with promoters composed of rare earths, can lead to an improvement in the oxygen storage capacity in the solids, which evidently enhances the oxidation processes [13]. On the other hand, the use of mixtures of elements of rare earths (Ce and Pr) incorporated to the hydrotalcite during its reconstruction, is a new field in the synthesis of mixed oxides and in particular, for oxidation reactions of VOCs.

In this work, Co and Cu hydrotalcites were synthesized as precursors of mixed oxides, in order to obtain total oxidation catalysts of ethanol. Also, mixed oxides promoted with rare earths (Ce–Pr) were synthesized starting from the corresponding chelates ($EDTA^{4-}$) by interchanges in the reconstruction stage of the hydrotalcites and the effect of these rare earth elements in the solid physical properties and catalytic performance was investigated.

## 2. Experimental

### 2.1. Synthesis of catalysts

The synthesis of Cu and/or Co hydrotalcites were obtained using the simultaneous co-precipitation technique at a constant pH [30], and for the modification with rare earth elements (RE) [33], the reconstruction in the presence of chelates [Ce–EDTA] and/or [Pr–EDTA] was used. In all cases the molar ratio $M^{2+}/M^{3+}$was 3.

The complex [RE–EDTA] was synthesized at room temperature adding a solution of the corresponding metal (0.15 mmol) drop by drop on a solution of EDTA tetra-sodium salt (0.15 mmol) at pH 10.5. The complex formed was aged for two hours at room temperature. Then, the chelate solution was added on mixed oxide previously synthesized and aged for 24 h at room temperature with constant stirring. The solid obtained was washed and dried at 80 °C and calcined at 500 °C in air for 16 h.

In Scheme 1 the synthesis methodology of the catalysts and the corresponding terminology is outlined.

### 2.2. Characterization

The X-ray diffraction was carried out with a SHIMADZU LAB–X XRD-6000 difractometer with a Cu anode ($\lambda = 1.54056$ Å), using a step size of 0.02° $2\theta$ at 1° $min^{-1}$. Textural characterization was carried out by nitrogen adsorption at liquid nitrogen temperature using a Micromeritics ASAP 2020. Samples were previously degassed for 5 h at 350 °C in vacuum. The bulk chemical composition was determined by X-ray fluorescence (XRF) with (PhilipsMagiXpro PW2440) equipment.

The $H_2$–TPR and $O_2$–TPD profiles were performed using CHEMBET 3000 (QUANTACHROME) equipment provided with a thermal conductivity detector.

For $H_2$–TPR the samples (<250 μm) were previously degasified at 400 °C for 1 h in a flow of Ar and then reduced at 10 °C $min^{-1}$ using 10% (v/v) $H_2$/Ar at 30 mL $min^{-1}$. The consumptions of $H_2$ were determined by means of the injection of pulses of known volumes of pure $H_2$.

For $O_2$–TPD, 200 mg samples were pre-treated with helium gas, and the temperature was increased from room temperature to 450 °C (10 °C $min^{-1}$). The samples were oxidized with a 10% $O_2/N_2$ mixture at a total flow rate of 30 $cm^3$ $min^{-1}$ at 450 °C for 30 min. Then, they were cooled to room temperature in the oxidizing mixture and flushed with a stream of purified helium for 30 min. When the baseline was stabilized, the desorption was carried out from room temperature to 1200 °C at an ascending rate of 10 °C $min^{-1}$ in a helium gas stream.

### 2.3. Catalytic evaluation

The ethanol oxidation reaction was carried out using a conventional continuous flow U-shape glass reactor working at atmospheric pressure. Mass flow controllers (Brooks 5850TR) were