



## Research paper

# Influence of the synthetic conditions on the composition, morphology of CuMgAl hydrotalcites and their use as catalytic precursor in diesel soot combustion reactions

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## ABSTRACT

In this work, a series of Cu-Mg-Al hydrotalcites and the oxide mixture obtained by their calcination at 600 °C were synthesized by coprecipitation from metal nitrates. The effect of the coprecipitation temperature of the precursor on the structure and texture of these materials was investigated. The solids were characterised by inductively coupled plasma (ICP), atomic absorption spectrophotometry (AAS), an energy dispersive spectrometer (EDAX), thermogravimetric analysis (TGA-DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR). It has been studied the activity of these solids as catalysts for diesel soot combustion. The materials are formed by nanoparticles, and the coprecipitation temperature has influence in the morphology of hydrotalcites. Moreover, the catalytic performance of calcinated solids is influenced by the synthesis conditions. A low temperature coprecipitation is beneficial for the diesel soot combustion. In this sense, the solid obtained by coprecipitation at 40 °C shows the best catalytic activity ( $T_{\max} = 375$  °C). This catalyst contains copper oxides, potassium and nitrate ions which can act as promoters of the soot combustion. The studied solids showed activity and high resistance to the deactivation caused by hydro-treatment.

## 1. Introduction

The partial combustion that takes place in diesel engines leads to enormous emissions of pollutants as volatile organic compounds (VOCs), nitrogen oxides (NOx) and particulate matter (PM) (Van Setten et al., 2001). PM is a main constituent of air pollution, being associated to cardiovascular and respiratory diseases as well as skin cell alterations (Frank et al., 2013). PM is generally composed by elemental carbon (soot), soluble organic fraction (solid or liquid substances finely distributed in gases), sulfates (hydrated sulfuric acid, metal sulfates and liquid, depending on the sulfur content of the fuel) and ash (inorganic materials) (Guan et al., 2015). Soot particles can also be classified according to their aerodynamic diameter in large particles ( $> 10$  μm), coarse particles (PM<sub>10</sub>, 2.5–10 μm), fine particles (PM<sub>2.5</sub>, 0.1–2.5 μm), ultra-fine particles (PM<sub>0.1</sub>, 50–100 nm) and nanoparticles ( $< 50$  nm), being reported that the smaller particles are the most harmful to human

health (Prasad and Bella, 2011; Ristovsky et al., 2012).

The effect of the PM in the health and the environment has led to stringent environmental regulations for diesel emissions, being limited the PM emissions to 0.0021 g km<sup>-1</sup> for light-duty vehicles and 0.01 g k Wh<sup>-1</sup> for heavy-duty engine in the European Union (EU) and United States (US) (Johnson, 2014).

Diesel Particulate Filters (DPF) are sustainable processes to remove soot particles coming from the exhaust stream (Van Setten et al., 2001; Maricq, 2007). These filters are monoliths with channels in the form of honeycomb structure, where the soot particles get stuck. DPF are used as support to collect a metal-based catalyst to diminish the temperature of the soot combustion. Several active phases have been proposed to accelerate the soot combustion, such as noble metals catalysts mainly Pt (Oi-Uchisawa et al., 2000; Oi-Uchisawa et al., 2003), perovskite type oxide (Teraoka et al., 2001; Peng et al., 2007), spinel type oxides (Shangguan et al., 1998), rare earth metal oxides (Liu et al., 2005; Zhu

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et al., 2005; Bueno-López, 2014).

In order to cheapen costs and to meet future expectation favoring Diesel engines, it is necessary the developing of inexpensive catalytic systems with higher performance and robustness to substitute the use of precious metals in soot combustion processes. In this sense, layered double hydroxides are inexpensive materials with potential to be used for the removal of the diesel soot particulate.

Layered double hydroxides, also denoted as hydrotalcites (HT), are classified as anionic clays, with general formula of:



where M(II) are divalent cations, M(III) are trivalent cations, A is an anion with charge  $m^-$ , and  $x$  is the  $M(III)/(M(III) + M(II))$  molar ratio (Cavani et al., 1991; Vaccari, 1998 and Rives et al., 2001).

The intrinsic physicochemical properties of hydrotalcites present interesting applications as adsorbent (Nogueira et al., 2016), wastewater treatment (Aguilar et al., 2013), in separation processes (Kudinalli et al., 2015), ion exchanger (Lv et al., 2009) or polymer additives (Kalouskova et al., 2004). Moreover, the calcination of the layered double hydroxides leads to the formation of mixed oxides, which display interesting properties as heterogeneous catalyst (Rives et al., 2003; García-Sancho et al., 2011; Zhou et al., 2011; Alvarez et al., 2012; Helwani et al., 2013) or catalytic supports (Narayanan and Krishna, 2000) due to their large surface areas, basic character, high dispersion of the metal species. In addition, the presence of a transition metal cation in the chemical composition of the hydrotalcite can also provide redox properties for these solids. Several authors have evaluated the influence of variables such as pH and calcination temperature in the framework and the physicochemical behaviour of the hydrotalcites.

The most frequently synthesized hydrotalcite is the Mg-Al double hydroxide. Nonetheless, this hydrotalcite can be modified by cationic substitutions. In the present research have been incorporated  $Cu^{2+}$  species in the synthetic procedure. Previously, Rosales Suarez et al. (2007) evaluated the influence of the precipitating solution, pH, copper content, and mechanical milling on the structure and texture of hydrotalcites, finding that the pure hydrotalcite phase was obtained in all cases and that coprecipitation at pH 10. However, the use of large copper content causes changes in the cell parameters of the hydrotalcite increasing the values of the parameters “ $a$ ” and “ $c$ ”, the crystallite size. Lwin et al. (2001) prepared a series of hydrotalcites by coprecipitation using metal nitrates as precursors and an aqueous solution of  $Na_2CO_3$  as a precipitant agent, varying the Cu:Al atomic ratio between 0.5 and 4. These authors found that samples with very low Cu:Al ratio were amorphous, while an increase of the Cu:Al ratio led to the formation of malachite phase. Auer et al. (1999) prepared two series of Cu-Mg-Al hydrotalcites, one of them containing 33% Cu based on the total content of metals and another one with 67% Cu from their respective metal nitrates and with sodium carbonate as the precipitating agent, also obtaining malachite for the samples with higher copper content.

The use of hydrotalcite-based catalysts have received attention because they are rather stable materials that are able to deliver oxidizing species and promote diesel soot combustion and  $NO_x$  decomposition (Wang et al., 2007, 2012, 2014; Li et al., 2009a and Li et al., 2009b; Jiang et al., 2012; Comelli et al., 2013; Fino et al., 2016). The oxidizing capacity of diesel soot catalysts can be improved by the incorporation of copper or cobalt species (Sánchez et al., 2013; Jakubek et al., 2015).

The aim of the present research evaluates the influence of synthetic conditions of Cu-Mg-Al layered double hydroxides in their physicochemical properties as well as the textural properties of the mixed oxides obtained from the calcination of their respective hydrotalcite precursors at 600 °C. The obtained mixed oxides were tested in the diesel soot combustion reaction carrying out a detailed analysis of their resistance to the deactivation processes and the regeneration of the catalysts in successive catalytic cycles.

## 2. Experimental

### 2.1. Catalysts preparation

Hydrotalcites were synthesized by the co-precipitation method by mixing of an aqueous solution, solution A, which contain copper nitrate 0.66 M,  $(Cu(NO_3)_2 \times 3H_2O)$ , Anedra), magnesium nitrate 0.66 M,  $(Mg(NO_3)_2 \times 6H_2O)$ , Sigma-Aldrich) and aluminum nitrate 0.44 M  $(Al(NO_3)_3 \times 9H_2O)$ , Sigma-Aldrich). In all cases, the atomic ratio between the divalent and trivalent cations in the solution was 3:1, while the Cu:Mg atomic ratio was 1:1. On the other hand, another aqueous solution (B) is prepared with the precipitating agents, i.e. potassium hydroxide 2 M (KOH, Cicarelli) and potassium carbonate 0.06 M  $(K_2CO_3 \times 1.5H_2O)$ , Sigma-Aldrich). Later, solutions A and B were putted in different burettes and added dropwise into distilled water simultaneously, which was collected form a purification system in the laboratory, maintaining the pH between 9 and 10 under vigorous stirring at the chosen temperature (25 °C, 40 °C, 70 °C and 90 °C) and controlling the water evaporation. The samples were aged in the mother liquor maintaining the precipitation temperature for 3 h in the same beaker used for the reaction, covered with a glass lid. Then, the solids were filtered, washed several time with distilled water and dried at 110 °C for 12 h. In addition, an additional sample was synthesized by co-precipitation of their respective precursors at 40 °C, avoiding the washing step before the drying. The resulting solids exhibited different colours ranging from dark maroon to bluish green. Finally, the catalysts were obtained by calcining the precursor at 600 °C for 4 h.

The precursors were denoted as Pxyw or Pxynw, where P indicates the hydrotalcite precursor, xy indicates the coprecipitation temperature, w and nw indicate if the sample was washed or not washed, respectively. The catalysts were denoted as Cxyw or Cxynw, where C indicates that it is a calcined solid. All of the solids obtained were: P25w, P40w, P40nw, P70w, P90w, C25w, C40w, C40nw C70w and C90w.

### 2.2. Characterization of materials

The semiquantitative analysis and the surface morphology of the precursors and catalysts were performed with a scanning electronic microscope (SEM) LEO 1450 VP attached to an energy dispersive spectrometer (EDS) EDAX Genesis 2000, 20 Kv, with a working distance (WD) of 15 mm.

The elemental composition was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES), with the use of a 1 m-Czemy Turner monochromator with a holographic grating with 1800 grooves  $mm^{-1}$ .

The temperature of the formation of the basic mixed oxides from hydrotalcites was determined by a TA-60 Shimadzu thermogravimetric (TG) and differential thermal analysis (DTA) instrument. In each experiment, 15 mg of hydrotalcite and  $\alpha-Al_2O_3$ , as an inert reference material, were heated in Pt cups with a rate of 10 °C  $min^{-1}$ , from 20 °C to 700 °C, with a  $N_2$  flow of 20 mL  $min^{-1}$ .

The crystalline structure of precursors and catalysts was studied by X-ray diffraction (XRD) using a D-Max III (Rigaku) with Cu  $K\alpha$  1 radiation ( $\lambda = 1.5405 \text{ \AA}$ , 40 kV, 30 mA), with Ni filter, and scanning an angular range of 2 $\theta$  between 10° and 70°, at a 3°  $min^{-1}$  rate.

Some samples were also studied by X-ray photoelectron spectroscopy (XPS) with a Physical Electronics PHI 5700 spectrometer with non-monochromatic Mg  $K\alpha$  radiation (300 W, 15 kV and 1253.6 eV) and a multi-channel detector. Spectra of samples were recorded in constant pass energy mode at 29.35 eV, using a 720  $\mu m$  diameter analysis area. Charge was referenced against adventitious carbon (C 1s at 284.8 eV). A PHI ACCESS ESCA-V6.0 F software package was used for data acquisition and analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were fit using Gaussian–Lorentzian curves in order to determine the binding energies

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