Developing Bifunctional Catalysts from Mg-Me-Al (Me: Cu, Fe, Ni, Zn)
Calcined Hydrotalcite-Like Compounds
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Introduction
Throughout previous decades, hydrotalcite-like (HT) compounds have been extensively studied as catalysts or catalyst precursors [1]. Since calcination of HTs yields mixed oxides which are basic solids, HT compounds have found applications in many organic reactions considered to be catalyzed by bases [1,2,3]. The structure of hydrotalcite resembles that of brucite, in which magnesium is octahedrally surrounded by hydroxyls. Replacing some of the Mg$^{2+}$ divalent cations by Al$^{3+}$ trivalent cations results in HT, turning the layered array positively charged. These positively charged Mg-Al double hydroxide layers are electrically compensated for by carbonate anions which are located in the interlayer region. A wide variety of synthetic hydrotalcite-like materials can be prepared and are represented by the general formula $\left[M^{2+}_{x-y}M^{x+}_{y}(OH)_{2}\right]\left(A^{n+}\right)_{y}mH_{2}O$, where $M^{2+} = \text{Mg}^{2+}$, $\text{Ni}^{2+}$, etc.; $M^{x+} = \text{Al}^{3+}$, $\text{Ga}^{3+}$, etc.; $A^{n+} = \text{CO}_3^{2-}$, $\text{Cl}^{-}$, etc.

Conventional HT-MgAl can be used to incorporate and disperse one or more reducible cations in the layers when partially replacing Mg$^{2+}$ or Al$^{3+}$ cations. These reducible cations, when they are indeed located in the layers and not as separate metal hydroxide or oxide entities, are imbedded in a mostly basic matrix. Accordingly, it is possible to modulate the basic strength of a series of binary hydrotalcite-like clays, depending on the nature of the cations in the layers [4]. In HTs containing three or more cations, one of them being reducible, when calcining and collapsing the layered array, solid solutions of the divalent cations in higher concentration, e.g. $\text{Mg}_{3-x}\text{Zn}_x\text{Al}_{y}$$\text{O}_6\text{CO}_3\text{H}_2$ or highly disperse small crystals of the reducible metal oxides, may result and may show interesting catalytic properties. In this work a series of HTs $\text{Mg}_{3-x}\text{Me}_x\text{Al}_{y}(\text{OH})_2$$\text{CO}_3\text{H}_2$; Me: Cu, Fe, Ni, Zn; $x=0$–0.23 and $y=0.29$–0.34, were synthesized, characterized and calcined and then tested as catalysts in the gas-phase decomposition of 4-Methyl Pentan-2-ol (4Me2Pol).

Materials and Methods
The HT materials were prepared by co-precipitation following the procedure described elsewhere [4]. Chemical composition of solids was determined by inductively coupled plasma atomic emission spectrometry. The crystalline structure of the solids was studied by X-ray diffraction using a Siemens D-500 diffractometer. Weight loss and temperatures associated with HTs thermal decomposition were determined by thermogravimetry (TG) using a Perkin-Elmer TG-7. DRIFT spectra were recorded in situ using a Bruker Equinox 55 spectrometer equipped with a Harrick diffuse reflection attachment and a Harrick reaction chamber. The texture of the calcined samples was analyzed by N$_2$ adsorption-desorption at -196°C on an AUTOSORB-1. The surface areas were calculated by using the Brunauer-Emmett-Teller (BET) method, and the pore size distribution and total pore volume were determined by the BJH method. The gas-phase decomposition of 4-Methyl Pentan-2-ol was used as catalytic test.

Results and Discussion
All samples presented the XRD pattern corresponding to HT structure and no different crystalline phases were detected. The real molar ratios varied from 2.20 for MgZnAl-15 to 3.09 for MgCuAl-7; these differences were attributed to an incomplete incorporation of the cations inside the layers. All samples exhibited type IV isotherms which are characteristic of mesoporous materials. Their specific surface areas ranged from 138–251 m$^2$/g.

Fig. 1. Activity recovery after in situ reactivation and effect of air as a carrier gas using MgZnAl-15 in the decomposition of 4Me2Pol.
(a) First cycle using He as a carrier gas, (b) second cycle after reactivation, and (c) third cycle using air.

The recovery of activity and the influence of the type of carrier gas were examined using MgZnAl-15 and the results are shown in Fig. 1. The catalyst was used under He as a carrier gas, conversion drops from 70 to 43%, while selectivity to methyl isobutyl ketone (MIBK) is less affected, after a total of 200 min. A second reaction cycle was started using the same conditions as in the first one, pointing out that the deactivation process is a reversible. After this, a third reaction cycle was started, this time using air as the carrier gas. In this run, the initial selectivity to MIBK dropped considerably, clearly indicating its strong dependence upon the electronic state of Zn, so we can assume a RedOx mechanism, then O$_2$ in air will impede this route to proceed. Alcohols are able to reduce transition metal cations. Thus, it is clear that Zn or other reducible cations play a crucial role in the selectivity of the catalysts.

Significance
HTs containing three or more cations, one of them being reducible, can produce highly disperse small crystals of the reducible metal oxides on a basic solid solution matrix, the catalytic properties could be easily regulated for the amount and nature of cations in the HT's network. Thus, we could design a bifunctional catalyst for an intended reaction.

References