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## Synthesis and characterization of metal mixed oxides from Layered Double Hydroxides

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### Abstract

This work reports the synthesis and characterization of metal mixed oxides (MMOxs) obtained from precursors like Layered Double Hydroxides (LDHs). These materials were synthesized with two hydroxides of Mg-Al with the incorporation of mono, di and trivalent metal ions, such as Li, K, Ca, Ba, Ce, and La. The third metal incorporation took place through two different ways: the direct incorporation by the co-precipitation method and the incorporation through the impregnation of the mixed oxides by the wet impregnation method. All materials were characterized by XRD, SEM-EDX and specific surface area. The samples synthesized by both methods show the characteristic structure from the LDHs compounds derived and the third metal incorporated. However MMOxs obtained by co-precipitation method showed higher specific surface area and smaller particle size.

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*Keywords:* Layered double hydroxides; Metal mixed oxides; Co-precipitation method; Wet impregnation method.

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## 1. Introduction

Layered double hydroxides (LDHs) with the hydrotalcite-like structure are materials attracting interest to many research groups due to their use in many different fields, such as anion scavengers, catalysts, catalyst precursors, hosts for drugs controlled delivery, etc. The thermal decomposition through calcinations of LDHs is a well known method for preparing homogeneous mixed oxides characterized by intimate mixing of components, Nalawade et al., 2009.

The use of LDHs and their MMOs as solid catalysts is a promising alternative for the decontamination of soils, groundwater, sediments, and industrial process and effluents. The versatility in chemical composition and physico-chemical properties of synthetic LDHs offers a large variety of applications for these materials. They are used in polymer processing, adsorption and decontamination processes, pharmacy, and in the preparation of new materials based on LDH host structures intercalated with various organic and inorganic species (Perioli et al, 2011; Ryu et al, 2010). Layered double hydroxides are also widely used in heterogeneous catalysis. The low cost and environmentally friendly nature of these materials are an added advantage.

Additionally, García-García et al., 2007 suggested that the introduction of nanoparticles in heterogeneous catalytic processes has led to appreciable improvements in catalytic efficiency.

As it was mentioned before, in the case of LDHs and MMOs as solid catalysts, they must fulfill a number of requirements, such as high activity in terms of conversion and selectivity, marginal leaching of active cations and stability over a wide range of pH and temperature. For practical applications, citing Garrido-Ramírez et al., 2010, these materials should also be available at a reasonable cost.

As many other authors, Rives and Ulibarri, 1999, proposed that the structure of the LDHs consists of brucite-like layers, where a partial substitution of Magnesium for Aluminum has taken place, so anions are located in the interlayer, where water molecules also exist, to balance the positive charge of the layers. Their formula can be written as  $[M(II)_{1-x}M(III)_x(OH)_2]^{x+} (A^{n-})_{x/n} \cdot mH_2O$ , where M(II) and M(III) represent the di and trivalent metal ions and  $A^{n-}$  is the interlayer anion, which is carbonate in natural hydrotalcite,  $[Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O]$  or many diverse anions depending on the different synthesis routes. The structure and surface properties of hydrotalcite and the resulting mixed oxides strongly depend on chemical composition and synthesis procedures as Cavani et al., 1991 affirmed.

On the other hand, the precise nature of the layer cations can be changed in a wide range, the limits being their molar ratio, and their ionic radii as noted by de Roy et al, 2001. LDHs containing  $Mg^{2+}$  and  $Al^{3+}$  are usually preferred because of their lack of toxicity, those with alkaline metal cations are generally used as catalysts or catalyst precursors for mild and total oxidation, alcohol synthesis, hydroxylation, etc. as Dubey et al, 2002 mentioned.

MMOs obtained by thermal decomposition of LDHs have been largely studied (Melo and Morlanés, 2008). The introduction of several elements in the structure could influence the metal electronic configuration, reducibility, particle size, dispersion and surface area modifying its catalytic performance. Magnesium and aluminum from basic catalysts have been substituted by different elements.

Specially, MMOs tuning with high specific surface areas has actually great interest for researchers due its many applications in several fields. For instance in  $N_2O$  decomposition using Co-Mn-Al mixed oxide (Karáskova et al, 2010); transesterification processes with MgAl and MgCa (Albuquerque et al, 2008); total oxidation of volatile organic compounds on mixed oxides with transition metal (Kovanda et al, 2011); synthesis of monoglycerides on calcined Li-Al hydrotalcites; etc. It is well known that the morphology of particles directly influences the catalytic activity of a supported metal, Nadgeri et al., 2008.

In this work, two different synthesis methods for LDHs containing  $Mg^{2+}$  and  $Al^{3+}$  with a third metal ion incorporated and their metal mixed oxides as well as their structure characteristics are reported. By using different molar ratios of several cations (mono, di and trivalent) such as  $Li^+$ ,  $K^+$ ,  $Ba^{2+}$ ,  $Ca^{2+}$ ,  $Ce^{3+}$  and  $La^{3+}$ ,

stoichiometric and non-stoichiometric LDHs were prepared, which undergo transformation to non-stoichiometric and stoichiometric mixed oxides by calcinations. LDHs were prepared by co-precipitation method and the third metal was introduced by two different approaches: wet impregnation or direct co-precipitation. The interlayer anion was carbonate in all cases, because it is easy to remove it by calcination.

## 2. Experimental

### 2.1. Synthesis

The preparative methods adopted in this study were direct co-precipitation and impregnation methods. In the direct co-precipitation method, the samples were prepared by the low supersaturation method at constant pH ( $10 \pm 0.2$ ), with  $M^{2+}/M^{3+} = 3$  molar ratio constant. Two solutions designated as A and B, were prepared. In order to obtain A solution,  $Mg(NO_3)_2 \cdot 6H_2O$ ,  $Al(NO_3)_3 \cdot 9H_2O$  and the metal nitrate to be incorporated were dissolved together in distilled water; while the solution B contains 0.085 M of  $Na_2CO_3$ . Both solutions were dropped simultaneously to 50 mL of distilled water at 60 mL/h. The pH was kept constant by adding a NaOH solution, 2 M. The co-precipitation was carried out at room temperature and the gel was continuously magnetically stirred. The mixture was kept under magnetic stirring for 4 hours. The precipitate was aged in the mother liquor overnight at room temperature, and then it was washed with distilled water and separated, by centrifugation at 2800 rpm, until pH=7. The resulting material was dried overnight at 90 °C in the open air. The solids were finally calcined in open air at 450 °C for 9 h (Crivello et al, 2007).

In the impregnation method, the metal ions were added to the mixed oxides using a salt aqueous solution containing the required metal concentration to obtain samples with 10 wt% of metal. The suspension was kept under stirring at constant temperature (25 °C) for 20 minutes and then it was dried in a vacuum rotary evaporator. The resulting solid was dried at 85-90 °C overnight. Then it was calcined in air at 350 °C for 1 h and then at 500 °C for 8 h (Papadopoulou et al, 2004)

LDHs samples and MMOxs samples were named by the symbol of the third metal incorporated, the synthesis method used: co-precipitation (c) and impregnation (i), and the stage of the sample: precursor (p) and calcined (c); i.e., in the case of the sample with Lanthanum incorporated: *La cp*, *La cc*, *La ip* and *La ic*.

### 2.2. Samples Characterization

All samples were examined by XRD on a Philips PW 3838 diffractometer, using monochromatic Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) at a scan speed of  $1/4^\circ/\text{min}$  in  $2\theta$  range between 10 and 80° and a step size of 0.02°.

The specific surface area was determined by the BET method, which was recorded on a Micromeritics ASAP 2000 instrument. The precursors were degassed at 200 °C and the calcined materials at 390 °C, both during 50 min.

The scanning electron microscopy (SEM) studies of the MMOxs were made with a JEOL JSM-6380 LV, coupled with an energy dispersion analyzer (EDX) Oxford Instruments model 7582. The specimens were Au coated (sputtering) to make them conductive. The SEM acceleration voltage was 20 kV.

The MMOxs chemical composition was determined by ICP analysis for the samples having Lithium due to this metal can not be detected by EDX. The equipment was a VISTA-MPX CCD Simultaneous ICP-OES-VARIAN.

## 3. Results and Discussion

Figure 1 shows the XRD patterns of the most representative LDHs synthesized by direct co-precipitation.

They are typical of a pure layered double hydroxide structure with sharp and symmetric reflections for (003), (006), (110) and (113) planes and broad asymmetric for (012), (015) and (018) (JCPDS 70-2151). But in the sample with Ba it was observed that the intensity of the (003) reflection was lower than that of the (006) reflection. This fact may be due to a disorder in the stacking of the layers, which also decreases the symmetry. The shoulder in the 006 reflection could be associated at  $\text{Ba}^{2+}$  ions located in sites outside the brucite-type layer. The samples with La behave similarly; in this case, the  $\text{La}^{3+}$  ions are replacing the  $\text{Al}^{3+}$  ions. It is known that  $\text{La}^{3+}$  have lower charge density in comparison with  $\text{Al}^{3+}$  due to its larger ionic radius, thus the possible insertion of  $\text{La}^{3+}$  into hydroxide sheets would cause a distortion of the octahedral structure, forming other phases (Fig. 1) (Zhang et al, 2010).

The XRD profiles of the oxides, with the third metal incorporated by wet impregnation, showed the LDHs structure due to LDHs memory effect (XRD patterns are not shown here). The term ‘‘memory effect’’ means the capacity of the samples obtained by thermal decomposition of hydrotalcite-type precursors, containing a volatile anion such as carbonate, to reconstitute the original layered structure upon adsorption of various anions or, simply upon exposure to the air. Independently of the synthesis method, all samples incorporated the third metal despite the wide range of the ionic radii maintaining the characteristic structure of the LDH.

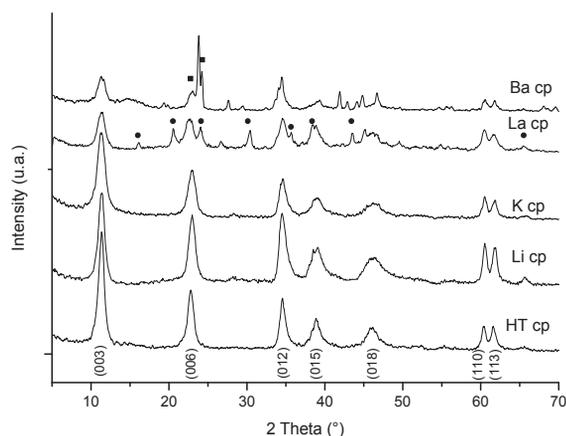


Fig.1. XRD profiles of LDHs synthesized by co-precipitation method: (■)  $\text{Ba}^{2+}$  species, (●)  $\text{La}^{3+}$  species.

Fig 2a and 2b show MMOxs XRD patterns. It can be seen that after calcination, hydrotalcite-type structure is lost, leading to a mixture of oxides with different diffraction bands. All profiles show the two characteristic MgO peaks (JCPDS 78-0430) as Domine et al, 2011 indicated. Chmielarz et al, 2002 proposed that the remaining peaks can be attributed to the third metal oxides:  $\text{Li}_2\text{O}_2$ , (JCPDS 74-0115),  $\text{K}_2\text{O}$  (JCPDS 77-2151),  $\text{CaO}$  (JCPDS 82-1691),  $\text{BaO}$  (JCPDS 74-1228),  $\text{La}_2\text{O}_3$  (JCPDS 83-1355) and  $\text{Ce}_2\text{O}_3$  (JCPDS 78-0484), and spinel-type mixed oxide ( $\text{MAl}_2\text{O}_4$ ); some of them are marked in Fig 2a. The XRD patterns of the oxides with the third metal incorporated by the wet impregnation method show the diffraction patterns similar to MMOxs obtained by co-precipitation method with two characteristic MgO peaks and the third metal oxides.

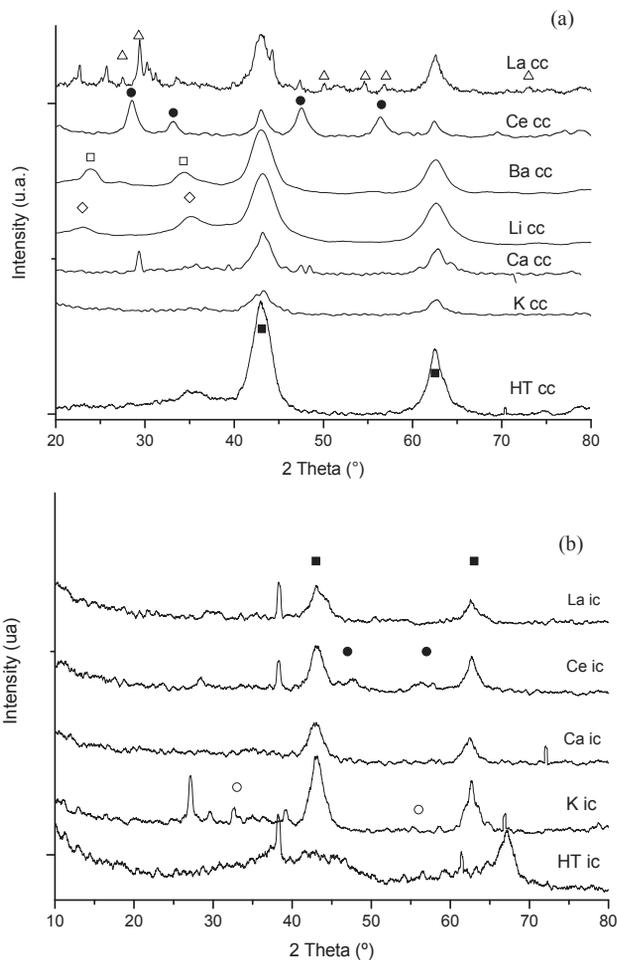


Fig.2. XRD profiles of (a) MMOx obtained by co-precipitation method: ( $\diamond$ ) Li<sub>2</sub>O<sub>2</sub>, ( $\blacksquare$ )MgO, ( $\square$ ) BaO, ( $\Delta$ )La<sub>2</sub>O<sub>3</sub>, and (b) MMOx with the third metal incorporated by wet impregnation method: ( $\blacksquare$ ) MgO, ( $\bullet$ )CeO<sub>2</sub>, ( $\circ$ ) K<sub>2</sub>O.

All surface areas of the oxides are higher than their corresponding precursors. These high areas are attributed to the removal of H<sub>2</sub>O and CO<sub>2</sub> during calcination, which leads to formation of channels and pores (Serrano et al, 2011). In Table 1 MMOx specific surface areas are shown. The MMOx synthesized by co-precipitation method present higher surface areas than the oxides with the third metal incorporated by the wet impregnation method. However, the wet impregnation plus calcination step has been the suggested method, up to now, to increase the specific surface area of the materials, as Ferretti et al., 2010 proposed. The largest area was obtained in the La-Mg-Al (impregnated samples and mixed oxides). It is noticeable that, this value is much higher than others reported on literature (Serrano et al, 2011). The increase of BET areas when La is added can be due to that the presence of small percentages of magnesium contributes in a significant extent to the dispersion of entities of La<sub>2</sub>O<sub>3</sub> on the surface of the calcined samples.

In addition, micrographs of all materials have been done. In Figure 3 some MMOxs SEM micrographs are shown. In general, the solid materials morphology analyzed by SEM presents particles with irregular grains.

In the case of mixed oxides with Potassium incorporated synthesized by wet impregnation method, their particles have more irregular shape and size than the ones of the oxides synthesized by co-precipitation method, which present particles of smaller size.

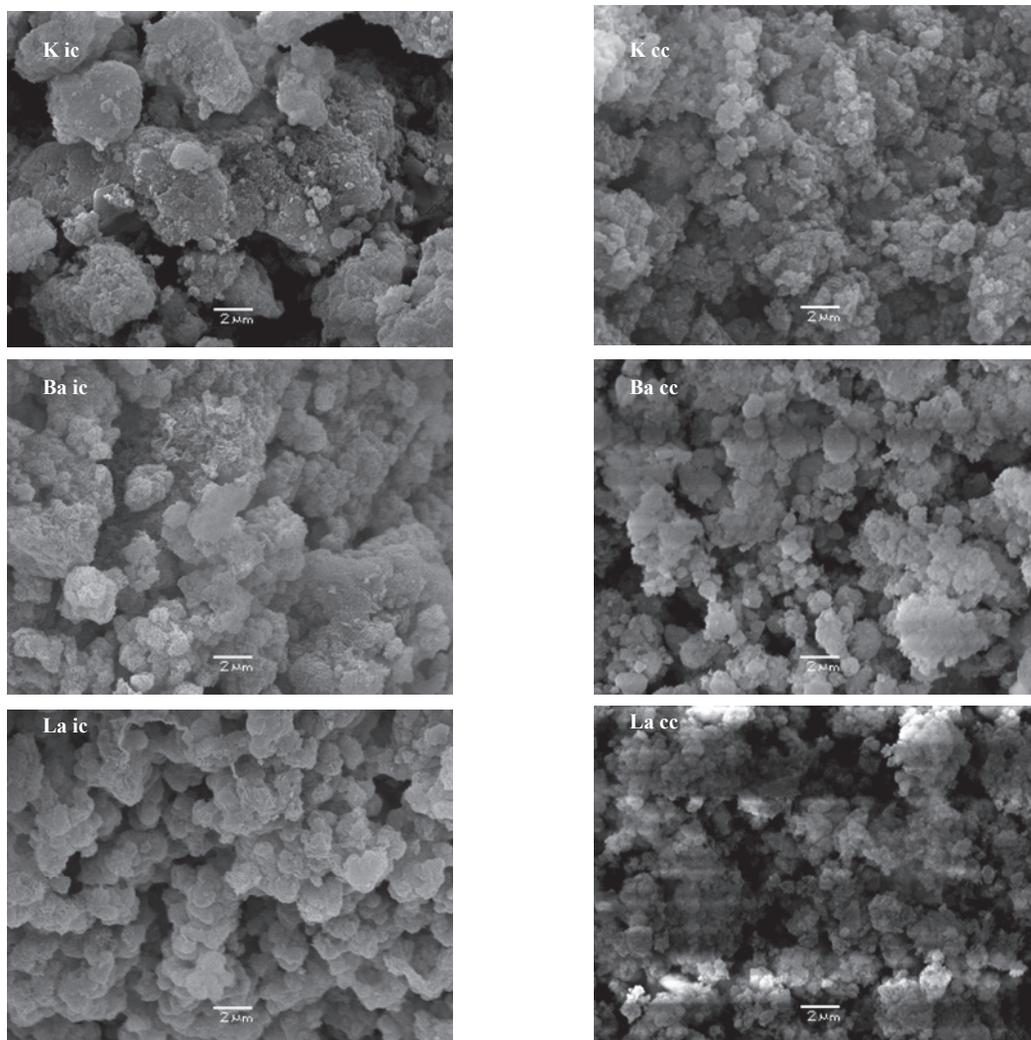


Fig 3. SEM micrographs from metal mixed oxides samples synthesized by wet impregnation and co-precipitation methods.

The mixed oxides with Barium synthesized by wet impregnation method show particles covering a size wide range. Its morphology is characterized by clusters of thin plates. On the contrary small and uniform particles of the oxides with Barium synthesized by co-precipitation method are observed.

The mixed oxides with Lanthanum, synthesized by co-precipitation method, show more uniform particle size and round shaped than those mixed oxides particles synthesized by wet impregnation method.

For the other materials (impregnated samples or mixed oxides) the photographs were similar.

ICP studies for the samples with Li and EDX studies for the rest of the MMOxs show that the third metal ion was incorporated (by both methods) in the solid structure.

Table I. MMOxs specific surface area ( $\text{m}^2\text{g}^{-1}$ ) synthesized by both methods.

MMOxs	Area Wet impregnation method	Area Co-precipitation method
MgAlOx	115	274
LiMgAlOx	142	268
KMgAlOx	150	282
CaMgAlOx	120	223
BaMgAlOx	172	213
LaMgAlOx	184	301
CeMgAlOx	181	212

#### 4. Conclusion

Structures characteristic of Layered Double Hydroxides were obtained by co-precipitation and wet impregnation methods. Independently of the synthesis method, all samples incorporated the third metal despite the wide range of the ionic radii maintaining the characteristic structure of the LDH; but the incorporation of La and Ba into the hydroxide sheets was very limited due to its larger ionic radius, which causes a distortion of the octahedral structure.

The X-Ray Diffraction patterns of the derived oxides show the characteristic peaks of MgO of the calcined precursor, which appeared together with those of the corresponding third metal oxides.

Otherwise, the metal mixed oxides synthesized by co-precipitation method present higher specific surface areas than the ones obtained from the wet impregnation method.

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