

## Effect of Mg/Al molar ratio on the basicity of Mg-Al mixed oxide derived from Mg-Al hydrotalcite

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**Abstract:** The fundamental character of the Mg-Al mixed oxide ( $Mg_n(Al)O$ ), derived from the Mg-Al hydrotalcite ( $Mg_nAl-CO_3-HT$ ), where  $n$  corresponds to the Mg/Al molar ratio ( $n$ : 2, 2.5, 3, 3.5 and 4), was studied by using the adsorption of phenol as a probe acid molecule. The hydrotalcite precursors were prepared by the coprecipitation method. Their derived mixed oxides were obtained by thermal treatment at  $450^\circ C$  in a flow of air. The resulting solids were characterized by X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), infrared spectroscopy (FTIR), thermogravimetric and differential thermal analysis (TG-DTA), nitrogen physisorption (BET) and phenol chemisorption. The phenol adsorption followed by UV-Visible spectrophotometry shows that the basicity increases with the Mg/Al molar ratio, such that maximum quantity of phenol adsorbed ( $Q_{ads} = 0.54 \text{ mmol/g}_{cat}$ ) was obtained with the mixed oxide derived from the Mg-Al hydrotalcite of Mg/Al molar ratio equal to 3.5.

**Keywords:** Layered double hydroxides; Hydrotalcite; mixed oxide; coprecipitation; basicity; adsorption.

### 1. Introduction

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds are anionic clays, of general formula  $[M^{2+}_{1-x} M^{3+}_x(OH)_2]^{x+} [A^{n-}_{x/n}]_x \cdot mH_2O$ , where the divalent metal ion  $M^{2+}$  maybe ( $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$ , etc.), and the trivalent metal ion  $M^{3+}$  ( $Al^{3+}$ ,  $Fe^{3+}$ ,  $Ga^{3+}$ , etc.). The compensating anions  $A^{n-}$  maybe ( $CO_3^{2-}$ ,  $NO_3^-$ , organic anions, etc) and  $x$  is equal to the  $M^{3+}/(M^{3+} + M^{2+})$  ratio, varying in the range of  $0.2 < x \leq 0.33$ <sup>1-3</sup>. Their structure consists of brucite-type layers  $Mg(OH)_2$ , where the substitution of  $M^{2+}$  by  $M^{3+}$  of relatively similar sizes ( $r_{M^{2+}} - r_{M^{3+}} < 0,18 \text{ \AA}$ ), results in a net positive charge of the layer, counterbalanced by anions, in the inter-sheets domain with water molecules<sup>2,4</sup>. Thus, the preparation of hydrotalcites with inorganic anions or organic anions has been described in the literature<sup>1-5</sup>.

Hydrotalcite-like Compounds have a wide field of application, as catalysts or catalyst supports, adsorbents for water treatment, ion exchangers, filters, stabilizers, and antacids in medicine.

The mixed Mg-Al oxides derived from hydrotalcites are widely used in heterogeneous catalysis. Their catalytic properties depend on several parameters, such as the nature and the molar ratio of the metal cations, and the type of anions of the hydrotalcite inter-layer<sup>5-7</sup>. The thermal decomposition of

hydrotalcites between  $450$  and  $500^\circ C$  affects the density of base sites<sup>8</sup> and textural properties, giving rise to materials with high porosity and surface area with medium and high primary sites<sup>9</sup>. This paper deals with LDHs containing  $Mg^{2+}$  as divalent and  $Al^{3+}$  as trivalent cations, which corresponds to the natural minerals hydrotalcites. The calcination of these solids leads to the collapse of the structure and the formation of mixed oxides  $Mg_n(Al)O$ .

The main objective of this work is to measure the basicity of the mixed oxides  $Mg_n(Al)O$ , derived from their precursor hydrotalcite ( $Mg_nAl-CO_3-HT$ ), by the phenol adsorption as a probe molecule, and examine the influence of the molar ratio Mg/Al on the fundamental properties of these materials.

Moreover, in this article, the results of the study of the basicity of Mg-Al mixed oxides derived from hydrotalcites by phenol adsorption were compared to those of the literature often using programmed temperature desorption of  $CO_2$  (TPD)<sup>8</sup> or the titration with benzoic acid<sup>10</sup> to understand the great difference in the basicity of these same solids studied by the two methods mentioned above.

### 2. Experimental

#### 2.1. Materials

The salts of the metal cations used, magnesium nitrate

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Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and aluminum nitrate Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, are Merck products, with a purity greater than 99%. Sodium hydroxide pellets (NaOH, ≥98%) and sodium carbonate anhydrous powder (Na<sub>2</sub>CO<sub>3</sub>, ≥ 99%) were Fisher products. The solutions used in this study were prepared with deionized water.

## 2.2. Sample preparation

The Mg<sub>n</sub>Al-CO<sub>3</sub>-HT precursors with different Mg/Al molar ratios (n: 2; 2.5; 3; 3.5 and 4) were prepared by the coprecipitation method at constant pH (10±0,2) under air, from an aqueous salt solution (1M) containing magnesium nitrate and aluminum nitrate, and a basic solution containing sodium hydroxide 1.5M and sodium carbonate 0.5M.

Both solutions were mixed dropwise under agitation at 25°C, and after the reactants were added, the slurry was aging for 24 hours at 65°C. The precipitate obtained was filtered, washed several times in distilled water, dried in an oven at 80°C for 24 hours. The precursors were calcined to 450°C in a flow of air. The temperature was raised at a rate of 5°C/min to reach 450°C and maintained for 8 hours. The generated mixed oxides obtained were denoted Mg<sub>n</sub>(Al)O.

## 2.3. Characterizations of the samples

The chemical composition of the synthesized hydrotalcites was determined by X-ray fluorescence spectroscopy, to check whether the molar ratios of Mg<sup>2+</sup>/Al<sup>3+</sup> are by the stoichiometry in the synthesis mixture. The samples were prepared by the pellet method (PROT-ELE03-v01) and then analyzed using the Axios type λ dispersive X-ray fluorescence spectrophotometer.

Powder X-ray diffraction patterns of samples were recorded with a PW 1800 Philips automated goniometer (Bragg-Brentano) using monochromatized Cu Kα radiation (λ = 1,5406 Å, 40kV, and 20mA). The angular 2θ diffraction range was between 5 and 70°.

The data were collected with an angular step of 0.04° at 2s per step.

Fourier transform infrared (FTIR) spectroscopy, was recorded by KBr pellet technique using a Shimadzu (JASCO 4100) instrument, in the wavelength range of 400-4000 cm<sup>-1</sup> with a nominal resolution of 4 cm<sup>-1</sup>. KBr pellets were prepared by mixing very well dried of about 2wt % hydrotalcite with 98 wt.% KBr and pressing.

Thermogravimetric and differential thermal analysis (TG-DTA) were carried out in the air on a Shimadzu (TA-60). A few mg of samples were heated at 20°C/min up 600°C.

The surface area and pore volume measurements of the samples were carried out by nitrogen adsorption at -196°C on a Micromeritics ASAP 2010 system using the BET method. The BJH method (Barrett-Joyner-Halenda) applied to the desorption branch, was used to determine the size of the pores. Before the analysis, the samples were degassed in vacuum at 100°C for the Mg<sub>n</sub>Al-CO<sub>3</sub>-HT or at 250°C for mixed oxides (Mg<sub>n</sub>(Al)O).

The adsorption isotherms of phenol dissolved in cyclohexane at 25°C were used to estimate the density of base sites of the Mg<sub>n</sub>AlO-mixed oxide<sup>11</sup>. The amount of phenol adsorbed by the solids was measured by UV-Visible spectrometer (Shimadzu, UV-1240) at λ = 271 nm.

## 3. Results and discussion

### 3.1. Chemical analysis by X-ray fluorescence

The chemical study by XRF of Mg<sub>x</sub>Al-CO<sub>3</sub>-HT showed that the Mg/Al molar ratios found in solid samples are close to those in solution. This indicates that the operating conditions such as pH, the choice of the precipitating agent, the crystallization temperature lead to the complete precipitation of aluminum and magnesium ions. Also, these chemical analyzes allow us to deduce the approximate formulas of the hydrotalcites studied (Table 1).

**Table 1.** Chemical composition and formulas of the samples studied.

sample	Wt % MgO	Wt % Al <sub>2</sub> O <sub>3</sub>	Mg/Al Molar ratio	( <sup>a</sup> ) x	( <sup>b</sup> ) Formula [Mg <sub>1-x</sub> Al <sub>x</sub> (OH) <sub>2</sub> ] <sup>x+</sup> [X <sup>n</sup> <sub>x/n</sub> .yH <sub>2</sub> O] <sup>x-</sup>
Mg <sub>2</sub> Al-CO <sub>3</sub> -HT	29.70	19.40	1.95	0,34	[Mg <sub>0,66</sub> Al <sub>0,34</sub> (OH) <sub>2</sub> ] [(CO <sub>3</sub> ) <sup>2-</sup> <sub>0,17</sub> .0,49H <sub>2</sub> O]
Mg <sub>2.5</sub> Al-CO <sub>3</sub> -HT	38.00	19.41	2.47	0,29	[Mg <sub>0,71</sub> Al <sub>0,29</sub> (OH) <sub>2</sub> ] [(CO <sub>3</sub> ) <sup>2-</sup> <sub>0,145</sub> .0,565H <sub>2</sub> O]
Mg <sub>3</sub> Al-CO <sub>3</sub> -HT	41.20	17.60	2.91	0,26	[Mg <sub>0,74</sub> Al <sub>0,26</sub> (OH) <sub>2</sub> ] [(CO <sub>3</sub> ) <sup>2-</sup> <sub>0,13</sub> .0,61H <sub>2</sub> O]
Mg <sub>3.5</sub> Al-CO <sub>3</sub> -HT	42.67	14.89	3.65	0,22	[Mg <sub>0,78</sub> Al <sub>0,22</sub> (OH) <sub>2</sub> ] [(CO <sub>3</sub> ) <sup>2-</sup> <sub>0,11</sub> .0,67H <sub>2</sub> O]
Mg <sub>4</sub> Al-CO <sub>3</sub> -HT	43.92	13.51	4.19	0,19	[Mg <sub>0,81</sub> Al <sub>0,19</sub> (OH) <sub>2</sub> ] [(CO <sub>3</sub> ) <sup>2-</sup> <sub>0,095</sub> .0,72H <sub>2</sub> O]

(<sup>a</sup>)x=Al<sup>3+</sup>/(Mg<sup>2+</sup>+Al<sup>3+</sup>). (<sup>b</sup>)Formula obtained from Ref<sup>1</sup>. Parameter y= 1-3\*x/2 obtained from Ref<sup>2</sup>.

### 3.2. X-ray Diffraction

The X-ray diffraction patterns of Mg<sub>n</sub>Al-CO<sub>3</sub>-HT (X: 2, 2.5, 3, and 3.5) are depicted in Figure 1A; the diffractograms of these materials present sharp and symmetric reflections of the (003), (006) planes at low values of 2θ angles (2θ ≈ 11- 24°), as well as other reflections at 2θ ≈ 34.5, 38.8, 45.9, 60.5, and 62°

respectively corresponding to the (009), (015), (018), (110) and (113) planes. These reflections are characteristic of a highly crystalline structure of hydrotalcites<sup>2,8,12</sup>. The values of the unit cell parameters can be determined for the hexagonal cell using the R $\bar{3}$ m space group in rhombohedral symmetry.

The diffraction corresponding to the (003) plane was used to calculate the basal spacing between the layers,  $c = 3d_{003}$ , while the (110) reflection was used to calculate the unit cell dimension,  $a$ , where  $a = 2d_{110}$ .

The obtained values are in good agreement with those found in the literature<sup>13</sup>. The crystallite size of the samples was calculated from X-ray line broadening, using the Scherrer equation ( $L = 0.9\lambda / \beta \cos \theta$ )<sup>14</sup>, considering the basal reflections (003) and (110) for the hydrotalcites, and (200) for the mixed oxides. The results of these calculations are summarized in Table 2.

In accord with previous measurements by Yun<sup>15</sup> and Di Cosimo<sup>8</sup>, it is seen that the value of the lattice parameter increases with the Mg content indicating that the mean distance between cation-cation in the brucite layer increased by the substitution of smaller  $Al^{3+}$  radius ions by larger  $Mg^{2+}$  ions<sup>16,17</sup>.

Simultaneously the increase of the  $c$  parameter with the increasing Mg/Al molar ratio (i.e., with a decrease in the  $Al^{3+}$  cations) is coherent with the decreased attractive forces between the brucite-like layers with a positive charge and the interlayer anions.

After thermal decomposition of  $MgAl-CO_3-HT$  at  $450^\circ C$ , the X-ray patterns of the calcined materials, shown in Figure 1B, present two new intensive diffractions lines at around  $43.1$  and  $62.5^\circ$ , which correspond to the (200) and (220) reflections of the MgO periclase-type structure<sup>8,17</sup>.

The average crystallite size of the mixed oxides is widely lower than the hydrotalcites. It decreases with an increase in the Mg/Al molar ratio (exception for the molar ratio equal to 4). It is seen that the crystallite size of  $Mg_{3.5}Al-O$  ( $34\text{\AA}$ ) is slightly smaller than in the other mixed oxides (Table 2).

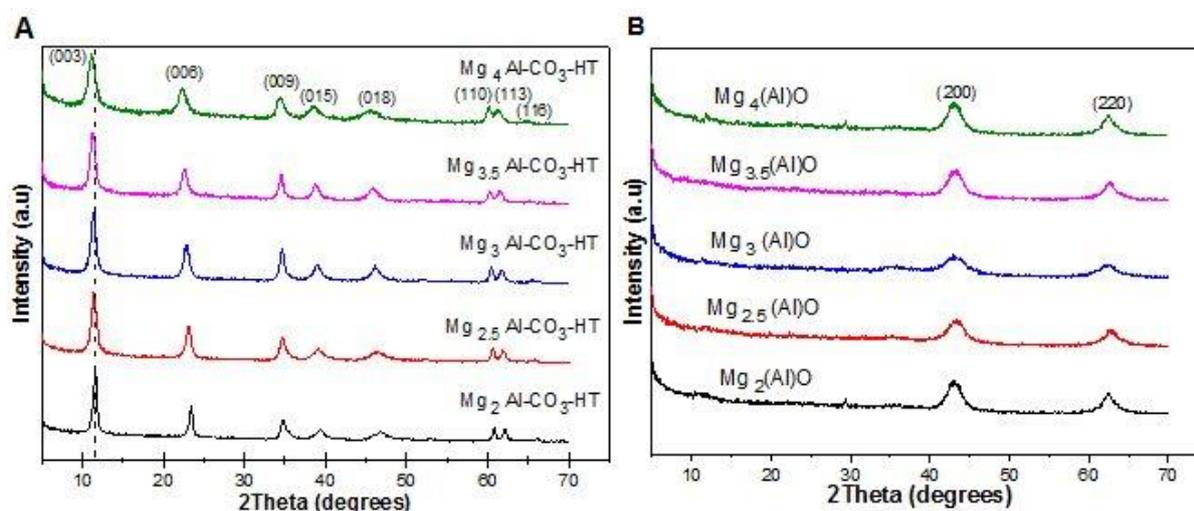


Figure 1. X-ray patterns of fresh (A) and calcined (B) materials

Table 2. Lattice parameters of hydrotalcites and crystallite size ( $L(\text{\AA})$ ) of the samples.

Sample	$d_{003}$ ( $\text{\AA}$ )	$c$ ( $\text{\AA}$ )	$d_{110}$ ( $\text{\AA}$ )	$a$ ( $\text{\AA}$ )	The crystallites size of hydrotalcites		The crystallites size of mixed oxides $L_{(200)}$ ( $\text{\AA}$ )
					$L_{(003)}$ ( $\text{\AA}$ )	$L_{(110)}$ ( $\text{\AA}$ )	
$Mg_2Al-CO_3-HT$	7.59	22.75	1.52	3.037	92.8	151.7	48
$Mg_{2.5}Al-CO_3-HT$	7.70	23.08	1.53	3.048	93.8	150.8	42
$Mg_3Al-CO_3-HT$	7.80	23.44	1.53	3.059	96.7	147.8	37
$Mg_{3.5}Al-CO_3-HT$	7.84	23.45	1.54	3.068	97	147	34
$Mg_4Al-CO_3-HT$	7.89	23.47	1.54	3.069	99	150	50

### 3.3. Infrared spectroscopy (FTIR)

Infrared spectroscopy has been widely used to characterize hydrotalcite and related materials<sup>2,8,18</sup>. The FT-IR spectra of  $Mg_nAl-CO_3-HT$  with Mg/Al molar ratios from 2 to 4 are shown in Figure 2. In all cases, these spectra show the main active IR vibrations in  $Mg_nAl-CO_3-HT$ . An absorption band centered at  $3460\text{ cm}^{-1}$ - $3537\text{ cm}^{-1}$ , is attributed to the hydroxyl groups. A slight shift towards higher frequencies is observed when the Mg/Al molar ratio

increases from 2 to 4. This effect can be explained by the increase in Mg-OH bond strength when the average load in the sheet increases by the decrease in the value of  $d_{003}$  observed by XRD<sup>1,19,20</sup>. The shoulder around  $3050\text{ cm}^{-1}$  can be attributed to the  $H_2O-CO_3^{2-}$  interlayer bridging mode by hydrogen bonds. The band around  $1630\text{ cm}^{-1}$  is attributed to the deformation vibration due to interlayer water  $\delta H_2O$ <sup>1,20</sup>. The sharp, intense vibration bands observed around  $1370\text{ cm}^{-1}$ - $1380\text{ cm}^{-1}$  were assigned to the asymmetric

stretching of  $\text{CO}_3^{2-}$  anions. This band is broad, which suggests the presence of nitrate ions from the starting salts, especially since the mode of vibration of  $\text{NO}_3^-$  is largely overlapped by the mode of vibration of  $\text{CO}_3^{2-}$ <sup>21</sup>. The bands observed at lower wavenumber

( $400 < \nu < 1000 \text{ cm}^{-1}$ ) are caused by metal-oxygen (M-O) stretching vibrations (close to  $700 \text{ cm}^{-1}$ ) and metal hydroxide (M-OH) vibrations (between  $600$  and  $400 \text{ cm}^{-1}$ )<sup>22,23</sup>.

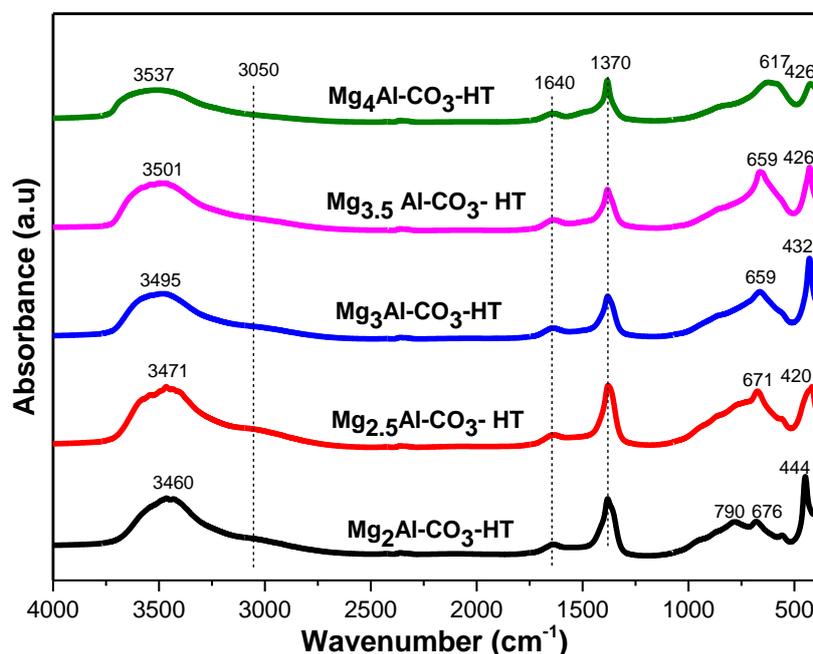


Figure 2. FTIR spectra of  $\text{Mg}_n\text{Al-CO}_3\text{-HT}$  ( $n=\text{Mg}/\text{Al} = 2; 2.5; 3; 3.5$  and  $4$ )

### 3.4. TG - DTA analysis

Figure 3 shows the thermal decomposition of samples in the air by TG-DTA analysis in the range of temperature  $25\text{-}600^\circ\text{C}$ . The decomposition profiles are in good agreement with those in the literature for

hydrotalcite-like compounds, with a total weight loss in the range of  $35\text{-}46 \text{ wt}\%$ <sup>24,25</sup>. The thermograms of all solids presented two weight loss regions, corresponding to endothermic events in the DTA analysis, as classically found for LDH materials<sup>26,27</sup>.

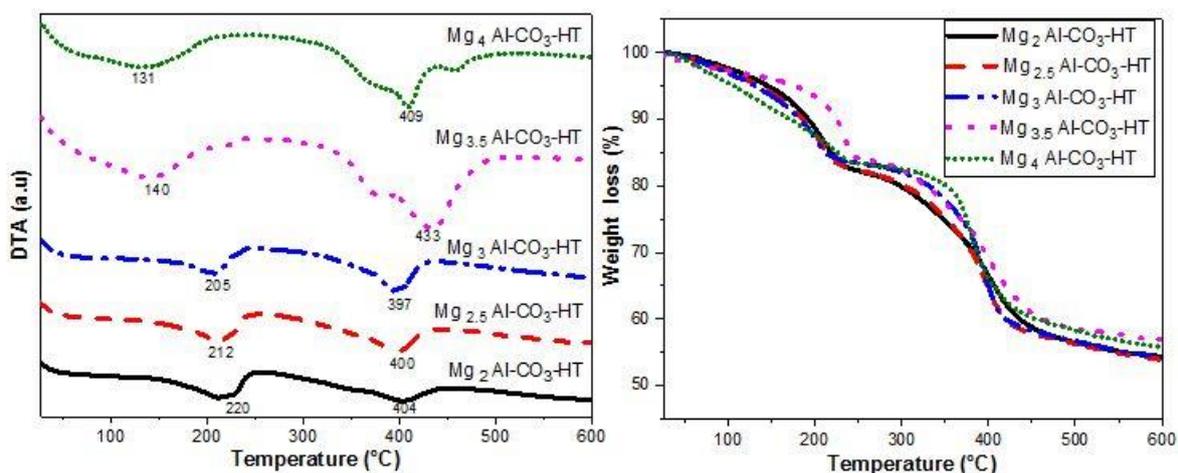


Figure 3. TG-DTA profiles of  $\text{Mg}_n\text{Al-CO}_3\text{-HT}$  ( $n=\text{Mg}/\text{Al} = 2; 2.5; 3; 3.5$  and  $4$ )

The first region at temperatures below  $207^\circ\text{C}$ , corresponding to a weight loss of  $11\text{-}18 \text{ wt}\%$ , is related from weakly connected water molecules located in the interlayer domain or adsorbed on the outer surfaces of the crystals<sup>4</sup>. In contrast, the second peak at ( $300\text{-}500^\circ\text{C}$ ) stems from the dehydroxylation of the brucite-like sheets and decomposition of the compensating anions in the interlayer<sup>28</sup>.

In our case, the shapes of the TGA curves and the positions of the DTA peaks show similarities between the synthesized materials; the differences only concern the total weight loss and the thermal stability of the samples.

The  $\text{Mg}_{3.5}\text{Al-CO}_3\text{-HT}$  sample had the lowest weight loss of all the samples and showed high thermal stability since the second DTA peak is extended at a high temperature equal to  $433^\circ\text{C}$ .

### 3.5. Adsorption of N<sub>2</sub>

The values of the BET surface areas and porosities of Mg<sub>n</sub>Al-CO<sub>3</sub>-HT and mixed oxides Mg<sub>n</sub>(Al)O are presented in Table 3. All materials have an average pore size in the range of 9-21nm, suggesting that all the samples are mesoporous materials.

The surface areas and pore volumes for mixed oxides Mg<sub>n</sub>(Al)O are higher than those of their precursors Mg<sub>n</sub>Al-CO<sub>3</sub>-HT (Table 3), Indeed, during the calcination, the departure of water and carbonates leads to a considerable increase in the surface and volume of the pores. The mixed oxide with Mg /Al ratio equal to 3.5 shows smaller crystallites size

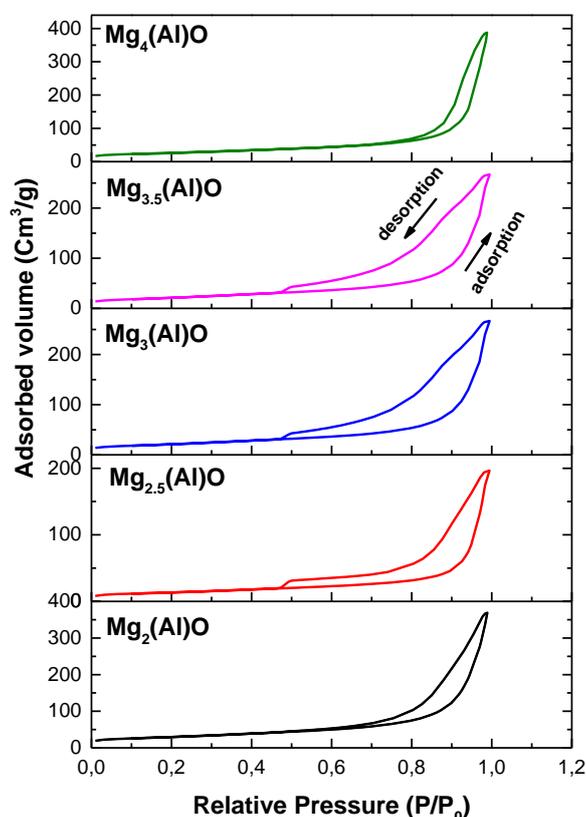
(L= 34 Å), higher surface area (214 m<sup>2</sup>/g), and higher pore volume (0.80 cm<sup>3</sup>/g).

The adsorption-desorption isotherms of the mixed oxides, which is shown in Figure 4, corresponds to type IV<sup>29</sup> according to IUPAC classification with a hysteresis loop characteristic of mesoporous materials<sup>8,30</sup>.

Moreover, the hysteresis loop begins at a high relative pressure, which further justifies the mesoporous nature of these materials. The type H3, according to the IUPAC classification, is observed for all the samples, which have non-rigid aggregates of platelet like particles forming slit-like pores<sup>31</sup>.

**Table 3.** Textural properties of the samples.

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	Pore diameter (nm)	Pore volume (cm <sup>3</sup> /g)
Mg <sub>2</sub> Al-CO <sub>3</sub> -HT	75	14	0.41
Mg <sub>2.5</sub> Al-CO <sub>3</sub> -HT	93	21	0.61
Mg <sub>3</sub> Al-CO <sub>3</sub> -HT	105	16	0.50
Mg <sub>3.5</sub> Al-CO <sub>3</sub> -HT	101	18	0.57
Mg <sub>4</sub> Al-CO <sub>3</sub> -HT	56	12	0.33
Mg <sub>2</sub> (Al)O	168	11	0.53
Mg <sub>2.5</sub> (Al)O	198	20	0.78
Mg <sub>3</sub> (Al)O	210	15	0.72
Mg <sub>3.5</sub> (Al)O	214	13	0.80
Mg <sub>4</sub> (Al)O	154	9	0.42



**Figure 4.** Nitrogen adsorption/desorption isotherms for Mg<sub>n</sub>Al-mixed oxides

### 3.6. Basic properties of the Mg-Al mixed oxides

#### 3.6.1. Phenol adsorption

To probe the basic properties of mixed oxides, the adsorption of phenol ( $pK_a = 9.9$ ) at  $25^\circ\text{C}$  was used. It has been reported to be an effective method to measure the strong basic sites of porous solids<sup>32,33</sup>.

Standard solutions of phenol in cyclohexane were prepared at room temperature. A quantity of 25ml for each standard solution was taken in separate conical flasks to which 50 mg of solid was added, and each mixture was kept in a shaker for 3h. After equilibrium was reached, solids were separated from the solution by vacuum filtration. The concentration of phenol in the cyclohexane solvent after adsorption was evaluated by a Shimadzu, UV-1240 spectrometer ( $\lambda = 271$  nm). The phenol adsorption isotherms of all catalysts are presented in Figure 4. All five isotherms were of the Langmuir type, indicating chemisorption of phenol.

Figure 4 shows that all the samples can adsorb phenol, which means that they own basic surface sites, and

$\text{Mg}_{3.5}(\text{Al})\text{O}$  has the highest amount of strong basic sites. It was observed that the number of strong basic sites of the solids was increased with the Mg/Al molar ratio and came up to the maximum value at the Mg/Al molar ratio of 3.5. Numerous authors have shown that the basic properties of the surface of MgAl-mixed oxides derived from Mg-Al hydrotalcites depend on their composition; a straightforward correlation has been established between the composition and the basicity: when the amount of Al increases, the total number of basic sites decreases<sup>34,35</sup>.

However, the strength and the proportion of more robust sites are also changed; this may compensate for the decrease in total basicity. Indeed, lowering the Mg/Al ratio results in the creation of stronger basic sites. In the case of Mg-Al mixed oxides, the active basic sites are associated with hydroxide groups and different  $\text{Mg}^{2+}\text{-O}^{2-}$  acid-base pairs. The basicity of the Lewis sites associated with  $\text{O}^{2-}$  anions depends on their coordination.

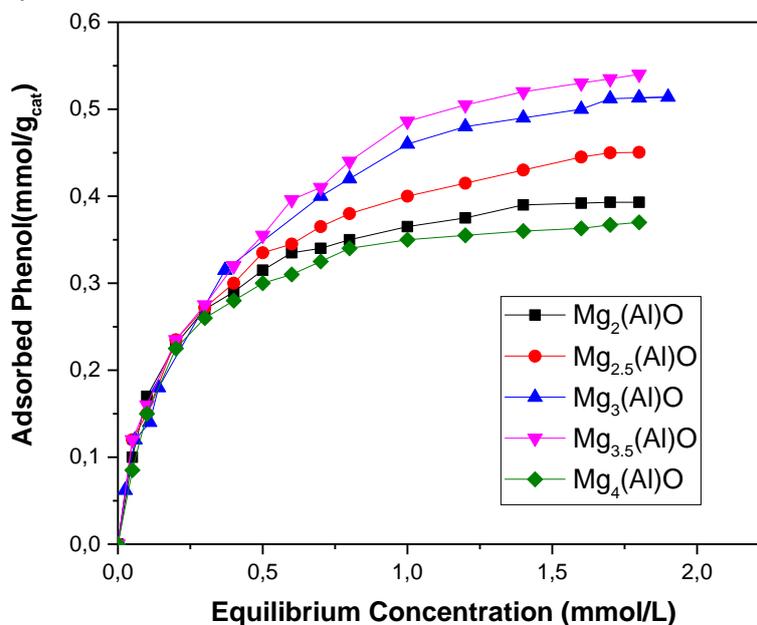


Figure 5. Phenol adsorption isotherms studies of  $\text{Mg}_n\text{Al}$ -mixed oxides

#### 3.6.2. Effect of Mg/Al molar ratio on amount phenol adsorbed and on the BET specific surface

The amount of phenol adsorbed at  $25^\circ\text{C}$  and the surface area on each mixed oxide, are plotted according to the Mg/Al molar ratio in Figure 5. It can be seen that the quantity of phenol adsorbed, and the surface area of mixed-oxides increase in parallel with the increases Mg/Al molar ratio, to obtain maximum values with Mg/Al = 3.5, then decrease sharply towards the lower values for Mg/Al = 4. Therefore, the results suggest that Mg/Al molar ratio equal to 3.5 presents the highest amount of strong basic sites in the interval of the molar ratios studied. These results may agree with several authors who have evaluated the acid-base properties of Mg-Al mixed oxides using other methods with other probe molecules. The effect of the Al content on the basicity of Mg-Al mixed

oxides was studied by Nakatsuka et al.<sup>36</sup> (for  $1 < \text{Mg}/\text{Al} < 9$ ) and by Fishel et al.<sup>37</sup> (for  $3 < \text{Mg}/\text{Al} < 6$ ) and by Di Cosimo et al.<sup>8</sup> (for  $1 < \text{Mg}/\text{Al} < 5$ ). Nakatsuka et al.<sup>36</sup> reported that the basic site density measured by titration with benzoic acid depends on the Al content, reaching a maximum for Mg/Al of about 2.6. Fishel et al.<sup>37</sup> and Di Cosimo et al.<sup>8</sup> measured the number of basic sites by Temperature-programmed desorption of chemisorbed  $\text{CO}_2$ . For Fishel et al., the basic site density increases for lower Mg/Al values, reaching a maximum at Mg/Al = 3. For Di Cosimo et al., in samples of Mg/Al > 4 the basic site density is lower, but in samples of  $1 < \text{Mg}/\text{Al} < 4$ , a highly interacting Mg-Al oxide phase is formed, to increase the basic site density.

Table 4 summarizes specific results reported in the literature on the number of strong basic sites of the same mixed oxides measured by temperature-

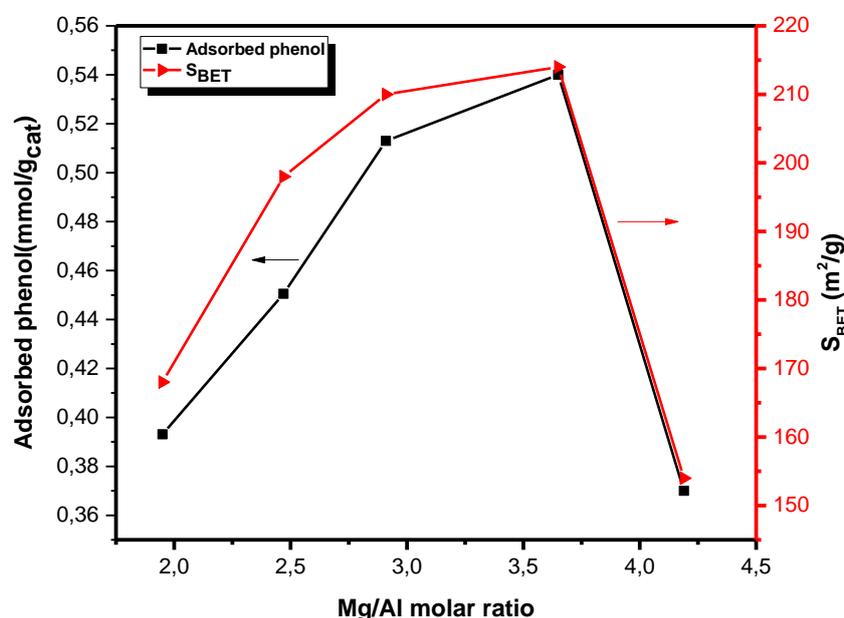
programmed desorption of CO<sub>2</sub> and by titration with benzoic acid, with our results using the adsorption of phenol.

**Table 4.** Strong basic sites of Mg<sub>n</sub>Al-mixed oxides (mmol/g).

Mg/Al			Strong basic sites by TPD of CO <sub>2</sub> Ref. 8 <sup>a</sup>	Strong basic sites by titration Ref. 10 <sup>b</sup>	Strong basic sites by phenol adsorption This work
Ref. 8	Ref. 10	This work			
/	2	1.95	/	0.45	0.39
/	2.33	2.47	/	0.80	0.45
3	/	2.91	0.064	1.35	0.51
/	3.54	3.65	/	1.05	0.54
4.5	4	4.19	0.039	0.90	0.37

a: strong basic sites calculated from reference 8

b: strong basic sites took directly from the results of the reference 10



**Figure 6.** The relation between amount phenol adsorbed, surface area, and Mg/Al molar ratio

#### 4. Conclusions

Mg-Al hydrotalcite-like materials at different Mg/Al molar ratio, containing CO<sub>3</sub><sup>2-</sup> interlayer anions, were prepared by the coprecipitation method. The thermal treatment under air at 450°C of the synthesized materials, led to the decomposition of the hydrotalcite structure, and formation of Mg-Al mixed oxides.

The basic properties of these mixed oxides have been evaluated by chemisorption of phenol as a probe molecule and compared with the results of the literature using other probe molecules, such as benzoic acid or carbon dioxide.

From the results obtained, it appears that:

- The composition of the synthesized materials has been confirmed by different physicochemical techniques (XRD, FTIR....).
- BET analysis has shown that these mixed oxides are mesoporous materials, and their specific surface area

increases with the Mg/Al molar ratio and come up to the maximum value at the Mg/Al molar ratio of 3.5.

- The influence of the aluminum content on the basic properties showed that the basicity of these materials increases with the decrease in the amount of aluminum (i.e., with the increase in the Mg/Al molar ratio, up to 3.5).

- The evaluation of the basicity by chemisorption of phenol showed that the number of basic sites varies in parallel with the Mg/Al molar ratio and the specific surface of these materials.

- The disparity noted in the determination of the basicity of the solids with one of the three methods (TPD of CO<sub>2</sub>, titration with benzoic acid or absorption of phenol) perhaps due to the divergence of the technique itself, or to the non-reproducibility of sample preparation, conducting to solids with different basic properties.

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