

# Structural Characterization of Some Mg/Zn-Al Type Hydrotalcites Prepared for Chromate Sorption from Wastewater

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**Abstract:** Five hydrotalcite-like compounds with different Mg/Zn ratio were prepared and characterized from a structural point of view, in order to be used for chromate uptake from wastewater. The chemical composition of the materials was determined using EPMA (electron probe microanalysis). The thermal behavior was investigated by DTG method. The structure of as-synthesized hydrotalcite-like samples was confirmed by X-Ray Diffraction and FTIR Spectroscopy methods. A part of the samples were activated in an oven, at temperatures of 500°C in air, with a rate of 5°C/min for 4 hours and the specific surface area of calcined compounds was measured.

**Keywords:** hydrotalcite-type compound, structural characterization, thermal behavior, specific surface area, morphology

## 1. Introduction

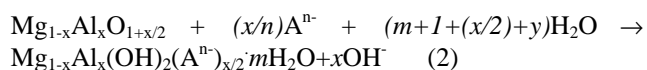
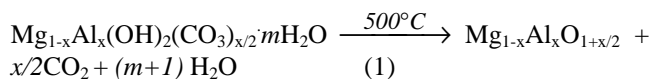
Hydrotalcite, first discovered in Sweden around 1842, is a hydroxycarbonate of magnesium and aluminum and it occurs in nature in forms of foliated and contorted plates and/or fibrous masses [1]. The chemical formula of hydrotalcite is  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ . Its structure can be explained by analogy with the crystal structure of brucite,  $\text{Mg}(\text{OH})_2$ . Brucite consists of a hexagonal close packing of hydroxyl ions with alternate octahedral sites occupied by  $\text{Mg}^{2+}$  ions. The metal hydroxide sheets in brucite crystal are neutral in charge and they overlap one another by Van der Waal's interactions. In hydrotalcite, some of the  $\text{Mg}^{2+}$  cations of these brucite-like sheets are isomorphously substituted by  $\text{Al}^{3+}$  cations and thus formed mixed metal hydroxide layers,  $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}]^{2+}$ , acquire a net positive charge. This excess charge on the metal hydroxide layers is neutralized by  $\text{CO}_3^{2-}$  anions accumulated in the interlayer region. The interlayer region also contains some water molecules for the stabilization of the crystal structure.

The hydrotalcite-like compounds, also called anionic clays or layered double hydroxides, have similar structure as hydrotalcite and the general formula is  $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+} [\text{A}^{n-}_{x/n} \cdot m\text{H}_2\text{O}]^{x-}$ , where  $\text{M}^{\text{II}}$  is a divalent cation ( $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  etc.),  $\text{M}^{\text{III}}$  a trivalent cation ( $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{In}^{3+}$ ,  $\text{Cr}^{3+}$  etc.) and  $\text{A}^{n-}$  charge compensating anions ( $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^-$  etc.).

Interest in hydrotalcite-like compounds has grown due to their role in controlling the mobility of aqueous metals in the environment [2-6] as well as their use as catalysts [1,7-9] and catalysts precursors [10-12].

The decomposition of hydrotalcite-like compounds when heated at around 500 °C leads to mixed metal oxides,

which are characterized by a high specific surface area and homogeneous dispersion of the metal cations. The mixed metal oxides can take up anions from aqueous solution, resulting in a concomitant reconstruction of the original layered structure, the so-called "memory effect", as expressed by the following equations [13]:



Therefore, the calcined hydrotalcite-like compounds can be used as potential ion exchangers/adsorbents for the removal of toxic anions from wastewaters.

In this work, five hydrotalcite-like compounds containing  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$  in different proportions as divalent cations were synthesized and characterized from a structural, textural and morphologic point of view, in order to be used as adsorbents for chromate anion removal.

## 2. Experimental

The hydrotalcite-like compounds were prepared by using a classic procedure: the co-precipitation method [1]. All used nitrates originated from Sigma. A solution of NaOH was slowly added to a 1 mol/L solution of zinc nitrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and aluminum nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) in distilled water, under magnetic stirring, so that the pH was kept at a constant value under the command of a

Hanna HI 991003 pH-meter. The mixing step was carried out for 1 h, at room temperature, under stirring, and then for 18 h on an oil bath at 80°C, under magnetic stirring and reflux. The hydrotalcite powders were recuperated by centrifugation and washed several times with demineralized water until pH = 7. This step was followed by drying at 80°C overnight. Then, the dried samples were crushed and sieved. The as-synthesized samples were denoted HTa (with the a values from 1 to 5).

A part of the samples were activated in an oven, at temperatures of 500°C in air, with a rate of 5°C/min for 4 hours, in order to be transformed into the mixed oxide type (denoted hereafter as CHTa, with a = 1 - 5).

The chemical composition of the as-synthesized products was determined using a JEOL JCXA 733 superprobe EPMA (electron probe micro analysis).

The thermal analysis was performed under an inert atmosphere (nitrogen), from 20 to 500 °C, with a heating rate of 5 °C/min by using a TG 209 Netzsch analyzer.

Powder X-ray diffraction patterns were recorded on a Bruker D8 Advance diffractometer using MoK $\alpha$  radiation (0.70930 nm).

Fourier transform infrared (FTIR) spectra were performed within the range of wavenumbers from 4000 to 400 cm<sup>-1</sup> on a Shimadzu IRPrestige-21 FTIR spectrophotometer, with a nominal resolution of a 4 cm<sup>-1</sup>. The samples were prepared by mixing the powdered solids with KBr.

Morphology was observed with a Philips XL20 scanning electron microscope.

Surface areas, pore volumes and the adsorption-desorption isotherms of the calcined samples were determined by N<sub>2</sub> adsorption-desorption at 77 K, using the BET analysis method, with a Micromeritics ASAP 2020 instrument.

### 3. Results and Discussion

The cationic ratio in the as-synthesized hydrotalcite-like samples was in good agreement with the initial one, as the EPMA results showed no major changing in the final composition (Table 1).

TABLE 1. Results of EPMA analysis

Sample	Initial Mg/Zn/Al ratio (nitrate solutions)	Elemental analysis			Final Mg/Zn/Al ratio (as-synthesized samples)
		% wt Mg	% wt Zn	% wt Al	
HT1	2 / 0 / 1	35.8	-	20.0	1.98 / 0 / 1
HT2	2 / 1 / 1	19.5	35.4	12.3	1.76 / 1.19 / 1
HT3	1.5 / 2 / 1	12.4	48.8	9.5	1.45 / 2.12 / 1
HT4	1 / 2.5 / 1	8.6	54.8	9.0	1.06 / 2.52 / 1
HT5	0 / 4 / 1	-	68.7	6.5	0 / 4.37 / 1

According to TG analysis in Table 2, the samples showed the presence of the first weight loss step around 100 °C corresponding to the loss of physically adsorbed water. Mass loss values corresponding to this process range from 3 to 7 %. Heating the samples at temperatures around 160 °C leads to loss of interlayer water molecules, with a weight loss from 5 – 7 %. The weight loss at low temperatures for HT1 sample occur in a single step (92.5 °C – physically adsorbed water and 144.8 °C – interlayer water). Substitution of Mg<sup>2+</sup> with Zn<sup>2+</sup> cations leads to a loss of physically adsorbed and interlayer water molecules in several stages. The structure of hydrotalcites is based on substitution of divalent cations (Mg<sup>2+</sup>) with trivalent cations (Al<sup>3+</sup>), so that Mg(OH)<sub>2</sub> · xH<sub>2</sub>O becomes Mg<sub>6</sub>Al<sub>3</sub>(OH)<sub>16</sub>CO<sub>3</sub> · mH<sub>2</sub>O. The latter becomes Mg<sub>x</sub>Zn<sub>y</sub>Al<sub>z</sub>(OH)<sub>16</sub>CO<sub>3</sub> · mH<sub>2</sub>O by Mg<sup>2+</sup> with Zn<sup>2+</sup> substitution. The several weight loss stages suggests that water molecules are different adsorbed on Mg-OH, Al-OH, and Zn-OH units.

The main mass loss process occurs in the range of 180 – 380 °C, when the weight losses are important, between 20 and 24 %. This weight losses are due to dehydroxylation and partial decarbonation of the compounds. By heating the hydrotalcite-like compounds at temperatures above 380 °C, the mass losses values are between 3 – 7 % and is due to total decarbonation of the samples [14].

TABLE 2. TG and DTG results for the hydrotalcite-like compounds

Sample	Heat flow step(°C)	Temperature (°C)	Weight loss (%)
HT1	20 – 126	92.5	6.75
	126 – 181	144.8	5.41
	181 – 368	315.8	24.11
	368 – 500	438.6	6.88
HT2	20 – 103	55.2	5.69
		73.7	
		96.1	
	103 – 180	129.2	7.20
		175.9	
HT3	180 – 373	211.8	22.34
		256.2	
	373 – 500	463.5	4.00
		424.5	
		424.5	
HT4	20 – 77	55.6	2.82
	77 – 160	131.9	7.31
	160 – 380	249.4	20.66
		286.9	
HT5	380 – 500	424.5	2.93
		424.5	
		424.5	
		424.5	
	20 – 86	57.7	3.31
		131.1	
		234.7	
		449.8	
	20 – 136	76.4	6.55
		129.1	
		188.2	
		284.1	
HT5	136 – 236	188.2	16.21
		284.1	
		421.6	
HT5	236 – 321	284.1	5.14
		421.6	
		421.6	

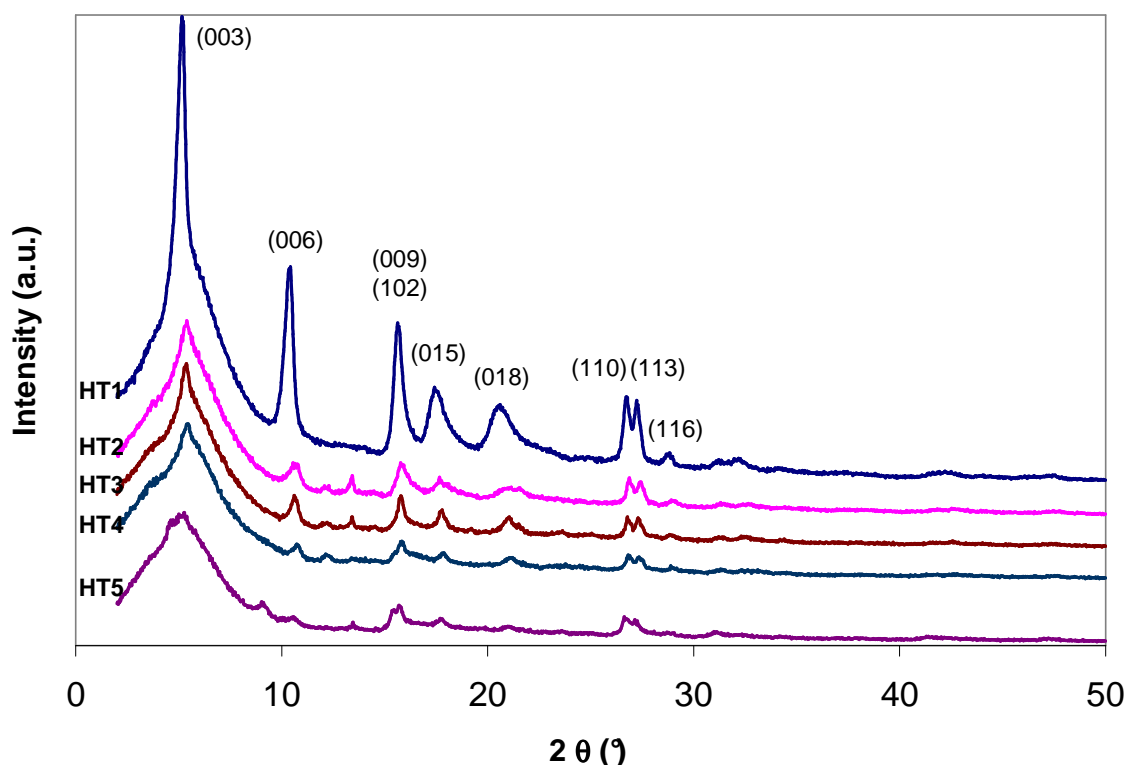


Figure 1. The XRD patterns of the samples

Figure 1 show the XRD patterns of the prepared hydrotalcites. The XRD patterns show that all the compounds have layered structure [7]. The peaks which correspond to basal planes (003) and (006) are present at low  $2\theta$  angles. Also, the reflections (110) and (113) observed at  $2\theta$  angles between 25 and 30°, are characteristic for hydrotalcite-like compounds. The difference in the intensities of the reflections from one sample to another indicates different degrees of crystallinity when the cationic composition varies. The calculation of unit cell parameters was done by the peaks indexing in the hexagonal crystal system (Table 3).

TABLE 3. The unit cell parameters for the as-synthesized samples

Sample	Unit cell parameters			Polytype
	$a$ (Å)	$c$ (Å)	$c'$ (Å)	
HT1	3.04	23.64	7.88	3R
HT2	3.02	22.83	7.61	3R
HT3	3.02	22.95	7.65	3R
HT4	3.02	22.65	7.55	3R
HT5	3.08	23.68	7.79	3R

The parameter  $a$  represents the distance between two adjacent cations (bi- or trivalent) in the layer, the parameter  $c'$  is related to the total thickness of the brucite-like layer and the interlayer distance, whereas  $c = 3c' = 3d_{003}$ . The values obtained here are close to previously reported data for similar materials [15,16]. It can be noticed that the unit cell parameter  $a$  value is not influenced by the nature of divalent cations incorporated in the brucite-like layers because they do not have too different ionic radii ( $r_{\text{Mg}^{2+}} = 0.65 \text{ Å}$  and  $r_{\text{Zn}^{2+}} = 0.74 \text{ Å}$ ) and do not lead to distortions in

the octahedral planes. The decrease of the parameter  $c$ , therefore, the decrease of the interlayer spacing  $c'$ , can be attributed to a distortion of the hydrotalcite network induced in the substitution process of magnesium by zinc [17].

The FTIR spectra of all the resultant hydrotalcite-type compounds are characteristic for this type of materials, as it shows in Figure 2.

The broad and strong absorption band in the range of  $3600\text{--}3200 \text{ cm}^{-1}$  is due to the O-H stretching vibration of the surface and interlayer water molecules. The broad shoulder close to  $3000 \text{ cm}^{-1}$  has been attributed to hydrogen bonding between water and carbonate anions in the interlayer galleries. The adsorption band in the range  $1650\text{--}1620 \text{ cm}^{-1}$  is due to the bending vibration of the interlayer water molecules ( $\delta_{(\text{HOH})}$ ) [1].

The absorption bands located around  $1500 \text{ cm}^{-1}$ , identified in the spectra of HT2, HT3, HT4 and HT5 samples, are due to the stretching vibrations ( $\nu_3$ ) of carbonate anions [18]. The presence of a multiple band between  $1200\text{--}1600 \text{ cm}^{-1}$  and not a single intense band at  $1383 \text{ cm}^{-1}$  indicates that the symmetry of the carbonate anions is lowered from the planar  $D_{3h}$  to the  $C_{2v}$  symmetry. The lowering of the symmetry also causes the activation of the  $\nu_1$  mode at  $1050 \text{ cm}^{-1}$ . Weakly resolved shoulders present between  $850\text{--}820 \text{ cm}^{-1}$  are attributed to bending vibrations ( $\nu_2$ ) of carbonates.

The band located around  $783 \text{ cm}^{-1}$ , identified in the FTIR spectra of HT2, HT3 and HT4 samples, are due to the Al – O or Zn – Al – O bond vibrations in the brucite-like layer [19].

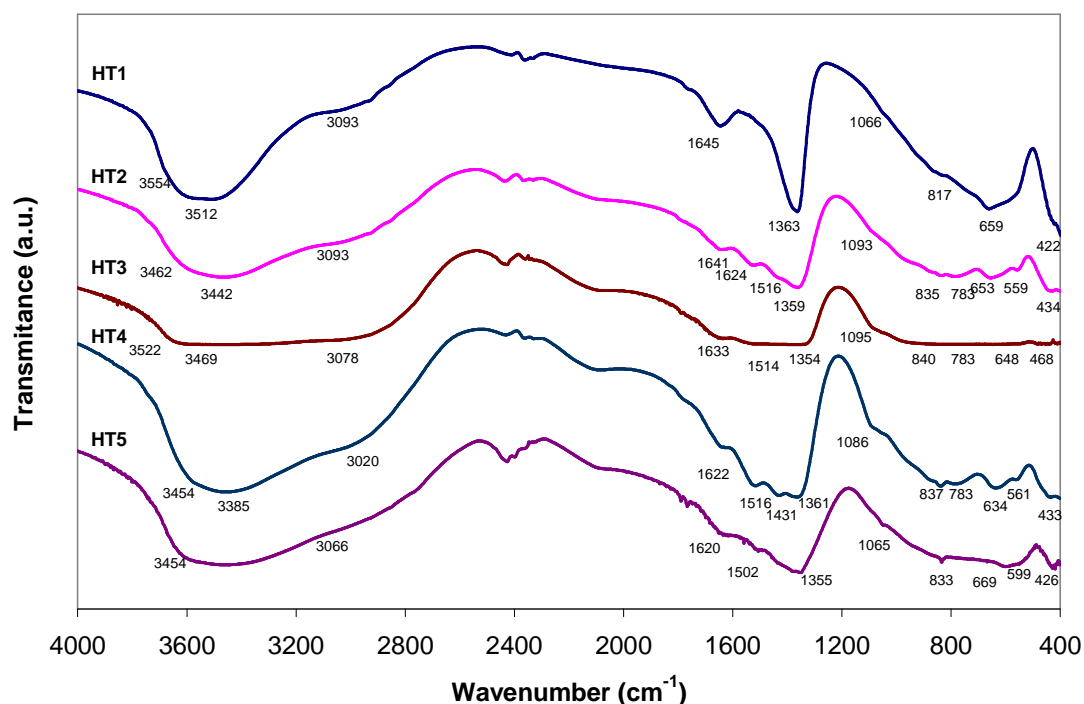


Figure 2. The FTIR spectra of the hydrotalcite-like compounds

In addition, the spectra contains absorption bands at  $670\text{--}620\text{ cm}^{-1}$  ( $\nu_4$  bending vibrations of carbonate bonds),  $590\text{--}560\text{ cm}^{-1}$  (may be due to stretching and bending vibrations of  $\text{M} - \text{O}$ ,  $\text{M} - \text{O} - \text{M}$  and  $\text{O} - \text{M} - \text{O}$  bonds) and  $460 - 420\text{ cm}^{-1}$  (vibrations of  $\text{Mg} - \text{OH}$ ,  $\text{Al} - \text{OH}$  and  $\text{Zn} - \text{OH}$  bonds from hydrotalcite octahedral networks). The last two absorption bands are typical for brucite-like layer.

The analysis of SEM micrographs (Figure 3) reveals that the prepared hydrotalcites-like compounds have good crystallinity, however the crystals are in great cohesion and have variable dimensions. Agglomerated and irregular sheets, lying on top of one another can be observed. These aspects are typical for hydrotalcites obtained by co-precipitation method at low supersaturation [20].

Figure 4 shows the  $\text{N}_2$  adsorption-desorption plots at 77 K for the calcined samples CHT1, CHT4 and CHT5. In all cases, the patterns correspond to the IV type but the hysteresis loops are different. The sample CHT1 shows the H2 type hysteresis loop while the presence of the H1 type in the Zn-containing samples is observed. Therefore, the pore shapes are different when the  $\text{Zn}^{2+}$  cations are introduced. In the first case, the H2 hysteresis loop is broad, the desorption branch being much steeper than the adsorption branch, associated with the interconnected pores and evidencing the mesoporous materials with a more complex morphology. In the former case the H1 hysteresis loop is relatively narrow with the adsorption and desorption branches nearly parallel, associated to compact packings of homogeneous spheres and narrow pore size distributions. The specific surface area values range is between  $244\text{--}32\text{ m}^2/\text{g}$ . The values decrease systematically upon increasing the  $\text{Zn}^{2+}$  content in the samples.

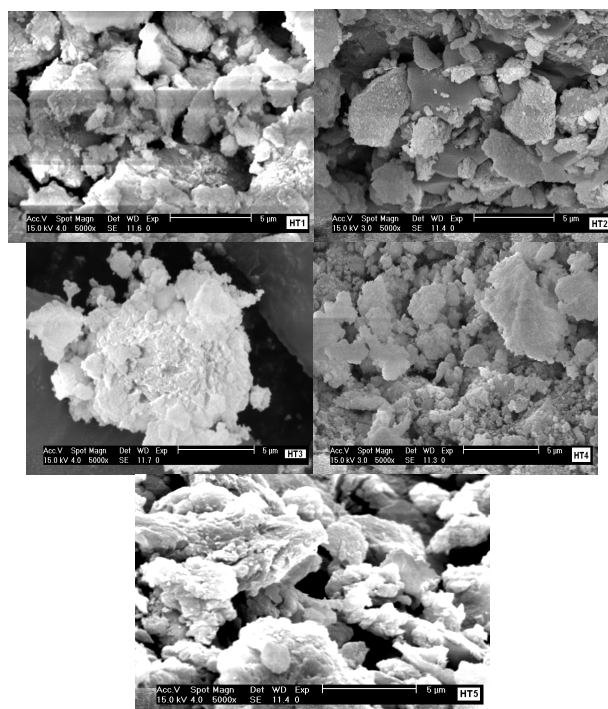
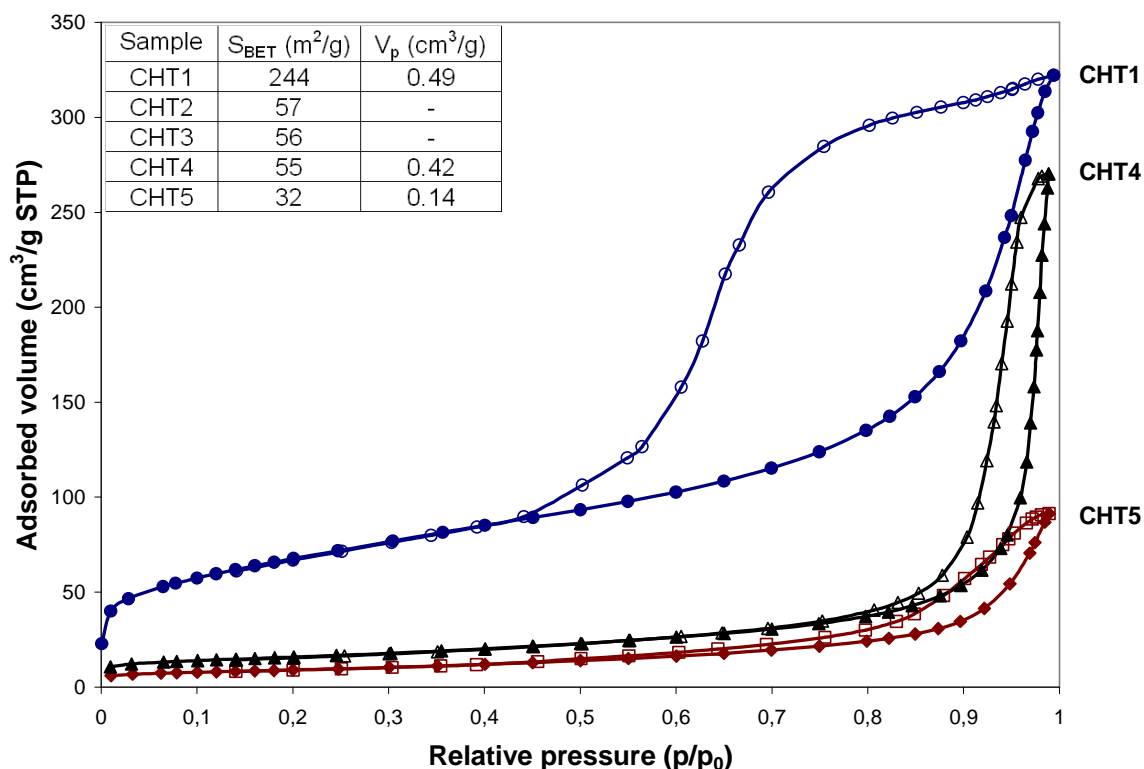


Figure 3. The SEM images of as-synthesized samples

The hydrotalcite-like compounds with two divalent metals in the brucite-like layer have similar values for their specific surface area but substantially lower than CHT1 sample.

Figure 4. N<sub>2</sub> adsorption-desorption isotherms of calcined samples CHT1, CHT4 and CHT5

#### 4. Conclusions

Five hydrotalcite-like compounds with different Mg : Zn : Al molar ratio were synthesized based on aqueous solutions of corresponding nitrates.

EPMA analysis showed that, after synthesis, the molar ratio between the cations remained unchanged.

According to thermal analysis, the samples showed the presence of four weight loss steps corresponding to: the loss of physically adsorbed water, the loss of interlayer water molecules, dehydroxylation and decarbonation of compounds.

The XRD analysis allowed the calculation of unit cell parameters  $a$ ,  $c$  and  $c'$ , respectively. With the introduction of the second divalent cation in the brucite-like network, the parameter  $a$  value has not changed significantly, however, also for the other parameters values have changed due to the deformation of the hydrotalcite network.

FTIR analysis showed that in the interlayer region only carbonate is present as charge compensating anion. The vibration domains of interlayer anion, physically adsorbed water and vibrations of the specific bonds from hydrotalcite octahedral network were identified.

Morphological analysis, by SEM method, revealed the formation of layered double hydroxides crystals, but also their cohesion, resulting in different particle sizes.

Textural analysis was performed for the five hydrotalcite-like compounds thermally treated at 500 °C for 4 hours.

The specific surface area values decreased systematically upon increasing the Zn<sup>2+</sup> content in the samples. The hydrotalcite-like compounds with two

divalent metals in the brucite-like layer have similar values for their specific surface area but substantially lower than CHT1 sample (244 m²/g).

The patterns of N<sub>2</sub> adsorption-desorption plot correspond to the IV type but the hysteresis loops are different. The sample CHT1 shows a H2 type hysteresis loop while the presence of a H1 type in the Zn-containing samples is observed. Therefore, the pore shapes are different when Zn<sup>2+</sup> cations are introduced.

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