

SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOR OF HYDROTALCITE-TYPE Mg_xZn_yAl

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A series of hydrotalcite-type anionic clays with different compositions, containing Mg^{2+} and Zn^{2+} as divalent cations and Al^{3+} as trivalent cation, were prepared by the coprecipitation method at constant pH.

The structure of as-synthesized samples was confirmed by X-Ray Diffraction, FTIR-PAS and UV-VIS Diffuse Reflectance Spectroscopy methods. The thermal behavior was investigated by DSC method.

The XRD patterns exhibit sharp and symmetric peaks which gives a clear indication that all samples are well crystallized. UV-VIS diffuse reflectance spectroscopy is used to investigate the spectral changes with Zn-loading in Mg_3Al -HTlcs. Thermal behavior of samples depends of nature of anions and both the nature and the cationic ratio comparing with the reference sample Mg_3Al -HTlc.

INTRODUCTION

Layered double hydroxides (LDHs), also known as hydrotalcite-type compounds or anionic clays represent an important class of materials with numerous potential applications as catalysts, precursor of catalysts and composite materials, catalyst supports, anion exchangers or adsorbent.¹

The structure of hydrotalcite-type anionic clays can be described as $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+} A^{n-}_{x/n} \cdot mH_2O$, where $M^{II} = Mg^{2+}$, Zn^{2+} , Ni^{2+} , etc., $M^{III} = Al^{3+}$, Fe^{3+} , Ga^{3+} , etc., and $A^{n-} = CO_3^{2-}$, Cl^- , HO^- , etc. Structurally they consist of stacked brucite-like ($M^{2+}(OH)_2$) layers in which M^{2+} ions are partially substituted by M^{3+} ions. The substitution of M^{3+} for M^{2+} on the layers demands the incorporation of interlayer anions to balance the resulting positive charge. In addition to divalent and trivalent cations, a wide range of cations in monovalence or higher valence such as Li^+ , Sn^{4+} , Zr^{4+} , Ti^{4+} , etc., may be also accommodated in the octahedral sites of the layers.

Coprecipitation method is the most widely used method to synthesize LDHs, in which an alkali solution is added to a mixed salt solution and the resultant slurry is aged at a desired temperature.²

The aim of this work is to investigate the possibilities of synthesizing hydrotalcite-type compounds with different cations, different cationic ratio and to establish a correlation between the cationic identity and ratio and the characteristics of the resulting materials.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the hydrotalcite-type samples with Mg/Zn molar ratio of 3, 2, 1 and 0. The samples exhibit the characteristic reflections of LDHs with sharp and symmetric peaks at low 2θ angle, but broad and asymmetric peaks at high 2θ angle. They are characteristic of materials with layered structure.³ The first two peaks with d value of $\sim 7.7\text{\AA}$ (d_{003}) and $\sim 3.8\text{\AA}$ (d_{006}) are due to the diffraction for the space between the adjacent layers in the hydrotalcites.^{2,4}

Comparing with the martor sample, the Mg/Zn-Al hydrotalcites have the same rhombohedral 3R symmetry ($c = 3c'$), in which the Zn^{2+} and Al^{3+} cations are incorporated in the brucite-like layers and the excessive positive charges are compensated by carbonate anions in the interlayer

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gallery. An additional ZnO phase was found in all the Zn-substituted Mg-Al hydrotalcites ($2\theta = 31.9$; 36.38 and 5.74 for sample 2, $2\theta = 31.82$; 36.36 and

56.82 for sample 3 and $2\theta = 31.82$; 36.32 and 56.66 for sample 5).

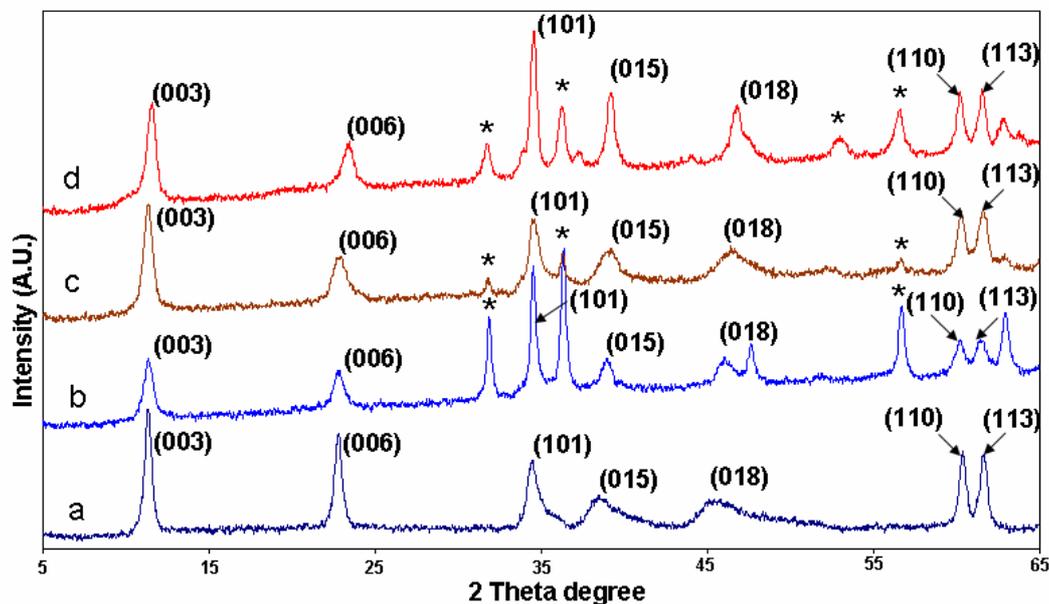


Fig. 1 – The XDR patterns of the (a) sample 1 ($R=3/0$), (b) sample 2 ($R=2/1$), (c) sample 3 ($R=1.5/1.5$) and (d) sample 5 ($R=0/3$), * represents the ZnO phase.

We have studied the influence of both the zinc introduction and the molar ratio R on the unit cell

parameters values. The calculated unit cell parameters $a(\text{\AA})$ and $c(\text{\AA})$ are given in table 1.

Table 1

The unit cell parameters $a(\text{\AA})$ and $c(\text{\AA})$ for the as-synthesized samples.

R	Sample	$a(\text{\AA})$	$c(\text{\AA})$
3	1	3.11	23.34
2	2	3.01	23.27
1	3	3.04	23.24
0	5	3.05	22.83

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 have not too different ionic radii ($r_{\text{Mg}^{2+}} = 0.65\text{\AA}$ and $r_{\text{Zn}^{2+}} = 0.74\text{\AA}$) and do not lead to distortions in the octahedral planes. The unit cell parameter c value decrease with the increase of the amount of Zn^{2+} incorporated in the brucite-like layers. These results are in agreement with the literature data.²

The FTIR spectra of all the resultant hydrotalcite-type compounds are characteristic for this type of materials.¹ Figure 2 shows the spectra of the as-synthesized samples.

On observed a broad and strong absorption band in the range $3600\text{--}3200\text{ cm}^{-1}$ centered at around 3590 cm^{-1} that is due to the O-H stretching

vibration of surface and interlayer water molecules. The shoulder observed near $1650\text{--}1700\text{ cm}^{-1}$ is assigned to the bending vibration of interlayer water molecules.

An another broad shoulder close to 3000 cm^{-1} may be attributed to hydrogen bonding between water and carbonate anions in the interlayer galleries. The absorption band at around 1350 cm^{-1} is due to the ν_3 stretching mode of the interlayer carbonate anions in a symmetric environment.⁵ It can be noticed that the intensity of this band decrease with the increase of Zn^{2+} content. A weak band is observed at around 1025 cm^{-1} . The symmetry of the carbonate anions is lowered from D_{3h} to C_{2v} resulting in activation of the IR inactive ν_1 mode around $1025\text{--}1060\text{ cm}^{-1}$.

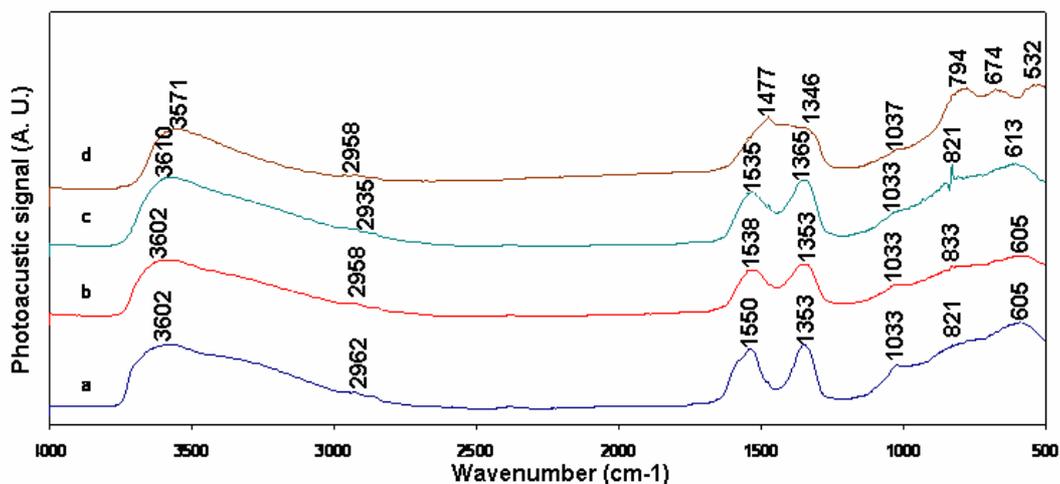


Fig. 2 – The FTIR spectra of (a) sample 1 (R=3/0), (b) sample 2 (R=2/1), (c) sample 3 (R=1.5/1.5) and (d) sample 5 (R=0/3).

The bands situated in the low-frequency region correspond to the lattice vibration modes such as the translation vibration of Zn-OH at 613 cm^{-1} and Al-OH at $740\text{--}800\text{ cm}^{-1}$ and 593 cm^{-1} and deformation vibration of HO-Zn-Al-OH and HO-Mg-Al-OH at 450 cm^{-1} which are typical for this class of materials.³

The UV-DR spectra of the reference sample 1 and the sample 5 were determined (figure 3). The results point out the influence of the identity of the divalent cation in the structure of our samples.

The reference sample 1 show a low intensity absorption edge in the reflectance spectra of 240 nm ; sample 5 (all the Mg^{2+} cations replaced with Zn^{2+} cation) show absorption edge in the reflectance spectra at 370 nm corresponding to the ZnO phase formed due to the longer periods of hydrothermal treatment, which corresponds well with the XRD data (figure 1). These data are consistent with those reported in literature⁶⁻⁸.

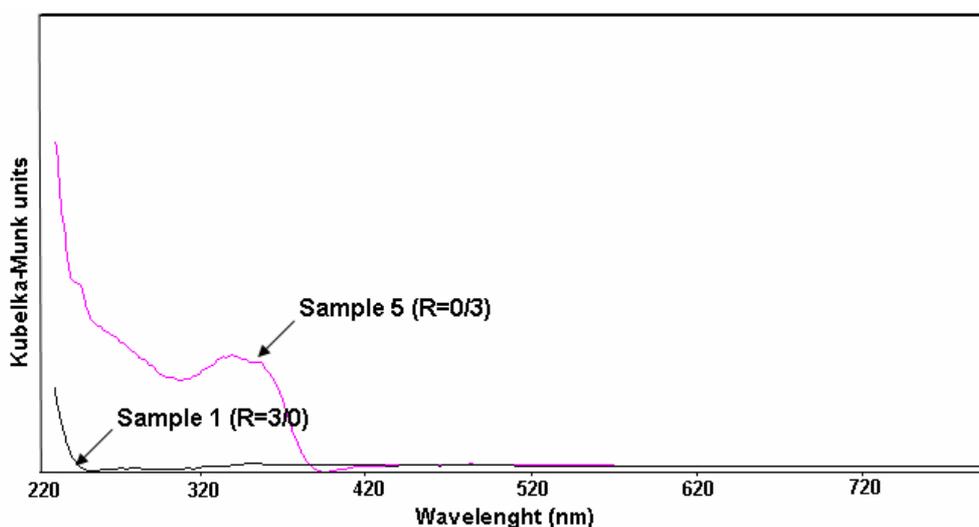


Fig. 3 – The UV-DR spectra of the sample 1 (R=3/0) and sample 5 (R=0/3).

All the TG, DTG patterns of the $\text{Mg}_x\text{Zn}_y\text{Al}$ -type hydrotalcites are characterized by a weight loss between 1.40 and 2.35% due to the loss of adsorbed water with a maximum between $89.4\text{--}100^\circ\text{C}$. The DTG curve (figure 4) for the reference sample 1 involves a dehydration process in one minor step (loss of the adsorbed water) followed

by two larger steps at 212°C and 379°C . These steps can be interpreted as being due to the loss of interlayer water coordinated to the interlayer carbonate.^{9, 10} The interlayer carbonate anions are released as CO_2 simultaneously with water around 379°C . The water loss at 379°C is due to the dehydroxylation of the Mg/Al-hydroxide sheets.¹¹

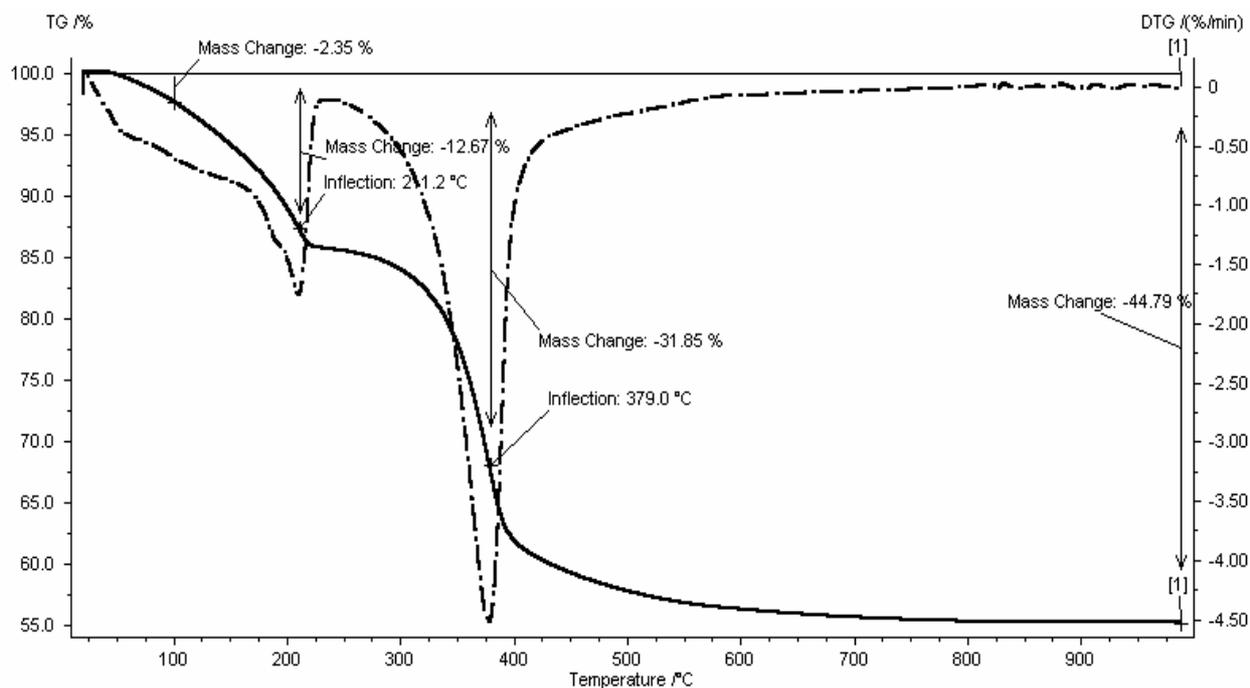


Fig. 4 – TG and DTG curves for the Mg_3Al product (sample 1).

Upon substitution of the Mg^{2+} by Zn^{2+} cations the temperature values corresponding to the dehydroxylation of the hydroxide sheets and decarbonatation decrease. For the $Mg/Zn = 0:3$ this

step is at $216^\circ C$. This observation suggests that the strength of the $Zn-OH$ bond is lower than the strength of the $Mg-OH$ bond. Table 2 shows the results obtained for all the as-synthesized samples.

Table 2

TG, DTG results for the hydrotalcite-type Mg_xZn_yAl

Heat flow step	Hydrotalcites-type Mg_xZn_yAl									
	R = 3 : 0		R = 2 : 1		R = 1.5 : 1.5		R = 1 : 2		R = 0 : 3	
	T, °C	Weight loss, %	T, °C	Weight loss, %	T, °C	Weight loss, %	T, °C	Weight loss, %	T, °C	Weight loss, %
1	100	2.35	100	2.29	89.4	2.04	100	2.17	100	1.40
2	212.2	12.67	175.8	8.16	100	2.61	183.1	9.85	176.5	9.01
3	379.0	31.85	302.3	15.56	182.6	9.01	270.5	17.80	216.6	14.62
4	-	-	363.2	23.89	261.0	17.01	372.1	28.42	-	-

EXPERIMENTAL PART

The hydrotalcite-type samples were obtained by the coprecipitation at low supersaturating method at a constant pH value. The metal hydrated nitrates (Merck) were dissolved in distilled water in order to obtain a 1 M solution. The solution was poured in a plastic flask at a 4 mL min^{-1} flow, under magnetic stirring, and a 2 M sodium hydroxide (Merck) was

added in order to maintain a constant pH value of the liquid medium. The synthesis conditions are listed in table 3. After aging under magnetic stirring at 353 K for 18-20 h, the samples were filtered, washed with distilled water until a neutral pH of the washing water was reached and dried for several hours at 363 K, crushed and sieved.

Table 3

The preparation conditions for the hydrotalcite-type solids.

Sample	M(II)	M(III)	R=Mg/Zn	pH
1- reference	Mg	Al	3 : 0	10
2	Mg, Zn	Al	2 : 1	9-10
3	Mg, Zn	Al	1.5 : 1.5	8.5-9
4	Mg, Zn	Al	1 : 2	8-8.5
5	Zn	Al	0 : 3	7.5

The structural type was investigated by X-ray diffraction on powder, FTIR-PAS and UV-VIS Diffuse Reflectance Spectroscopy methods. The thermal behavior was investigated by TG and DTG method.

X ray diffractions were recorded on a Philips PW 1830 powder diffractometer (45 KV, 25 mA), using Ni filtered Cu_α (0.154 nm) radiation. FTIR-PAS spectra were recorded on a Nicolet 20SX spectrometer, equipped with a McClelland photo acoustic cell, to ensure IR measurements under dry condition. About 500 scans were taken with a resolution of 8 cm^{-1} . The PAS spectrometer was placed in an isolated bench, which was constantly purged with nitrogen to ensure that the samples were completely dried. UV-VIS-DR spectra were obtained at room temperature on a NICOLET EVOLUTION 500 UV-VIS Spectrometer, with a diffuse reflectance accessory using BaSO_4 standard white as reflectance.

Thermal and gravimetric analyses (TG and DTG) were performed using a TG – 209 analyzer (Netzsch, Germany).

CONCLUSION

A series of Zn-substituted Mg/Al-hydrotalcite-type materials were prepared by the coprecipitation method at constant pH. The structural type and the thermal behavior upon the Mg-Zn substitution were investigated by XRD, FTIR-PAS, UV-VIS-DR and TG, DTG methods, respectively. The XRD patterns showed that, for all the samples, the characteristic layered structure, with a rhombohedral 3R symmetry, was formed. The FTIR-PAS measurements evidenced the presence of the carbonate anions with a lowered symmetry characteristic for this type of materials. The UV-VIS-DR measurements, together with the

XRD results, revealed the presence of the ZnO phase formed due to the longer periods of hydrothermal treatment at 353 K. The thermal stability of the as-synthesized hydrotalcite-type samples increased upon the substitution of the Mg^{2+} by Zn^{2+} cations.

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