Journal of Optoelectronics and Advanced Materials Vol. 7, No. 6, December 2005, p. 2869 - 2874

SYNTHESIS OF HYDROTALCITE-TYPE ANIONIC CLAYS CONTAINING BIOMOLECULES

E. M. Seftel*, E. Dvininov, D. Lutic, E. Popovici, C. Ciocoiu[a]

Faculty of Chemistry "Al. I. Cuza" University, 11 Carol I Blvd, Iasi, 700506, Romania
[a]Faculty of Horticulture "Ion Ionescu De La Brad" University of Agricultural Sciences and Veterinary Medicine, Aleea Mihail Sadoveanu nr. 3, Iasi, 700050, Romania

A series of hydrotalcite-type solids with different compositions containing aminoacids (D,L-alanine and L-triptophan) between the cationic layers were prepared by the coprecipitation method at constant pH. In parallel two hydrotalcite samples containing (Ni and Al) and (Mg and Al) respectively, as reference samples, were prepared. The structure of the as-synthesized solids was confirmed by X-Ray Diffraction and FTIR methods. The incorporation of the aminoacids during the synthesis in the interlayer anionic sheets was weighted by photocolorimetric analysis with ninhidrine. The lattice parameters values and the thermal behavior data show that the incorporation of the aminoacids in the hydrotalcite interlayers occured. The incorporation degree depends both on the aminoacid and the composition of solid.

(Received August 22, 2005; accepted November 24, 2005)

Keywords. Hydrotalcite-type solids, Aminoacids, Coprecipitation

1. Introduction

Layered double hydroxides (LDH), also known as anionic clays, can be structurally described as the stacking of positively charged layers with anions in the interlamellar space. The general formula of these materials is $[M(II)_{1-x}M(III)_x(OH)_2]^{x+} A^{n-}_{x/n} \cdot mH_2O$, where M(II) is a divalent cation (Mg^{2+} and/or Ni^{2+}, Zn^{2+}, Co^{2+}), M(III) is a trivalent cation (Al^{3+} and/or Fe^{3+}, Ga^{3+}, Cr^{3+}) and A is an anion with charge n (HO^-, CO_3^{2}, NO_3^-, Cl^-, SO_4^{2-}) [1-3].

The most important characteristic of the structural properties of the hydrotalcite-like compounds is the distance between the neighboring cationic layers, also known as the basal spacing. This parameter depends in a big extend of the nature of the anions in the interlayers.

The porous structure of LDH allows to use them as solid supports for different molecules, immobilized on the surface by adsorption and/or anionic exchange in the interlayer**.** Various species of anions inorganic, organic, polymeric, complex, iso- and heteropolyoxometalates and biochemical can be included in the anionic layer of double hydroxides [1, 2, 4, 5] or adsorbed at their surface. It is worthy to note the very different nature, structure, dimensions and charges of these species. Between the biological molecular species included in the porous structure of layered double hydroxides, amino acids and DNA have been reported, in order to study the possible role of these mineral materials in the origin of life [6]. The resulting materials find applications in food, pharmaceutical and other manufacturies.

---

* Corresponding author: elena_enculesi@yahoo.com

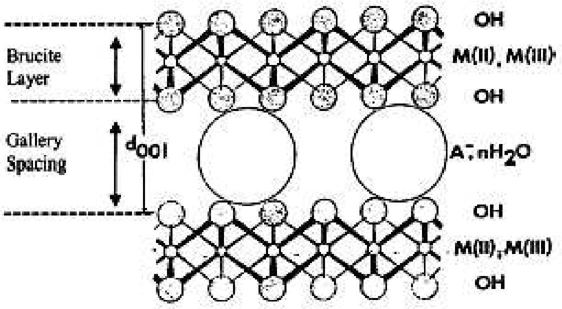


Fig. 1. Schematic representation of a LDH structure [3].

The aim of this work is to report the synthesis of some hydrotalcite-type anionic clays, using the coprecipitation method in the Mg/Al and Ni/Al systems, in the presence of biomolecules, such as D,L-alanine and L-triptophan. This paper is a preliminary study aiming to reveal some data about the mechanism of aminoacids incorporation into the structure of Mg_3Al and Ni_3Al layered double hydroxides.

2. Experimental

A series of hydrotalcite-type solids with different compositions (Table 1) containing aminoacids (D,L-alanine and L-triptophan), by the coprecipitation method [1,3] at constant pH, were prepared. In a polypropylene flask, 100 mL of aminoacid solution (10g/L) in water was placed, then 2 g of sodium carbonate and 10 mL NaOH 2M were added under magnetic stirring. To this solution, a constant flow of metal (Al and Mg or Ni) nitrates solutions mixture (1 $mol.L^{-1}$ in total) obtained by previous individual dissolution were poured at a constant flow under stirring. Suitable flows of 2M NaOH solution were added so that the pH was kept at a constant value. The suspension was aged about 1 h at room temperature under and then placed for 14 h on oil bath at 353 K under magnetic stirring and reflux. The hydrotalcite powder was recuperated by filtration and washed several times with demineralized water till pH=7, dried at 353K overnight, crushed and sieved. In parallel, as reference samples, two hydrotalcite samples containing (Mg / Al-sample 1) and (Ni / Al-sample 4) respectively, using distilled water instead the aminoacid solution, were prepared.

The morphological characteristics of the samples were investigated by optical microscopy at a magnification degree of 2×10^2 and registered using a digital camera.

The structure of the as-synthesized solids was investigated by X-Ray Diffraction method. The X-ray diffraction patterns were measured with a DRON-3 diffractometer using Ni-filtered Cuα radiation, 25KV, 20 mA.

Table 1. The preparation conditions of the hydrotalcite-like samples.

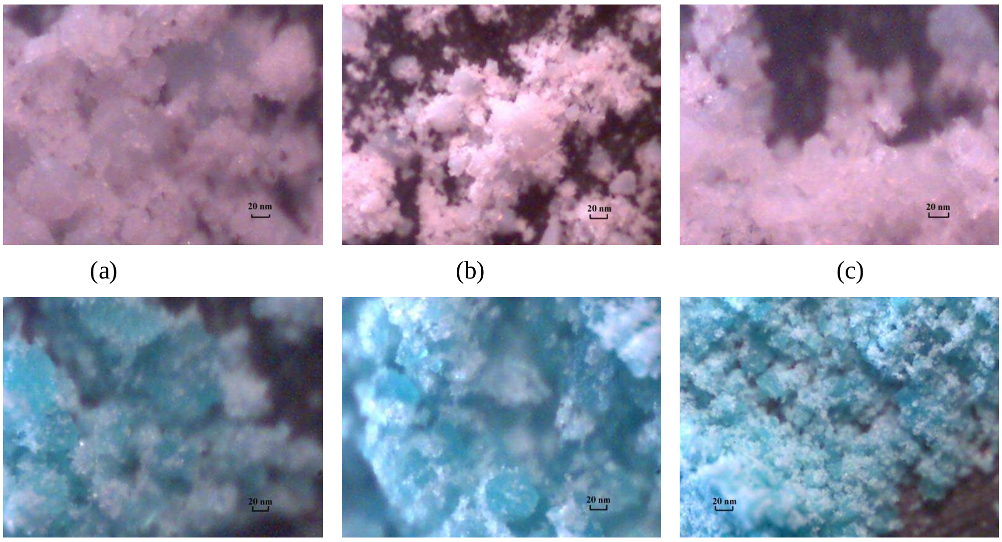
Sample	M(II)		M(III)		M(II)/ M(III)	pH	Aminoacids				
	R_i (nm)	X	R_i (nm)	x			a	b	c	d	e
1	Mg-0.072	1.2	Al-0.054	1.5	3/1	10	-	-	-	-	-
2	Mg-0.072	1.2	Al-0.054	1.5	3/1	10	T	2.38	9.39	5.66	282
3	Mg-0.072	1.2	Al-0.054	1.5	3/1	10	A	2.38	9.39	5.66	297
4	Ni-0.069	1.9	Al-0.054	1.5	3/1	8	-	-	-	-	-
5	Ni-0.069	1.9	Al-0.054	1.5	3/1	8	T	2.34	9.69	6.00	282
6	Ni-0.069	1.9	Al-0.054	1.5	3/1	8	A	2.34	9.69	6.00	297

R_i - ionic radius (nm); x-electronegativity (L.Pauling, General Chemistry (roum.), Ed.Stiintifica, Bucuresti,1972). a: **T**- L-Triptophan; **A**-(D,L)-Alanine; b: $pK_1(COOH)$; c: $pK_2(NH_3^+)$; d: pI; e: decomposition point , ºC

Thermogravimetric and differential thermal analyses of samples were performed on a Perkin Elmer instrument. The incorporation of the aminoacids during the synthesis in the interlayer anionic sheet was weighted by aminoacid quantitative analysis by photocolorimetry with ninhidrine.

3. Results and discussion

The microscopic images presented in Fig. 2 show the crystalline morphology for all synthesized samples.



(a) (b) (c)

(d) (e) (f)

Fig. 2. The microscopic images of samples a) sample 1; b) sample 2; c) sample 3; d) sample 4; e) sample 5; f) sample 6.

The series of samples synthesized in aqueous media with and without aminoacids showed significant differences in the XRD diffraction patterns, indicating the aminoacids influence in course of synthesis (Figs. 3 and 4).

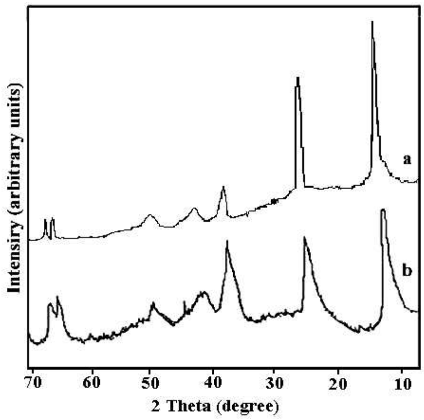


Fig. 3. The XRD patterns of the reference samples. a) sample 1, b) sample 4.

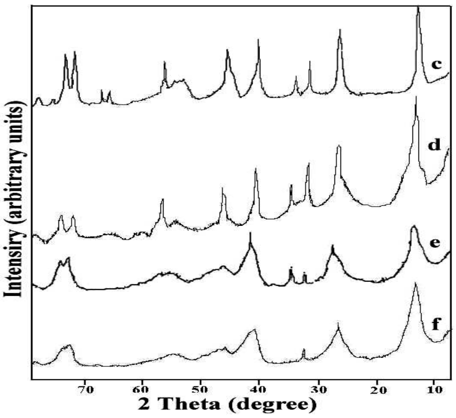


Fig. 4. The XRD patterns of the samples. c) sample 2, d) sample 3, e) sample 5, f) sample 6.

The XRD patterns exhibit sharp and symmetric peaks, which give clear indication that all samples are well crystallized. The peaks corresponding to (003), (006), (101), (110) and (113) planes and broad symmetric peaks for (102), (105) and (108) planes are characteristic for hydrotalcites [7].

The lattice parameters (Table 2) are calculated by indexing the peaks in a hexagonal crystal system. The parameter *a* corresponds to the cation-cation distance within the cationic layer, while the parameter *c* is related to the total thickness of the brucite-like layer and the interlayer distance [1,8].

For the reference samples, it is observed that the parameters *a* and *c* respectively, have almost the same values as for the natural hydrotalcite and takovite [2,11]. The aminoacids introduction in the course of hydrotalcite synthesis leads to the increase (Δa,%; Δc,%) of the values of these parameters of obtained samples, clearly indicating the incorporation of the aminoacids in the hydrotalcite interlayers.

Table 2. The unit parameters cell of the obtained samples.

Sample	The unit cell parameters			
	a, Å	Δa,%	*c*, Å	Δc,%
1	3.043	-	23.374	-
2	3.243	6.57	23.469	0.40
3	3.178	4.43	23.537	0.70
4	3.012	-	23.0	-
5	3.032	0.66	23.167	0.72
6	3.054	1.39	23.78	3.39
Literature data [2]				
Hydrotalcite (Mg3Al)	3.054		22.81	
Takovite (Ni3Al)	3.025		22.59	

In what concerns the behavior upon heating, major differences occur in the thermal behavior of samples (1 and 2) and (4 and 5), respectively, between 176-450 ºC and 220-450 ºC, respectively. While the loss occurring below 180 ºC and 220 ºC, respectively, is attributed to water elimination from the interlayer, the subsequent heating to higher temperatures is due to the decomposition of the interlayer labile species, namely the anions. Since the anionic species present in the samples 1 and 4 are mainly NO_3^- and traces of CO_3^{2-} resulted by the absorption of atmospheric carbon dioxide, it is supposed that in samples 4 and 5 certain amounts of aminoacid anions are present. The difference in mass loss, about 3%, between samples (1 and 2) and (4 and 5), respectively, is a confirmation of the above supposition, indicating a certain degree of triptophan intercalation in the hydrotalcite interlayers of Mg_3Al and Ni_3Al, respectively.

Table 3. DTA transformation temperatures and weight losses.

Sample	Temperature range, ºC	Temperature max.rate, ºC	Weight loss, %	Observations
1	20-110	55	6.33	The loss of the surface weakly held water;
	110-186	176	7.39	The loss of interlayer water;
	186-393	295	20.07	Dehydroxilation of the brucite-like layer; aminoacid decomposition;
	393-600	459	6.33	The carbonate ions decomposition.
2	20-110	51	7.14	The loss of the surface weakly held water;
	110-176	161	6.63	The loss of interlayer water;
	176-431	340	23.34	Dehydroxilation of the brucite-like layer; aminoacid decomposition;
	431-600	556	1.72	The carbonate ions decomposition.
4	20-220	55	14.78	The loss of surface and interlayer water;
	220-450	245	21.21	Dehydroxilation of the brucite-like layer; aminoacid decomposition;
5	20-110	48	6.33	The loss of the surface weakly held water;
	110-220	183	8.45	The loss of interlayer water;
	220-450	334	24.29	Dehydroxilation of the brucite-like layer; aminoacid decomposition;
				The carbonate ions decomposition.

The degree of aminoacids uptake from the initial solutions was calculated by subtracting the final amount of aminoacid in solution from the initial amount added to the coprecipitation medium.

The degree of aminoacid retention (D.R.) was calculated with the formula:

$$D.R. = \frac{C_i V_i - C_f V_f}{C_i V_i} \times 100, \qquad [\%]$$

where: - C_i, C_f are the aminoacid concentrations in the initial and mother liquor resulted in coprecipitation time;
- V_i is the volume of aminoacid added in aqueous initial medium;
- V_f is the volume of suspension where the coprecipitate was formed.

Table 4. Data of aminoacids retention.

Sample	Initial conc. aminoacid (mmol/L)	Final conc. aminoacid (mmol/L)	D.R.,%
2	49.0196	7.080	54.78
3	112.3596	9.545	45.41
5	49.0196	10.375	32.93
6	112.3596	8.885	50.73

The incorporation degree depends both on the aminoacid and the composition of solid.

4. Conclusions

Using a common coprecipitation technique at constant pH, the incorporation of aminoacids in a series of hydrotalcite-type solids containing Mg, Ni and Al was possible. The structural investigation by XRD and the thermal analysis of the samples confirm the incorporation of the aminoacids to a certain extent in the interlayer.

The incorporation degree depends both on the aminoacid nature and on the composition of solid.

Acknowledgements

The financial support from CNCSIS – grant nr.19-1450/2005 is gratefully acknowledged.

References

[1] Scott M. Auerbache, Kathleen A. Corrado, Prabir K. Dutta, Handbook of layered materials, New York (2004).
[2] F. Cavani, F. Trifirò, A. Vaccari, Catalysis Today **11(2),** 201-206 (1991).
[3] A. Clearfield, M. Kicke, J. Kwan, J. L. Colon, J. Inclusion. Phenom. Mol. Recogn. Chem. **11,** 361 (1991).
[4] G. Faradella, V. Ambragi, L. Perioli, G. Grandolini, “Intercalation of Indomatacin and Tolmetin in Hydrotalcite-like Compounds and in vitro Release”, In Proceedings of the International Symposium “Controlled Release of Bioactive Materials”, 1998, p. 774-775.
[5] K. Kuma, W. Paplawsky, B. Geduluin, G. Arrhenius, OLEB **19**, 573-602 (1989).
[6] J. W. Boclair, P. S. Braterman, B. D. Brister, J. P. Jiang, S. W. Lou, Z. M. Wang, F. Yarberry, OLEB **31**, 53-69 (2001).

[7] A. Vaccari, M. Gazzano, in: G. Poncelet, j. Martens, B. Delmon, P. A. Jacobs, P. Grange (Eds.), Preparation of Catalysts VI, Studies in Surface Science and Catalysis, Elsevier, Amsterdam **91,** 309 (1995).
[8] S. Velu, N. Shah, T. M. Jyothi, S. Sivasanker, Micropor. Mesopor. Mater. **33,** 61 (1999).
[9] F. Leroux, J. P. Besse, Chem. Mater. **13**, 3507 (2001).
[10] P. Kustrowski, A. Rafalska-Lasocha, D. Majda, D. Tomaszewska, R. Dziembaj, Solid State Ionics **141/142**, 237 (2001).
[11] U. Costantino, F. Marmottini, M. Nocchetti, R. Vivani, Eur. J. Inorg. Chem. **10**, 1439 (1998).