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SCIENTIFIC PAPER

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SYNTHESIS OF ORGANO–MINERAL NANOHYBRID MATERIAL: PHENOXYACETATE ANIONS IN THE LAMELLA OF Mg–Al–LAYERED DOUBLE HYDROXIDE

An organo–mineral nanohybrid material in which the organic moiety is interleaved inside the inorganic lamella was prepared by using phenoxyacetate anions as a guest in the Mg–Al–layered double hydroxide lamella (as an inorganic host) by the self–assembly technique, anion exchange and the reconstruction methods. The powder XRD patterns of the resulted materials show that the basal spacing of the Mg–Al–layered double hydroxide with carbonate as the counter anions expanded from 7.7 Å to around 16.6 Å in the nanohybrid materials. IR studies show that the absorption bands of the resulting materials correspond to the characteristic functional groups of the host and the guest structures. When the two results are taken together, the expansion can be attributed to the intercalation of the phenoxyacetic acid in the inorganic interlamella for the formation of the nanohybrid material. The intercalation of phenoxyacetate anions was also confirmed by thermogravimetric analysis (TG).

Key words: Layered double hydroxide, Hydrotalcite, Phenoxyacetic acid, Nanostructures.

The development of new organic–inorganic hybrid materials opens promising prospects for applications in various areas of science and technology. Apparently, these types of material have better or improved properties than their counterparts, or the property can be tailor–made to a specific application such as in photochemical reactions (1), selective optical transmission (2), photochromic coating (3), controlled release (4), and gene reservoir (5), to name a few.

Hydrotalcite–like materials or layered double hydroxides (LDHs) are one of the popular inorganic hosts for the formation of organic–inorganic hybrid type nanolayered composites, or so–called nanocomposite materials (6). Layered double hydroxides (LDHs) belong to a large class of layered materials the structure of which can be described as containing brucite–like ($Mg(OH)_2$) layers in which some of the divalent cations have been replaced by tri–valent ions giving positively charged sheets (7). These charges are balanced by the intercalation of anions in the hydrated interlayer regions. LDHs can be represented by the general formula $[M^{2+}_{1-x} M^{3+}_{x} (OH)_2]^{x+} (A^{n-})_{x/n} \cdot mH_2O$. The identities of the di– and trivalent cations (M^{2+} and M^{3+}, respectively) and the interlayer anion (A^{n-}) together with the value of the stoichiometric coefficient (x) may be varied over a wide range, giving rise to a large class of isostructural materials. Anions can range from simple inorganic species (7), through polyoxometallates (8) to organic anions (9) and polymers (10). Due to the bulky size of the guest and its orientation in the inorganic lamellae together with the presence of water molecules and other species, an expansion of the interlayer distance to a nanometer size dimension is usually observed and the formation of a so–called nanohybrid or nanocomposite material takes place.

The insertion of guest anions into the inorganic lamella, or the intercalation process, can be approached by two routes: direct or indirect insertion. In the direct route, the guest can be inserted by spontaneous self–assembly (11) or the co–precipitation technique. The host and the guest species are included in the mother liquor, followed by an aging process to form a well–ordered nanolayered structure. On the other hand, in the indirect route, insertion of the guests can be done by preparing the well–organized host first, followed or not by the modification or further treatment of the host and, finally, insertion of the guest molecule into the interlayer [12].

The present study forms part of a wider investigation aimed to understanding the mechanisms of interaction between LDHs and organic pollutants in view of LDH use in environmental applications to remove organic pollutants from agricultural or industrial wastewater effluents. This paper presents the formation of a new layered organic–inorganic nanohybrid material by the intercalation of phenoxyacetic acid (PhA) into the Mg–Al–LDH.

Phenoxyacetic acids (2,4D: 2,4– dichlorophenoxyacetic acid; MCPA: 4–chloro–2– methylphenoxyacetic; 2,4,5T: 2,4,5–trichlorophenoxyacetic acid) are used for the treatment of grain, corn, sugar, cane and rice and the pollution from these chemicals is well known. The salts and free acids are soluble in water and the ester form can accumulate in aquatic and terrestrial organisms

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[13]. Also, the exposure of such materials to light, rain, etc., can lead to dangerous products. Therefore, besides the use of LDHs as anionic exchangers or scavengers, another interesting application of these materials consists in the preparation of stable nanocomposites with controllable release of the physiologically active species

In order to determine the optimum synthesis method for which a stable nanohybrid material is obtained with good crystallinity and a high exchange level, several methods of intercalation were applied: direct synthesis by the coprecipitation, at fixed pH, of metal nitrates and the sodium form of phenoxyacetic acid, the anion exchange reaction of a nitrate LDH precursor, and the calcination – reconstruction method.

EXPERIMENTAL

The phenoxyacetic acid and inorganic reagents were purchased from Aldrich and used without any further purification.

Preparation of parent-layered double hydroxides

Mg–Al–layered double hydroxide carbonate ($MgAl–LDH–CO_3$) was prepared by the co–precipitation method. Fifty milliliters of aqueous Mg and Al nitrate solution with the Mg^{2+}/Al^{3+} molar ratio of 3.0 and a base solution of sodium hydroxide (7 g) and sodium carbonate (7.95 g) were added to a beaker containing 50 ml deionized water. The pH mixture was held constant at 9.5 ± 0.1. The resulting precipitate was aged for 18 h at 65°C, and then recovered by filtration, washed thoroughly with deionized water and dried at room temperature.

Mg–Al layered double hydroxide nitrate ($MgAl–LDH–NO_3$) was prepared by the co–precipitation method. Fifty milliliters of aqueous Mg and Al nitrate solution with the Mg^{2+}/Al^{3+} molar ratio of 3.0 was added dropwise to a flask containing 50 ml of deionized water at 55°C under vigorous magnetic stirring and nitrogen flow. A base solution of sodium hydroxide (2 M) was simultaneously added to fix the pH of co–precipitation at 9 ± 0.5. The resulting precipitate was aged for 18 h at 65°C, also under nitrogen flow, and then recovered by filtration, washed thoroughly with deionized water and dried at room temperature.

Preparation of hybrid materials

The following methods of intercalation were applied in the present study:

The direct ion exchange. MgAl – layered double hydroxide intercalated with organic phenoxyacetate anions (PhAE) was prepared by ion exchange under nitrogen atmosphere and vigorous magnetic stirring. An aqueous solution with a three–fold excess (with respect to Al content) of sodium phenoxyacetate (PhA) was added slowly to 50 ml of deionized water, where the Mg–Al layered double hydroxide nitrate precursor had previously been dispersed. The exchange process was kept at 70°C for 2 h. The temperature was then decreased to 35°C and the resulting solid was filtered, washed thoroughly with deionized water at 60°C and dried at room temperature.

LDH reconstruction. $MgAl–LDH–CO_3$ was calcined in air at 500°C for 5 hours. A three–fold excess of sodium PhA was dissolved in deionized water at 60°C under nitrogen flow. The calcined product was added into solution at 60°C and the suspension was maintained at this temperature for 4 hours under vigorous magnetic stirring. The solid was filtered, washed with deionized water at 60°C and dried at room temperature, leading to the sample labeled as PhAR.

Direct synthesis by coprecipiation. A mixture of $Mg(NO_3)_2 \cdot 6H_2O$ (14.35 g, 0.05 mol) and $Al(NO_3)_3.9H_2O$ (7.0315 g, 0.02 mol) was dissolved in 50 ml of deionized water. The aqueous solution was slowly added to 25 ml of solution containing 14.30 g of PhA in deionized water at 35°C under vigorous stirring. The pH = 9 was maintained at constant value by the controlled addition of NaOH. The resulting suspension was stirred for 18 hours at 65°C. The solid was filtered, washed with distilled water at 60°C, and finally dried at room temperature; the sample was labeled PhAC.

Characterization

Powder XRD patterns of the samples were recorded using a Philips X'Pert diffractometer (Cu–Kα radiation and curved copper monochromator).

Infrared spectra were collected in the transmission mode, with potassium bromide–pressed disks, by accumulating 64 scans at 2 cm^{-1} resolution between 400 and 4000 cm^{-1} using an EQUINOX55 instrument.

Thermogravimetric and differential thermal analysis (TG–DTA) were performed under airflow at a heating rate of 5°C/min with Al_2O_3 reference, using a NETZSCH TG 209 thermoanalyser.

Scanning Electron Microscopy (SEM) photographs were taken with a Philips SEM 501 instrument. Before observation, the dried samples were sputtered and coated with gold, for ca. 5 min under nitrogen atmosphere.

RESULTS AND DISCUSSION

The molecular structure of phenoxyacetic acid and its carboxylate anion is presented in Figure 1.

The phenoxyacetate anion was formed by dissolving the organic acid in alkaline aqueous solution and the anion was intercalated between the inorganic lamella of the Mg–Al–LDH by applying various methods. The resulting materials were first investigated by powder X–ray diffraction taking into account the fact that the incorporation of larger organic anions would distance the brucite–like layers and this modification could be

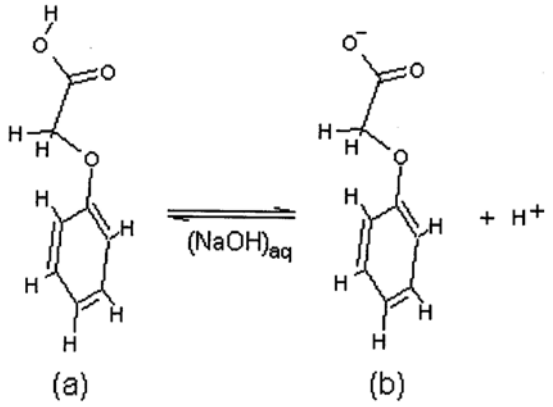

Figure 1. Molecular structure of phenoxyacetic acid (a) and its anion (b)

evidenced by the DRX patterns. Indeed, as seen from Figures 2 and 3, all the three methods applied to the synthesis of hybrid materials led to structural changes of the parent-layered double hydroxide.

Figure 2 shows the XRD patterns of the three precursors. Mg–Al–LDH precursors showed the characteristic reflections corresponding to a well–crystallized layered phase with an interlayer spacing of 7.7 Å and 8.2 Å for the carbonate and nitrate forms, respectively (patterns (a) and (c)), similar to that reported in the literature. The height of the interlayer was estimated to be approximately 2.9 Å and 3.4 Å because, as previously referred by Miyata [14], the thickness of the brucite–like octahedral hydroxide layer made with Mg and Al is 4.78 Å. The c and a lattice parameters were evaluated to be 23.12 Å and 3.02 Å, respectively, for carbonate precursor, and 24.66 Å and 3.02 Å, for the nitrate form (Table 1). The XRD pattern of the calcined sample (at 500°C) shows that calcination destroyed the layered structure (Figure 2, pattern b) and a solid

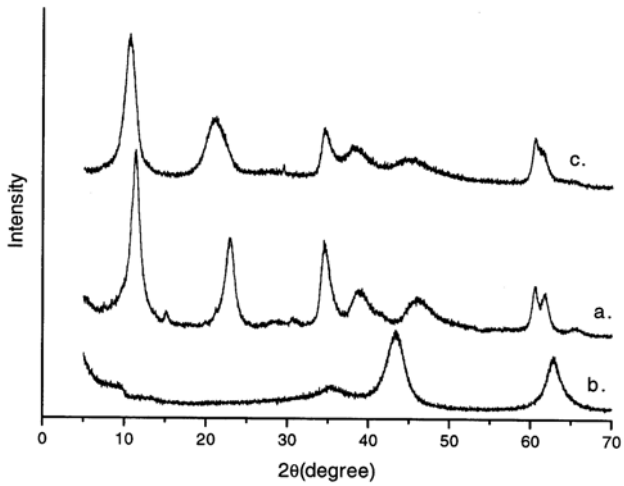

Figure 2. Powder XRD patterns for MgAl–LDH–carbonate (a), LDH–calcined (b), (c) LDH–nitrate

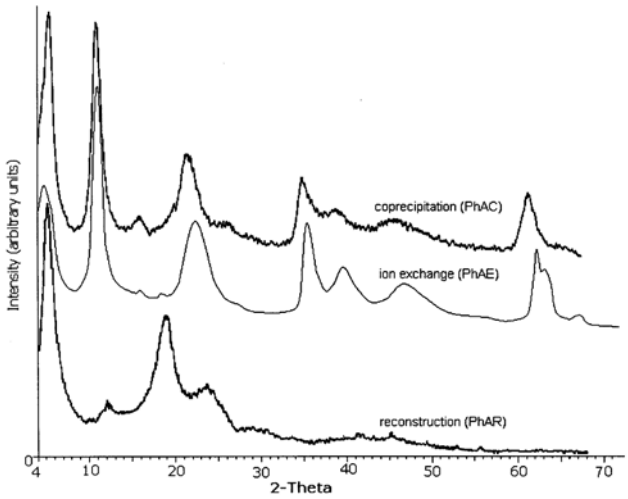

Figure 3. Powder XRD patterns for: (a) PhAC , (b) PhAR and (3) PhAE

solution was formed by the dissolution of a small amount of Al^{3+} in the MgO lattice [11].

Although the XRD patterns of all the organic derivative compounds are typical of layered materials of relatively good crystallinity (Figure 3), several of the (hkl) reflections characteristic of hydrotalcite disappeared or were broadened. This is typical of a turbostatic effect caused by a decrease of the ordering along the stacking axis due to the loss of the van der Waals interaction between adjacent layers and the absence of a densely packed interlayer space formed by high–charge–density anions. The intercalation of organic molecules inside the lamellar host structure is clearly evidenced in all cases by the net increase of the basal spacing d_{003} from 7.7 and 8.2 ć for the precursors, MgAl–CO_3 and MgAl–NO3, respectively, to 16.2 – 16.7 Å for the nanohybrid samples. The lattice parameters of the intercalated samples, calculated from the positions of the maxima due to reflection by planes (003) for parameter c, and planes (110) for parameter a, are given in Table 1.

Given that the thickness of the brucite–like layer of LDH is 4.8 Å, the gallery height in phenoxyacetate–intercalated materials is 11.9 Å compared with 2.9 Å in carbonate–LDHs. Taking into account that the size of PhA is 8.34 Å, these data suggest a monolayer arrangement for the intercalated phenoxyacetic acid oriented perpendicular to the LDH layers (Figure 4).

The higher expansion of interlamella spacing than the size of the PhA molecule could be the consequence of some molecular associations of the guest species (e.g., hydrophobic interactions between the aromatic rings of two molecules of PhA with opposite orientations).

Harmonic diffraction lines were also recorded at the corresponding spacing 8.22 and 5.4 Å and they revealed that the crystallinity of the intercalated phases was lower than that of the MgAl–LDH. Intercalation caused a certain degree of disorder in the layers without

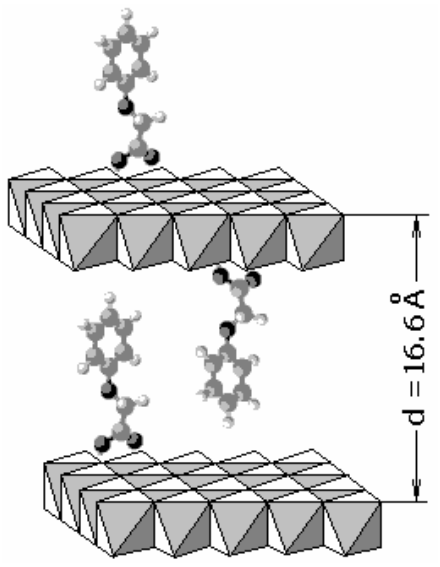

Figure 4. Structural model for the orientation of the PhA anion between the hydrotalcite layers.

destruction of the layered structure of the material or degradation of the PhA anion. This is the case of hybrid materials obtained by simultaneous coprecipitation or ion exchange. It could be observed from Figure 3 (patterns PhAC and PhAE) that a significant amount of inorganic anions (NO_3^-) remained to compensate the charge of brucite–like layers (see the reflections at approximately 11° 2 theta), while the sample obtained by reconstruction had only traces of inorganic anions. From these data it could be concluded that the method of preparation plays an important role as concerning the crystalline phases and chemical compositions.

Figure 5 shows the spectra of all the precursors used to prepare the hybrid materials. The IR spectrum of the Mg–Al–LDH sample presents a profile which resembles those exhibited by all the hydrotalcite–like phases. Typical of this spectrum are the strong absorbance at 3400 cm^{-1} and around 1600 cm^{-1} which correspond to the valence vibration of hydroxyl groups and the bending vibration of water, respectively. The bands observed in the low frequency region of the spectrum correspond to the lattice vibration modes and can be attributed to M–O (730 and 600 cm^{-1}) and O–M–O (522 cm^{-1}) vibrations. The strong adsorption bands which appear in the 1400 –1360 cm^{-1} region are due to the stretching vibration of C_3^{-2} and NO_3^- anions, respectively.

As concerns the spectrum of PhA, a broad band at 3436 cm^{-1}, could be observed which is attributed to the OH stretching vibration. Strong bands at 1585 and 1374 cm^{-1} are due to the asymmetric and symmetric stretching modes of $-COO^-$, respectively. The bands at 1439 and 1498 cm^{-1} are attributed to the stretching vibrations of aromatic rings. Strong bands at 690 and 755 cm^{-1} can be attributed to the presence of phenyl ring substitution.

The FTIR spectra of phenoxyacetate–intercalated LDHs are shown in Figure 6. As expected, the spectra resemble a mixture of both the spectra of PhA and LDH, indicating that both functional groups of PhA and Mg–AL–LDH are simultaneously present in all the intercalated compounds. All the stretching and bending vibration modes of the organic anion are observed in the spectra, beside the absorption bands of the hydroxylated layers. However, the more intense bands of adsorption observed for the sample obtained by the reconstruction method could be considered as proof that a higher amount of phenoxyacetate anions was intercalated in the interlamella of Mg–AL–LDH by the reconstruction method.

The bands at 1620 cm^{-1} can be attributed to the carboxylate ion vibrations. The C=C bond vibrations of the aromatic nuclei appear around 1490 and 1420 cm^{-1}. The bands observed at 1280 and 1060 cm^{-1} correspond to the asymmetric and symmetric vibrations of C–O–C, respectively. The bands at 770 and 800 cm^{-1} can be assigned to the C–H deformation vibrations out of the benzoic plane.

The TG and DTA curves obtained for the Mg–Al–LDH–CO^3 precursor and LDH–PhA phase are reported in Figure 7. The precursor underwent four

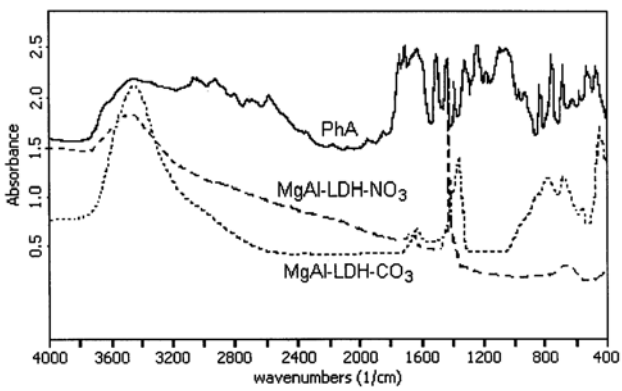

Figure 5. IR spectra of Mg–Al–LDH–carbonate, MgAl–LDH–nitrate and phenoxyacetic acid (PhA)

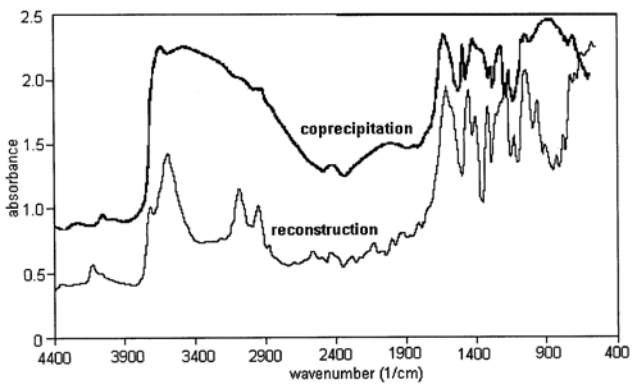

Figure 6. IR spectra of PhAC and PhAR

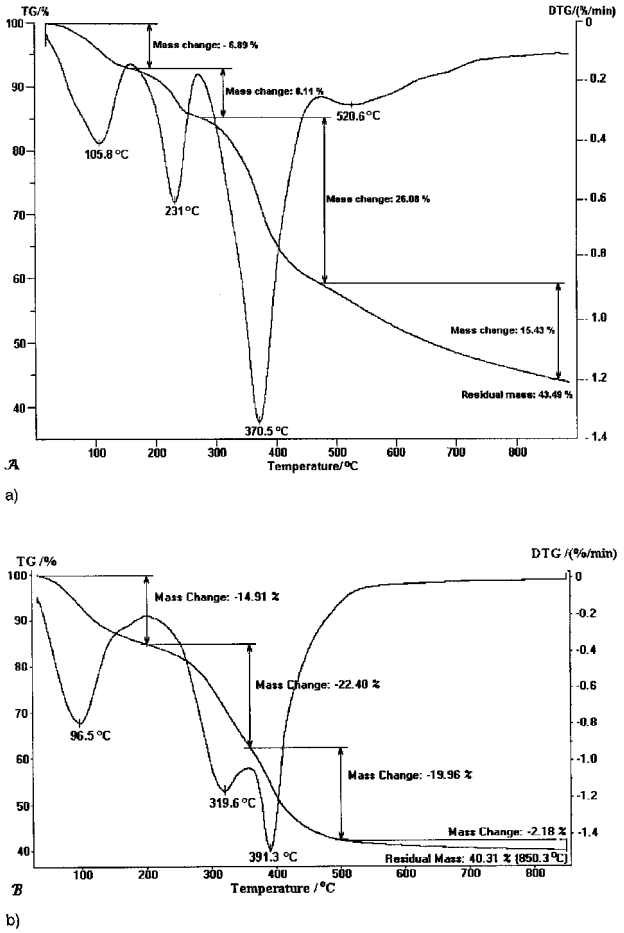

Figure 7. TG–DTG curves of Mg–Al–LDH–carbonate (a) and LDH–phenoxyacetate (b)

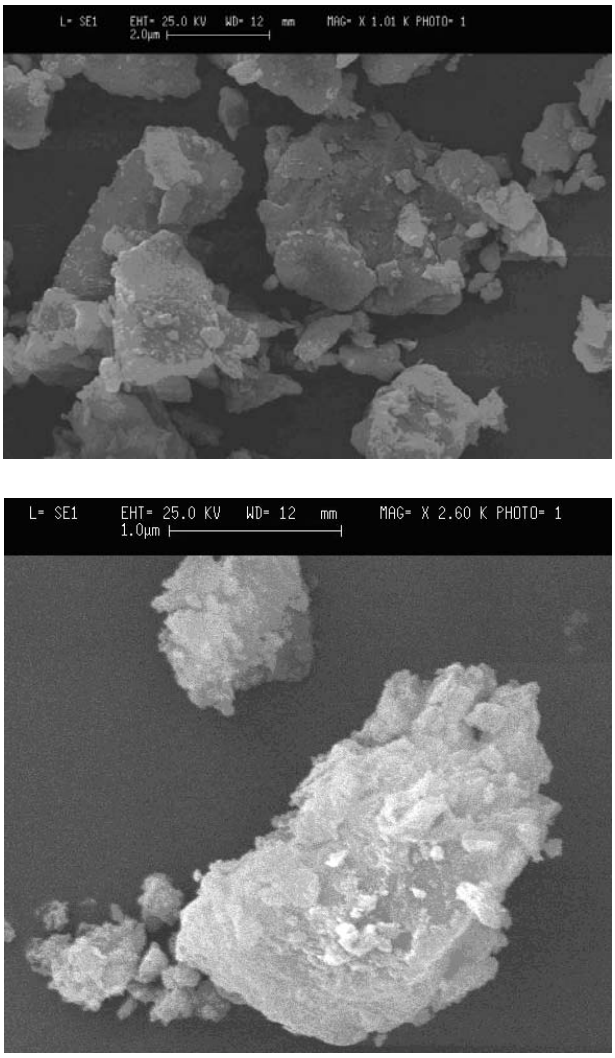

Figure 8. Electron micrographs of MgAl–LDH–nitrate (a), Mg–Al–LDH–carbonate (b) and phenoxyacetic acid (c)

weight losses occurring at the temperature maxima of 105.8, 231, 370.5°C and 520.6°C (Figure 7a). The first weight loss is associated with the removal of water physisorbed on the external surface of the crystals. The second weight loss is attributed to the removal of crystallization water present in the hydrotalcite structure. The third weight loss corresponds to removal of hydroxyl groups from the brucite–like layers and the removal of interlayer carbonate anions. Finally, the residual hydrotalcite carbonate groups decompose in the subsequent weight loss at higher temperatures. This indicates that below 400°C, the hydrotalcite CO_3^{2-} units still remain occluded in the solid.

The thermogravimetric results for LDH–phenoxyacetate show three major stages of weight loss. The initial distinct reduction in mass between 50°C and 200°C is due to the removal of water physisorbed on the powder particles. Since this first weight loss of the nanohybrid material is greater (about 15% w/w, Figure 7b) than those observed for the hydrotalcite precursor (ca. 7% w/w), it could be assumed that not only the water physisorbed on the external surface is removed, but also part of the interlayer water. This hypothesis is based on the enlargement of the interlayer space, due to the intercalation of phenoxyacetate anions, which probably facilitates the diffusion of water molecules.

The second one should be due to the simultaneous loss of carbonate and the dehydroxylation of the brucite–like layer and, especially, to the decomposition of the organic moiety in the interlayer lamella of the nanohybrid material. The last contribution is supported by the temperature maximum shifted from 231 to 319.6°C, which is relatively close to the boiling point phenoxyacetic acid (b.p. = 285°C, with decomposition), as well as by the exotherms in the temperature range 300–450°C (associated with combustion of the organic component) from the corresponding DTA curves. Also, it is worthy to mention that this peak corresponds to the greatest weight loss from the TG curves. The temperature difference between the boiling point of PhA and the maximum of the second peak proves that the PhA intercalated inside the LDH is thermally more stable than its free form. Finally, the weight loss at higher temperatures (temperature

maximum of 391.3°C) should be due to the residual inorganic anions.

The morphologies of the MgAl–LDH–NO_3 and MgAl–LDH–PhA obtained by scanning electron microscope are shown in Figure 8.

They show the typical morphology of the LDHs obtained by coprecipitation at low supersaturation and its nanocomposite, which are non–uniform, irregular agglomerates of compact and non–porous plate–like structure. There is no significant difference in the morphology of the two samples, but a certain degree of exfoliation may be observed in the case of the hybrid material and it could be attributed to the process of intercalation. They are also very similar to the morphology of other nanocomposites (e.g., ZnAl–α–naphtalenacetate–LDH [15]).

CONCLUSION

In this study, we chose phenoxyacetic acid, the simplest member of the family of phenoxyacetic acid derivatives, and its incorporation in the layered structure of Mg–Al–LDHs was investigated. The idea for the formation of the organic–inorganic nanohybrid composite is to protect and to control the release of pesticides in order to avoid the contamination of soils and water or to diminish it. With this possibility in mind, during this study, we synthesized a new stable organo–mineral nanohybrid material by different methods of intercalation of the phenoxyacetate, as the organic guest, within the layers of the MgAl–LDHs, as an inorganic host. Taking into account the interlamellar values of the hybrid compounds, the coprecipitation method appears to be a successful method for the intercalation of PhA, when the molar ratio of the precursor is around 3. Noteworthy that the sample obtained by the anionic exchange route, PhAE, seems to be the most crystalline, while the sample obtained by reconstruction indicated a layered structure mainly without inorganic anions (only a small contamination could be noted). FTIR study shows that the nanocomposite resemble the spectra of PhA and MgAl–LDH, indicating the presence of both the functional groups in LDH–PhA. Thermal analysis of the nanohybrid material showed that intercalated PhA is thermally more stable than its free form.

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IZVOD

SINTEZA ORGANO–MINERALNIH NANOHIBRIDNIH MATERIJALA:
FENOKSIACETATNI ANJONI U LAMELIZIRANOM Mg–Al–DVOSTRUKOM HIDROKSIDU

(Naučni rad)

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U radu je definisano dobijanje organo-mineralnog nano–hibridnog materijala tako što je fenoksiacetatni organski anjon povezan sa dvostrukim Mg–Al–hidroksidnim slojem (lamelama). Ova sinteza realizovana je u jednom stupnju primenom izmene anjona i rekonstrukcijske metode. Izvršena su detaljna XRD, IR i TG ispitivanja sintetizovanog materijala i definisan način povezivanja organskog i neorganskog dela u strukturi ovog materijala.

Ključne reči: Lameliziran dvostruki hidroksid, Nano struktura, Fenoksi sirćetna kiselina, Hidrotalcit.