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Interlayer intercalation and arrangement of 2-mercaptobenzothiazolate and 1,2,3-benzotriazolate anions in layered double hydroxides: *in situ* x-ray diffraction study

Maria Serdechnova^{a,b}, Andrei N. Salak^{*,a}, Filipe S. Barbosa^a, Daniel E.L. Vieira^a, João Tedim^a, Mikhail L. Zheludkevich^{a,b}, Mário G.S. Ferreira^a

^a*Department of Materials and Ceramic Engineering, CICECO – Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal;*

^b*Institute of Materials Research, Helmholtz-Zentrum Geesthacht, Max-Planck-Straße 1, 21502 Geesthacht, Germany*

ABSTRACT

2-mercaptobenzothiazole (MBT) and 1,2,3-benzotriazole (BTA) are very promising inhibitors for the corrosion protection of aluminum alloys. These inhibitors can be incorporated in protective coatings in the form of anions intercalated into interlayers of layered double hydroxides (LDHs). Capacity and performance of such LDH-nanocontainers depend on the arrangement of the anions in their interlayers. In this work, intercalation of MBT⁻ and BTA⁻ into Mg-Al-NO₃ and Zn-Al-NO₃ LDHs were studied in detail using X-ray diffraction (XRD) methods including *in situ* XRD. The nitrate-to-MBT(BTA) anion exchange is much faster than considered previously. Well-formed Mg-Al-MBT, Zn-Al-MBT, Mg-Al-BTA LDHs were obtained after a 20-min exchange reaction at pH 11.5 at room temperature. It was demonstrated that Zn-Al-BTA LDH cannot be obtained under the same conditions due to the reaction between BTA and the Zn-Al hydroxide layers. Substitution of nitrates by organic anions occurs with the participation of hydroxide anions. Although no intermediate LDH phase intercalated with the combination of NO₃⁻ and OH⁻ appears, formation of the LDH-MBT and LDH-BTA phases results also in appearance of an LDH phase intercalated with OH⁻ at the final stage of the anion exchange. In the LDH interlayer, MBT⁻ and BTA⁻ form a double layer in which these species have a tilted orientation against the layer plane (herringbone-like arrangement). Such an arrangement meets the LDH layer-interlayer electroneutrality and matches well with the observed values of the layer-interlayer distance.

* Corresponding author. Email: salak@ua.pt

INTRODUCTION

Nowadays, a great attention is given to the development of new protective materials that can replace toxic chromium (VI) compounds as effective corrosion inhibitors for aluminum alloys. A variety of new organic and inorganic compositions has been proposed and optimized for application in protective coatings [1,2]. It was shown that some of those inhibitors can be used more effectively and safely (both for the coatings and for the environment), if they are intercalated in their anionic forms into the solids with anion-exchange ability such as layered double hydroxides (LDHs) [3,4,5].

LDHs are typically composed of positively-charged mixed metal $M^{\text{II}}-M^{\text{III}}$ hydroxide layers and interlayers occupied by anions (A^{y-}) and water molecules. The general formula of the most common LDHs can be represented as $[M^{\text{II}}_{1-x}M^{\text{III}}_x(\text{OH})_2]^{x+}(A^{y-})_{x/y} \cdot z\text{H}_2\text{O}$ [6,7]. LDHs are typically characterized by hexagonal symmetry with the c -axis perpendicular to the layers. Parameter a is a function of both size and ratio of cations M^{II} and M^{III} , while parameter c depends mainly on size, charge and orientation of the intercalated species. The intercalated anions are arranged in the interlayer to compensate the charge of the hydroxide layer (which is $+xe$ per formula unit, where e is the elementary charge). Small anions with relatively high charge density are generally the most preferable; nevertheless, LDHs can be intercalated with low-charge large anions (including organic species) [6,7,8]. Miyata [9] has demonstrated that CO_3^{2-} leads a series of inorganic anions in terms of the preference for intercalation. NO_3^- which is almost equal in size but with half charge of carbonate is at the end of this series. Therefore, nitrate-containing LDHs are commonly used as parent compounds for further intercalations: LDH-nitrates of various cationic compositions can be easily synthesized and then intercalated with a desired anion through anion exchange reactions. The corrosive anions Cl^- and SO_4^{2-} are about in the middle of the anionic exchange preference series [9].

The protective action of LDHs loaded with inhibiting anions is based on the anion-exchange reaction induced by particular triggers, such as a change in pH and/or an appearance of the corrosive anions. Then the LDH nanocontainers release inhibitors and absorb those anions [3,4,10]. It has been demonstrated that Mg-Al and Zn-Al LDHs intercalated with 2-mercaptobenzothiazole (MBT) provide such an active protection effect [3]. The allied heterocyclic compound – 1,2,3-benzotriazole (BTA) – was later found to be an effective corrosion inhibitor as well [11]. A successful application of LDH intercalated with BTA for protection of aluminum alloy AA6061 has recently been reported [12]. As it often happens, the functionality of new protective materials was demonstrated before their fundamental characteristics (crystal structure, anion-exchange capacity, *etc.*) are studied. Meanwhile, such a

study is basic for optimization of the preparation procedure and the application ways. Both the LDH nanocontainer capacity and the anion-exchange behavior in various corrosive media depend on the manner how inhibiting anions are arranged in the interlayers.

It is generally easy to determine the anion arrangement in the case of intercalation of simple, monoatomic, and high-symmetry anions with a relatively high charge density: the interlayer height is usually equal to the minimal dimension of the anion [13]. The task is more complicated when the intercalated anion trends to the formation of polytypes [14,15,16]. Determination of the interlayer arrangement of large anions with a relatively low charge density (which is typical of organic species) is not straightforward. Organic anions usually form complex configurations of species tilted against the layer plane [7,8].

A similar arrangement behavior seems to take place in Mg-Al and Zn-Al LDHs intercalated with MBT: the interlayer height calculated from the position of the diffraction reflections in the XRD patterns exceeds the maximum size of MBT anion [3]. Besides, a second LDH phase which could not be associated with the parent LDH-nitrate was found to be always present in the as-prepared material along with the main LDH-MBT phase. It has been suggested that these two phases with different basal spacings (distances between the double metal hydroxide layers, d) correspond to two particular orientations of MBT anion in the interlayers; however, this issue has not been thoroughly considered [3]. As regards the BTA-containing LDHs, no crystal structure characterization has been reported yet. MBT and BTA anions are very similar in terms of the chemical structure. Hence, one can suggest that, in the LDH interlayer, these species are arranged in the same manner. On the other hand, the fixed difference in their linear dimensions can be used as a measure when comparing the basal spacings values of the same LDHs intercalated with either MBT⁻ or BTA⁻.

Intercalation of organic anions into LDHs was studied by O'Hare *et al.* through the time-resolved *in-situ* diffraction experiments using both laboratory and synchrotron x-ray facilities [17,18,19]. During some intercalation reactions, a second LDH phase with a small d was observed and associated with the *tilted* orientation of organic anion and grafting into the hydroxide layers.

In this work, methods of x-ray diffraction (XRD) including *in situ* XRD were applied to study in detail the processes that occur at different stages of intercalation of either MBT⁻ or BTA⁻ into Zn-Al-nitrate and Mg-Al-nitrate LDHs. Based on a comparative analysis of the XRD patterns, the arrangement of these organic anions in the LDH interlayers was modeled.

EXPERIMENTAL

Materials

Zinc nitrate hexahydrate ($\geq 99.0\%$), aluminum nitrate nonahydrate ($\geq 98.5\%$), magnesium nitrate hexahydrate (99%), sodium hydroxide ($\geq 98\%$), sodium nitrate ($\geq 99.5\%$), sodium carbonate ($>99.95\%$) and 2-mercaptobenzothiazole (97%) were purchased from Sigma-Aldrich, while 1,2,3-benzotriazole, ($>99\%$) was purchased from Riedel-de-Haën. Nitric acid (65%) was purchased from Merck. All the chemicals were used as received without further purification.

Preparation of the LDH compositions

The parent LDH compositions, Mg-Al-nitrate and Zn-Al-nitrate, were synthesized based on the previously described experimental procedure [3]. This procedure was optimized in order to improve both the reproducibility of the synthesis and the final product quality. The syntheses, hydrothermal treatment, intercalation reactions and drying procedure were carried out under a nitrogen atmosphere. All solutions were prepared in decarbonated water. Proportions of the reagents used were to meet the 2:1 ratio of Mg/Al (Zn/Al). A solution containing 0.5M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (or $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 0.25M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (200 ml) was instilled to a 1.5M NaNO_3 solution (400 ml) under continuous stirring and N_2 flow at room temperature. This procedure took about 90 minutes. During the reaction, pH of the mixture was controlled to be between 7 and 9 by addition of a 2M NaOH solution. Then the obtained suspension (pH 9-10) was kept in a water bath at about 100°C for 4 h to complete the crystallization. After this hydrothermal treatment, the suspension was centrifuged at 10^4 rpm for 90 s. The resulting dense slurry was washed with deionized water (in proportion of about 20 ml for 4 g of slurry) and centrifuged. This procedure was repeated three times. Such LDH slurry was estimated to contain about 85% of water.

The obtained Mg-Al-nitrate and Zn-Al-nitrate LDHs were intercalated with either MBT or BTA through anion exchange in a 0.1M solution of the respective organic compositions. In order to dissolve MBT and BTA and produce their anionic forms, the pH of the solution was adjusted with NaOH to 11.5 ± 0.1 . In the anion exchange reaction, 13 g of the LDH slurry were mixed with 100 ml of the MBT (BTA) solution. The mixture was stirred for 24 h at room temperature. Then the slurry was centrifuged and washed in the same manner as described above. In order to clarify pathways of the nitrate-to-MBT(BTA) substitution reaction, supplementary anion-exchange experiments were carried out. The descriptions of these experiments are given in *Results and Discussion*.

Certain amounts of the obtained LDH materials both before and after the anion exchange procedures were dried at 60°C for 6 h and used for further characterization along with the slurry samples.

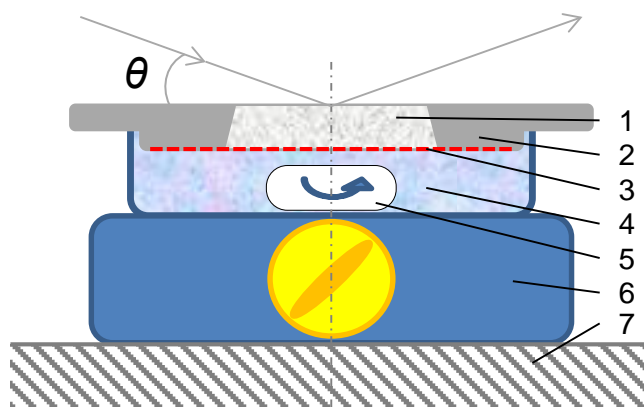
Characterization techniques

Morphology of the LDH powders was characterized using a Hitachi S-4100 scanning electron microscope (SEM) with an electron beam accelerating voltage of 25 kV and a beam current of 10 μ A.

An inductively coupled plasma (ICP) spectrometer (Horiba Jobin Yvon Ultima2C™) was used for chemical analysis of the parent LDH compositions. The samples were dissolved in a 0.1M HNO₃ solution and analyzed with a solution flow of about 3 ml/min. The spectral lines of 167.02, 213.84 and 279.55 nm were used for estimation of Al, Zn and Mg content, respectively.

Phase content and crystal structure of the samples were characterized using a PANalytical X'Pert Powder diffractometer (Ni-filtered Cu K α radiation, *Theta-Theta* goniometer in the reflection mode, PIXcel^{1D} detector, step 0.02°, exposition time ~1.5 s per step) at room temperature. *Theta-Theta* goniometer provides for horizontal position of a sample surface during an XRD scan and thereby allows to measure liquid samples. The measurements were performed using Spinner Sample Stage (a sample rotation of 4 s⁻¹). A zero-background holder made of obliquely cut Si crystal was used for powder samples. A standard steel holder with the cover ring of 16 mm in diameter and about 1.5 mm thick was applied for slurries. The obtained data were refined by the Rietveld method using the FULLPROF in the profile matching mode [20].

In situ study of the anion-exchange reactions (NO₃⁻ → MBT⁻ and NO₃⁻ → BTA⁻) was performed on slurry samples of the parent LDHs-nitrates. The cover ring of the standard steel sample holder was filled with the LDH slurry and put on the top of an open 20 ml cylindrical container with 0.1M MBT(BTA) solution at pH 11.5±0.1 (Scheme 1). The bottom surface of the slurry contacted the solution through a permeable film (approx. three 0.1 mm holes per 1 mm²). A magnetic stirrer provided a continuous agitation of the solution in the vicinity of the solution-slurry interface. The assembly was placed on a Multi-Purpose Sample Stage (MPSS) and aligned to position the horizontal surface of the slurry in the center of goniometer. The measurements were performed in a Static Mode: 30 s per scan; 2 min dwell between scans.



Scheme 1. Anion-exchange cell used in the *in situ* XRD study: LDH slurry (1), cover ring (2), permeable membrane (3), a Na-MBT (Na-BTA) solution (4), magnet (5), magnetic stirrer (6), MPSS (7).

RESULTS AND DISCUSSION

Phase content and chemical composition of the prepared LDHs

The XRD patterns of the parent LDHs-nitrates and the compositions intercalated with either MBT or BTA are shown in Figures 1 and 2. The diffraction reflections typical of the LDH structure are seen in all the patterns. Analysis has revealed that the parent compositions correspond to the single-phase Mg-Al-NO₃ and Zn-Al-NO₃ LDHs. The crystal structures of these compositions were successfully refined using the rhombohedral $R\bar{3}m$ space group¹. The calculated values of the lattice parameters were $c=2.682$ nm and $a=0.3042$ nm (Mg-Al-NO₃), and $c=2.673$ nm and $a=0.3070$ nm (Zn-Al-NO₃). The relative errors in determination of the parameters c and a were 0.1 % and 0.07 %, respectively.

As regards the LDH phases obtained as a result of the anion-exchange reactions, the diffraction reflections of the (00 l) family in the XRD patterns of Mg-Al-MBT and Mg-Al-BTA (Figure 1), and Zn-Al-MBT (Figure 2) turned out to be shifted to a lower-angle range indicating a considerable increase in the basal spacing values as compared with the respective values for the parent LDH-nitrates. These LDHs phases were the only phases found in the XRD patterns of the obtained compositions. No traces of the parent LDHs were detected. Therefore, it has been concluded that the substitution of nitrates by the organic anions was complete.

The anion exchange reactions were revealed to cause no change in positions of the (110) diffraction reflections (Insets in Figures 1 and 2). Since $a=2d_{(110)}$ and depends on the Mg/Al

¹ The XRD patterns of all the LDH compositions studied in this work were indexed in a three-layer 3R polytype [21,22].

(Zn/Al) ratio [7]), it implies that the chemical composition of the double metal hydroxide layers was not affected.

The lattice parameters obtained from the crystal structure refinement as well as other parameters that characterize the LDH compositions are listed in Table 1. The basal spacings were calculated as $d=c/3$; the interlayer thickness (gallery height, h) was found by subtracting the hydroxide layer thickness from the basal spacing value. The used layer thicknesses were 0.477 and 0.471 nm for Mg-based and Zn-based layers, respectively [23].

The relative error in determination of c -parameter in the case of MBT(BTA)-intercalated compositions was estimated to be about 0.6% which is considerably bigger than that for the respective parent LDHs, while the relative error in determination of a -parameter was the same (0.07%). Diffraction reflections of the $(00l)$ family of the LDHs phases intercalated with either MBT or BTA were broadened as compared with the respective reflections of the parent phases. The broadening effect estimated using the full width at half maximum turned out to be the strongest for the reflections with l =odd. The diffraction reflections of a second LDH phase with a much smaller d -value (as reported in Ref [3]) were observed in the XRD patterns of Zn-Al-MBT and Mg-Al-MBT along with reflections of the main phase. All these effects and features are discussed in detail below.

The intercalation of BTA⁻ into Zn-Al-nitrate was unsuccessful although various reaction conditions in terms of concentration of the BTA solution (0.01M, 0.1M, and 0.5M), temperature (from 30 to 100°C) and pH (from 6 to 12) were attempted. The only LDH phase observed in the XRD pattern of a typical product of the reaction (Figure 2, "Zn-Al-BTA") was a phase with the basal spacing of 0.756 nm that corresponded to the gallery height of 0.285 nm. The latter is very close to the double van der Waals radius of oxygen. The basal spacing value of about 0.76 nm is characteristic of Zn(n)Al LDHs ($n\approx 2$) intercalated with either CO₃²⁻ or OH⁻ [13]. Since the anion exchange was performed in a carbonate-free solution, it can be concluded that the observed LDH phase is actually Zn-Al-OH. Diffraction reflections of other phase(s) were observed in the XRD pattern of "Zn-Al-BTA" as well; however, the identification attempts using the ICDD database (PDF 4+, 2014) resulted in no reasonable matches.

Since zinc is known to form complexes with benzotriazole [24,25], we have assumed that the unidentified phase(s) can be a product of the reaction between the Zn-Al hydroxide layers and BTA. In order to test the assumption, the conditions of the anion-exchange reaction in the BTA solution (as described in *Experimental*) were reproduced using zinc oxide instead of Zn-Al-nitrate LDH. ZnO powder (99.99%, Sigma-Aldrich) was taken in the amount corresponding to the same molar fraction of Zn as that in the parent Zn-Al LDH used in the anion-exchange

experiments. Figure 3 shows the XRD pattern of the dried product of a 48-h immersion of zinc oxide in the BTA solution. The XRD pattern of "Zn-Al-BTA" is shown for comparison. As seen, the positions and the relative intensities of most of the diffraction reflections, which were not identified for the "Zn-Al-BTA" sample, match well the reflections of the ZnO+BTA reaction product. Thus, an attempt to intercalate BTA into Zn-Al-nitrate LDH results in the reaction with a partial substitution of NO_3^- by OH^- and a partial decomposition of the parent LDH followed by formation of the phase(s) based on zinc oxide/hydroxide and BTA. The exact chemical composition and crystal structure of this product is unknown. Identification would require a particular research which is out of the scope of the present work.

The above-mentioned case suggests the likely reactions between the double metal hydroxide layers of the LDHs and the organic species. Therefore, the samples of LDHs successfully intercalated with MBT(BTA) were analyzed aiming to reveal signs of possible recrystallization, dissolution and other morphology changes caused by the anion-exchange processes. Figure 4 shows the SEM images of the dried Zn-Al and Mg-Al LDH powders before and after the intercalation procedure. It is seen that the particles are flake-shaped which is typical of the LDH materials. The characteristic size (diameter) of the flakes was estimated to be from 2 to 5 μm and from 50 to 200 nm for the particles of the Zn-Al LDHs and the Mg-Al LDHs, respectively. No regular changes in the shape and/or size of the particles which could be associated with a process of anion substitution have been revealed. These observations are in agreement with the conclusion drawn from the analysis of the (110) diffraction reflections that the intercalation reactions induced no change in the chemical composition of the LDH hydroxide layers.

The cations ratio (n) in the hydroxide layers of the obtained LDHs was estimated using two independent methods. The ICP spectrometry chemical analysis found that the Mg/Al and Zn/Al ratios in the parent compositions were 1.9 ± 0.2 and 2.1 ± 0.1 , respectively. Comparison of the measured a -parameter values (Table 1) with the reported dependences $a(x)$ [$x = (n + 1)^{-1}$] for Mg-Al and Zn-Al LDHs [7] also showed the cations ratio in the obtained LDHs to be close to 2:1.

Nature of the second phase in the LDHs intercalated with organic anions

In order to monitor the formation of the second phase, the intercalation processes were studied in more detail. Phase content of the Zn-Al and Mg-Al LDH samples was characterized by XRD after immersion in the MBT solution for 20 min, 2, 6, 24 and 48 h under the conditions described in *Experimental*. The samples (slurry) were studied immediately after centrifugation.

The XRD patterns of all the samples were found to be surprisingly identical: the LDH phases intercalated with MBT^- were well crystallized; no traces of the parent LDH-nitrate were detected (Figure 5, Zn-Al-MBT slurry). The second LDH phase (with the basal spacing of ~ 0.76 nm) was revealed in all the samples in approximately equal amounts. It follows from this study that the nitrate-to-MBT anion exchange reaction is much faster than it was considered before [3] (cf.: 20 min *versus* 24 h). Furthermore, intercalation of MBT^- into the LDH-nitrate takes considerably less time than that of $\text{V}_2\text{O}_7^{4-}$ (about 6 hours at room temperature [26]), although the vanadate anion is more compact and with a higher charge. It should be noticed, however, that the nitrate-to-vanadate exchange was carried out at a relatively low pH (8.4).

We considered also the reaction time of the nitrate-to-BTA anion exchange. It was found that such an exchange in Mg-Al LDH is complete in about 20 min. Besides, an analysis of the XRD patterns of both the Mg-Al-BTA powders and slurry suggested a likely presence of a second LDH phase with $d_2 \approx 0.76$ nm. The value of the basal spacing in Mg-Al-BTA (Table 1) is almost exactly twice higher than d_2 . Therefore, the most intense diffraction reflections (003) and (006) of the second phase are overlapped with the (006) and (0012) reflections of the main phase (Figure 6). The presence of the second phase was concluded from the unusual ratios of the (00*l*) reflection intensities in the XRD patterns of both slurry and powder of the Mg-Al-BTA LDH samples.

In some cases, the anions in the adjacent interlayers are arranged in different ways resulting in a layer-interlayer sequence with two basal spacings: $\cdot d_1 \cdot d_2 \cdot d_1 \cdot d_2 \cdot d_1 \cdot$ [27]. Such a configuration causes an appearance of the diffraction reflections corresponding to the d_1+d_2 values. The same effect can be induced by presence of two or more different anions in the interlayers. To make certain that no LDH phase with such combined interlayers formed as a result of the intercalation, a supplementary XRD study was performed over a 2θ range between 1.5 and 5° . No reflections which could correspond to the d_1+d_2 spacing, where d_1 is the basal spacing value of the LDH intercalated with either MBT or BTA (Table 1) and $d_2 = 0.76$ nm have been detected.

Thus, the LDH phase with $d_2 = 0.76$ nm is an attribute of the anion exchange reactions between nitrate and MBT^- (BTA^-). Appearance of such a phase is often associated with the carbonate contamination, suggesting that carbonate anion is the most favorable for intercalation. We prepared LDHs intercalated by OH^- and LDHs intercalated by CO_3^{2-} from the respective parent Zn-Al- and Mg-Al-nitrates. Anion exchanges were performed in solutions of NaOH and Na_2CO_3 , respectively, at the same pH (~ 11.5) as that used for the MBT^- and BTA^- intercalations (see *Experimental*). As seen from Figures 5 and 6, the diffraction patterns of

LDHs intercalated with either hydroxide or carbonate are very similar; both LDH-OH and LDH-CO₃ are characterized by $d \approx 0.76$ nm. However, as the organic anions intercalation was carried out in a carbonate-free environment, one should conclude that the observed second LDH phase is a Zn-Al (Mg-Al) layered double hydroxide intercalated with OH⁻.

Mechanism of the organic anions intercalation into the parent LDH-nitrate

It is seen from Figure 5 that the amount of the LDH-OH phase in Zn-Al-MBT is about twice lower in slurry than in the dried powder of the same sample. Besides, drying was found to result in broadening of the diffraction peaks that correspond to the (003) and (009) reflections. The same feature was observed in Mg-Al-MBT and Mg-Al-BTA LDHs. The fact that the LDH-OH phase is always present in the as-prepared samples, as well as the observed correlation between the relative amount of this phase and the broadening of the diffraction reflections of the LDH phases intercalated with organic anions suggest that the hydroxide anions play an important role in the substitution mechanism. It can be assumed that at the initial stage of the substitution, hydroxide anions are the first which substitute nitrate anions. In such a scenario, the intercalated hydroxide anions increase the available space of the interlayer. It would lead to the rearrangement of the remaining nitrate anions to decrease the tilt angle against the hydroxide layers, thereby reducing the basal spacing. As a result, intermediate LDH phase(s) intercalated with the NO₃⁻+OH⁻ combinations of would appear.

In order to clarify the issue, the nitrate-to-MBT exchange was studied using *in-situ* XRD. As seen from Figure 7, for the most part of the 45-min process, Zn-Al-NO₃ and Zn-Al-MBT are the main phases. The amount of the former decreases with time, while that of the latter increases. Traces of the Zn-Al-OH phase are detectable only at the final stage of the exchange reaction. No regular displacements of the diffraction reflections of the observed LDH phases have been found. Thus, the nitrate-to-MBT substitution occurs without formation of any intermediate LDH phases. Therefore, a *direct* replacement of nitrate anions by the organic species in the presence of hydroxide anions should be suggested. It seems reasonable to assume that the Zn-Al-MBT phase in the slurry contains a relatively higher amount of hydroxides and crystal water in the interlayer in comparison with that in the dried material. In more hydrated form, the interlayer species (MBT⁻, OH⁻ and H₂O) have more flexibility in terms of arrangement: anions are effectively coordinated by water molecules which screen their charges. The basal spacing of such an LDH (~1.7 nm, Table 1) is determined by the biggest species arranged, namely MBT. Drying is believed to decrease the relative amount of crystal water in the LDH interlayer. Uncoordinated hydroxide anions cannot be accommodated in the gallery

with such a big height. This induces redistribution of the anions in the interlayer. OH-rich and MBT-rich crystallites appear that finally results in a phase separation into Zn-Al-MBT (less hydrated) and Zn-Al-OH. That is why the amount of the LDH-OH phase in the powder is detected to be higher than that in the slurry (Figure 5). In order to keep the layer-interlayer electroneutrality, the organic anions in the less hydrated Zn-Al-MBT have to be arranged closer to each other in the plane parallel to the layers. Symmetry of such an arrangement appears to mismatch the symmetry of the double-metal hydroxide layers that can result in local inhomogeneities of the MBT distribution in the interlayer indicated by broadening of the (00 l) diffraction reflections with $l=odd$.

Arrangement of MBT(BTA) in the LDH interlayer

As seen from Table 1, the gallery height (h) values of the Zn-Al and Mg-Al LDHs intercalated with MBT (1.207 and 1.190 nm respectively) are equal within the experimental error. It suggests that MBT anions are arranged in interlayers of these compositions in the same way. The h -value calculated for the Mg-Al-BTA LDH (1.044 nm) is lower than that for the MBT-intercalated LDH which is consistent with the difference in length of MBT and BTA: 0.741 and 0.546 nm, respectively. At the same time, the h -values are smaller than the double size of the respective anions. Therefore, one can suggest that in the LDH structure, MBT and BTA form a double layer in which these species have a tilted orientation against the layer plane. In other words, a herringbone-like arrangement [28, 29] of the organic anions is proposed (Figure 8). Such an arrangement is common for the benzene rings since provides the most expedient molecule organization [29] and characterized by “looking” of the ring of one molecule to the center of another one.

Provided the herringbone arrangement, the orientation of MBT(BTA) anions in the LDH interlayer can be characterized by two angles, α and β (Figure 8). The former (50-52° [28]) describes a slope between the anion plane and the double metal hydroxide layer (ab plane). The latter is the angle between the symmetry axis of the benzene rings lengthwise of the anion and the line through the atoms which are in contact with the hydroxide layer (see Insets in Figure 8). The β value depends on the chemical structure of negatively charged heterogenic ring.

Following the idea of distributed charge into heterogenic part of the organic species (between nitrogen atoms, in case of BTA [30], and between sulfur atoms or sulfur and nitrogen atoms, in the case of MBT [31]) we suggest those pairs of atoms to be in contact with the hydroxide layer for better charge compensation. This assures the maximal possible interaction between negatively charged part of the anion and the hydroxide layer. It follows from such a condition that slope β is about 60° and 85° for MBT and BTA, respectively. Taking into

account the estimated values of α and β angles as well as the van-der-Waals radii of sulfur (0.182 nm), nitrogen (0.155 nm) and hydrogen (0.110 nm), the height of the herringbone-arranged organic species is calculated to be within the ranges of 1.187-1.211 nm for the MBT intercalates and 1.035-1.056 nm for the BTA intercalates. These values are in very good agreement with the galleries heights calculated from the XRD data (see Table 1).

The suggested configuration of the organic anions was verified to meet a requirement of electroneutrality of the layer-interlayer system. Figure 9 shows a possible arrangement for the case of BTA anions in the interlayer of Mg-Al LDH with the cation ratio Mg/Al = 2. One can see that the herringbone-arranged organic species are distributed to compensate the hydroxide layer charge leaving enough space for the crystal water in the interlayer.

CONCLUSIONS

2-mercaptobenzothiazole (MBT) and 1,2,3-benzotriazole (BTA) are successfully intercalated into Mg-Al-nitrate and Zn-Al-nitrate LDHs at room temperature and at high pH (11.5) which is necessary to keep an anion form of these organic species. Intercalation of BTA⁻ into Zn-Al-nitrate is not possible because of irreversible formation of a compound based on zinc oxide/hydroxide and BTA.

Formation of Mg-Al-MBT, Zn-Al-MBT and Mg-Al-BTA LDHs occurs through a direct replacement of nitrate anions by the organic species without appearance of any intermediate LDH phase. The exchange takes about 20 min which is much faster than previously considered.

Hydroxide anions are present in the interlayer of the most hydrated form (slurry) of the LDHs intercalated together with the organic anions. OH⁻ and MBT⁻ (BTA⁻) are effectively coordinated by water molecules which screen their charges. Drying results in a decrease of the relative amount of crystal water. Then, the uncoordinated hydroxide anions cannot be accommodated in the interlayer. This induces the redistribution of the anions in the interlayer which results in a phase separation into Zn-Al-MBT (less hydrated) and Zn-Al-OH.

In the LDH structure, MBT⁻ and BTA⁻ form a double layer in which these species have a tilted orientation against the layer plane (herringbone-like arrangement). Such an arrangement mismatches the symmetry of the double-metal hydroxide layers.

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