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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-Straβe 1, 21502 Geesthacht, Germany*

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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–NO_3 and Zn–Al–NO_3 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 NO_3^- 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.

1. 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) [3–5].

LDHs are typically composed of positively-charged mixed metal M^{II}–M^{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 $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{y-})_{x/y}\cdot zH_2O$ [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) [6–8]. 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

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[*] Corresponding author.
E-mail address: salak@ua.pt (A.N. Salak).

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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 [14–16]. 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 [17–19]. 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.

2. Experimental

2.1. 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.

2.2. 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 $Mg(NO_3)_2 \cdot 6H_2O$ (or $Zn(NO_3)_2 \cdot 6H_2O$) and 0.25 M $Al(NO_3)_3 \cdot 9H_2O$ (200 ml) was instilled to a 1.5 M $NaNO_3$ solution (400 ml) under continuous stirring and N_2 flow at room temperature. This procedure took about 90 min. During the reaction, pH of the mixture was controlled to be between 7 and 9 by addition of a 2 M 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 0.1 M 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 Section 3.

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.

2.3. 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 μA.

An inductively coupled plasma (ICP) spectrometer (Horiba Jobin Yvon Ultimata2C™) was used for chemical analysis of the parent LDH compositions. The samples were dissolved in a 0.1 M HNO_3 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