

Preparation and Characterization of Hybrid Organic-Inorganic Composite Material: Polymerization of *m*-Aminobenzoic Acid-Intercalated Into Zn/Al-Layered Double Hydroxides

Rasheed M.A.Q. Jamhour

Department of Applied and Basic Science, Tafila Applied University College,
Al-Balqa' Applied University, P.O. Box 179, Tafila, Jordan.

Abstract: Layered double hydroxides of aluminum and zinc (Zn/Al-LDH's) were synthesized directly by hydrolysis at room temperature as reported elsewhere. After characterization, the material was reacted with *m*-aminobenzoate anion ($m\text{-NH}_2\text{C}_6\text{H}_4\text{COO}^-$) which undergoes polymerization in the interlayer space; resulting in the formation of a matrix with polymeric organic macromolecule. The resulting material along with the host LDH's compound of Zn/Al-Cl was characterized by X-Ray Powder Diffraction (PXRD), Thermal Analysis (TG), Differential Thermal Analysis (DTA), and Fourier Transform Infrared Spectroscopy (FTIR). The study confirms the intercalation of *m*-aminobenzoate anion. Diffusion of oxygen molecules between the contact region of two anions in the interlayer space and oxidation of the anion lead to the formation of a polymer macromolecule. This intercalation compound result in a gallery height of 15.8 Å, indicating that the guest anion stack to form a monolayer with the benzene rings perpendicular to the host layers, giving a suitable orientation for polymerization.

Key words: Layered double hydroxides, Intercalation compound, Aminobenzoic acid, Host-guest system

INTRODUCTION

Layered double hydroxides LDH's or anionic clays have been of interest to researchers of different discipline in chemistry due to their many applications specially as adsorbents, ion-exchangers, catalyst precursors and more recently in pharmaceuticals for drug release control^[1-7]. LDH are minerals and synthetic materials that consist of layered structure with positive charge brucite-type ($\text{Mg}(\text{OH})_2$) layers of mixed metal hydroxides. In brucite, magnesium atoms coordinate with hydroxyl groups in an octahedral geometry resulting in layers that interact with each other by weak forces. Exchangeable anions are located in the inter layer spaces to balance the positive charge of the layers. LDH's have a general formulation of $[\text{M}^{+2}_{1-x} \text{M}^{+3}_x (\text{OH})_2]^{+x} (\text{A}^{m-})_{x/m} \cdot n\text{H}_2\text{O}$, where M^{+3} and M^{+2} represent metal atoms arranged octahedrally within the structure and A^{m-} represents a general anion such as Cl^- , OH^- , CO_3^{2-} , etc. Trivalent metal atoms have substituted some divalent metal atoms, which creates positively charged layers^[8,9]. The generation of an organic-inorganic hybrid material is accomplished by incorporating an organic anion in the inter layer space of the layered inorganic matrix by a typical ion-exchange mechanism between the anion sited, which is free to move, and the organic anion. It is also possible to exchange not only organic but also inorganic anions, as well as complexes

at variable oxidation states^[10-12]. The layer surfaces of LDH's are structurally similar to Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5$), in which it is a dioctahedral layered aluminosilicate, consists of aluminum atoms coordinated octahedrally with oxygen atoms and hydroxyl groups on the outer surface of the layer. While the inside surface resembles the structure of silica, where silicon atoms are coordinated tetrahedrally with only oxygen atoms. Therefore, less hydroxyl groups are found when compared by LDH layers that are decorated with hydroxyl groups at both layer surfaces^[13,14]. This fact makes the LDH to be susceptible to the same type of reactions with Kaolinite and probably with higher reactivity, due to the availability of reaction sites. Therefore, many chemical modifications using the host - guest system for incorporating molecules in the interlayer space were found in the literature, for instant, different anionic dyes were incorporated into Zn/Al-LDH^[15], tetraphthalate, naphthalene-2,6-disulfonate, and anthraquinone-2,6-disulfonate anions were also incorporated with the same type LDH^[16], and different dicarboxylate anions with Zn/Al-LDH were synthesized^[17]. In most cases the intercalated molecules are often present as neutral molecules or anions.

The aim of this study is to incorporate *m*-aminobenzoate anion in the interlayer space of Zn/Al-LDH and to investigate the interlayer polymerization, which is expected to give a new avenue to a number of applications especially in the industrial processes.

MATERIALS AND METHODES

Reagents and Instrumental Techniques: The starting reagents were of standard analytical grade from Merck. All other necessary solutions were prepared freshly prior to use. Powder X-Ray Diffraction (PXRD) analyses was obtained using a Phillips APO 1700 instrument with Ni-filtered Cu- α radiation with the angle range $2\theta = 4-30^\circ$. Both thermogravimetry (TG) and differential thermal analysis (DTA) were carried out with a Rigaku Denki thermoflex-type thermal analyzer, model 8076 at a heating rate of 10°C mn^{-1} using $\alpha\text{-Al}_2\text{O}_3$ as reference material. FTIR spectra were recorded with a Perkin-Elmer FT-IR 1730 spectrometer using KBr disks. Analyses were performed at a transmission within $400\text{-}4000\text{ cm}^{-1}$ and 4 cm^{-1} resolution.

Preparation of the Host Material of Zn/Al- Double Hydroxides: The host material was directly synthesized by hydrolysis at room temperature following closely a method reported earlier^[18]. The amount of (13.6 g) 0.1 mole of an aqueous solution of ZnCl_2 was mixed with (6.5 g) 0.05 mole of AlCl_3 . The Zn/Al ratio close to 2 was maintained to give a good crystalline product. Another aqueous solution of NaOH (14 g) 0.35 the mole was added drop wise to the mixture at $\sim 22^\circ\text{C}$ and continue stirring over a period of 4 h. The pH kept around 10 throughout the reaction. The powder material so obtained was filtered, crystallized at 65°C for 18 h followed by cooling and washing several times with deionized water. The material was then dried overnight at 80°C . This material was named Zn/Al-Cl.

Preparation of the Zn/Al-*m*-Aminobenzoic acid Intercalated Compound: Approximately 1.0 g of the LDH material obtained as above, was dispersed in 20ml of (0.05-0.1 mole) solution of *m*-aminobenzoic acid in a 50-ml flat-bottomed reaction flask. The reaction was refluxed for 3 h. and kept for gentle stirring for 12h. The product was separated and washed several times with hot distilled water, dried at 40°C for 24 h. Once incorporated the Zn/Al-AB appears stable. The polymerized form was obtained when heating the Zn/Al-AB material in air at 90°C for four days ($\sim 100\text{ h}$).

RESULTS AND DISCUSSION

Preparation and Characterization of Zn/Al-AB Intercalation Compound: The starting host material of Zn/Al-Cl was directly synthesized through hydrolysis of ZnCl_2 and AlCl_3 with NaOH aqueous solution as described in the experimental section. By equilibrating the solid host with *m*-aminobenzoat anion results in a complete replacement of chloride in the solid phase by *m*-aminobenzoat anion. The host material of Zn/Al-Cl (a) and intercalated material Zn/Al-AB (b) were characterized by x-ray diffractograms shown in Fig. 1.

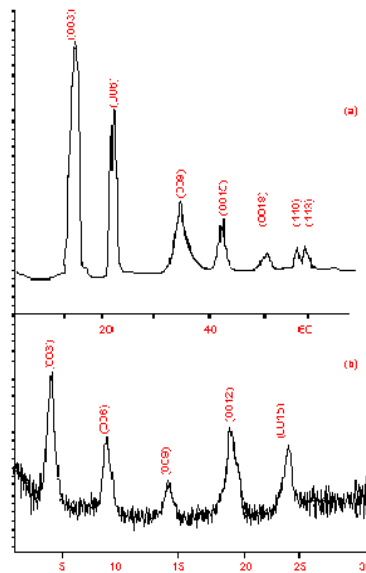


Fig. 1: X-ray diffractograms of the Zn/Al-Cl phase before (a) and after intercalation with *m*-aminobenzoic acid (b)

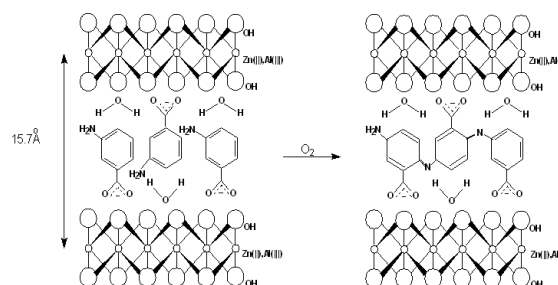


Fig. 2: Structure of $[\text{ZnAl}_2(\text{OH})_6][m\text{-NH}_2\text{C}_6\text{H}_4\text{COO}]_2 \cdot n\text{H}_2\text{O}$ (a), and after heating in air (b).

The x-ray diffraction pattern of the host material (a) agrees well with that previously reported^[16], with a basal spacing of 7.8 \AA , thus, the gallery height of Zn/Al-Cl is 3.0 \AA after subtracting the thickness of the layers (4.8 \AA). The new compound after intercalation (b) was confirmed by the increase in the interlayer distance for 15.7 \AA (gallery height of 10.9 \AA) which is 7.9 \AA more than the interlayer distance of the host material. From this result it can be said that the organic anion was readily exchanged by chloride ion and located in a perpendicular manner (with regards to the benzene rings) to the planes of Zn/Al hydroxide layers, see Fig. 2.

Moreover, the gallery height is 0.9 \AA large in comparison with the size of anion (which is about 10 \AA) that may account for the presence of voids of molecular size between the anion and the layers which are partially occupied by water molecules. The presence of water molecules was also confirmed by the data of thermal analysis.

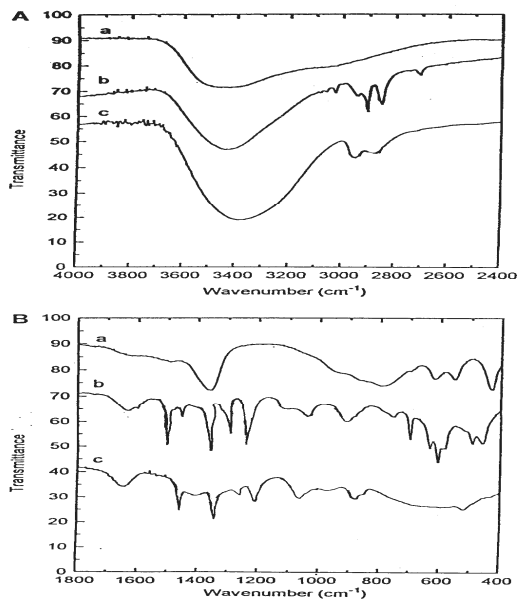


Fig. 3: FTIR spectra of: Zn/Al-Cl (a), Zn/Al-AB (b), and Zn/Al-AB after heat treatment (c). At higher (A) and lower wave numbers (B).

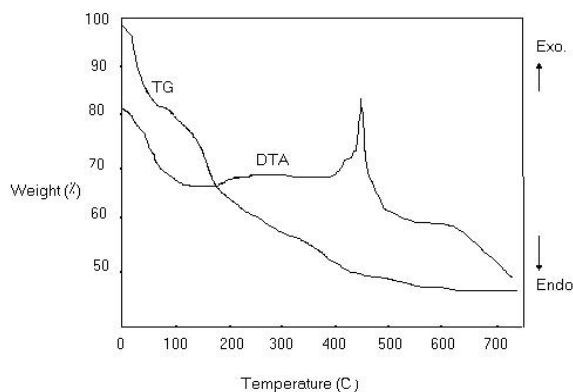


Fig. 4: TG and DTA Curves of Zn/Al-AB Intercalation Compound

Figure 3 shows the FTIR spectra of Zn/Al-Cl (a) and after intercalation (b). The intense bands at 1373 and 1533 cm^{-1} confirm the presence of the organic anion of *m*-aminobenzoic acid in the intercalation compound –spectrum (b) which are attributed to the stretching vibration of the carboxylic group. Less intense bands at 1250 and 1300 cm^{-1} may assign to the stretching vibration of the C-N bond of amino^[19]. Other interesting information about the structure those two bands found at 2700-3100 cm^{-1} attributed to the stretching vibration of C-H bonds. The broadband at 3100-3700 cm^{-1} assigned to the stretching vibration of O-H groups. The comparison of spectrum (b) with spectrum (c) taken over the polymerization process reveals a sharp decrease of the intense bands at 1250 and 1300 cm^{-1} which points to a substantial decrease in the number of amino groups $-\text{NH}_2$.

Figure 4 shows the thermograms TG and DTA for the synthesized Zn/Al-AB. The TG curve shows two steps for a mass loss. The first mass loss of 18%, up to 250°C, correspond to the loss of interlayer water molecules and surface adsorbed water (endothermic peak at DTA curve). The second step from 250-500°C a continuous loss of about 55% attributed to dehydroxylation of the material and loss of organic compound. An additional 3% mass loss observed between 500-950°C, which is attributed to reactions involving oxides.

The Mechanism of Polymerization of *m*- $\text{NH}_2\text{C}_6\text{H}_4\text{COO}^-$ Since polymerization is connected with the oxidation of the organic molecules, for the reaction to proceed, either oxidative properties of the host material are necessary or the treatment of the whole system with oxidative reagent like oxygen in this study.

The packing of *m*-aminobenzoate anion (benzene rings) in the perpendicular orientation gave a good site to every NH_2 group to be in molecular contact with the benzene ring of the other anion. The oxidation readily occurring by oxygen molecules that enter through the voids and take part in the oxidative polymerization in the presence of water molecules. This mechanism leads to the formation of a polyconjugated system (PCS). The polymerization was confirmed by the FTIR analysis as described, also in a change of color of the material upon polymerization that is over heating at 90°C in air.

The attention to this type of polymerization is connected with the possibility to obtain well-ordered conducting polymers in the interlayer space, which is difficult to achieve when polymerization is performed in solution.

CONCLUSION

The present characterization of Zn/Al-AB by X-ray diffractometry, FTIR, and thermal analysis have demonstrated the synthesis of Zn/Al layered double hydroxides intercalated with *m*- $\text{NH}_2\text{C}_6\text{H}_4\text{COO}^-$ anion and its further polymerization in the interlayer space by an expansion of layers up to 15.7 Å. The use of Zn/Al-AB layered double hydroxides allows to investigate and control the possibility of the formation of Polyconjugate Systems (PCS) by the oxidative polymerization mechanism of the organic anion in the interlayer space of LDH. The qualitative study of different forms of the organic anions would give a wide range of study, particularly when packing and orientation is taking into account. In this study one particular orientation was taken into account where the formation of the new bond should most probably take place between the nitrogen atom of the NH_2 group and the fourth carbon atom of the benzene ring of the neighboring molecule. For this reason it would be interesting to investigate the polymerization of organic molecules into layered double hydroxides with different

forms of m-aminobenzoate anions or with the more straightforward planar type of packing of the organic anions. These polymer-intercalated compounds can possess interesting physicochemical properties.

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