Elaboration and Physico-Chemical Characterization of the Gibbsite Li(OH)3 Hybrid Material

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Abstract-A hybrid material can be defined as a combination of two components of different chemical nature. The combination of a mineral matrix and organic matter has multiple significance. From a chemical point of view, it allows the obtaining of bi-functional materials that combine the chemical properties of their components. The development of new materials with specific properties and nanostructured Lamellar Double Hydroxides (LDHs) has been widely investigated due to their great importance. This study focuses on the development of a hybrid material consisting of a matrix of alumina trihydrate $Al(OH)_3$ (gibbsite). Previous studies on the synthesis of suspension LDHs by lithium salts intercalation in a gibbsite matrix were examined, while the obtained samples were characterized by different physicochemical methods.

Keywords-alumina; inorganic compounds; gibbsite; lithium-salts intercalation; lamellar double hydroxide components

I. INTRODUCTION

Nanotechnology has been used for synthesizing various polymer nanocomposites and examining their physical and chemical properties [1-3]. The presence of nanoparticles in polymers improves their mechanical, electrical, and chemical properties as it results in bi-functional materials that combine the chemical properties of their components. Layered Double Hydroxides (LDHs) have attracted considerable interest due to their potential applications as selective sorbent medicines [4, 5], precursors for ceramics [6], and nanocomposite materials [7, 8]. Crystalline aluminum hydroxides, such as gibbsite, bayerite, and nordstrandite, exhibit properties of intercalation matrices for lithium salts [9-12]. The reaction between aluminum hydroxides and lithium salts is represented by:

$$Li_nX + 2n\,Al(OH)_3 + qH_2O \rightarrow [LiAl_2(OH)_6]n\,X.qH_2O$$

The most remarkable synthetic procedure is the direct intercalation of lithium salts into crystalline $Al(OH)_3$ polymorphs [13, 14]. Intercalation of inorganic or organic ions into gibbsite matrices is used for creating Li/Al LDHs [15-17]. Gibbsite is intercalated with lithium cations obtained from various lithium salts, which dehydrate readily giving highly crystalline intercalates. These crystal structures display highly ordered lamellar phases consisting of eclipsed $[LiAl_2(OH)_6]^+$ sheets with sandwichlike layers of intercalated anions [17]. Li and Al-X can be prepared using different synthetic approaches. The products are obtained by the intercalation of lithium cations into the octahedral voids of aluminum hydroxide layers of trihydroxides, having anions and water molecules incorporated between the layers [18]. The compounds consist of layers with $[LiAl_2(OH)_6]^+$. Xn-anions of $[LiAl_2(OH)_6]$nX or Xn-anions and water of $[LiAl_2(OH)_6]nX.qH_2O$ are located between the layers. Therefore a structural study of these intercalation compounds and their synthesis mechanisms is very interesting from both theoretical and practical viewpoints.

This study investigates the physicochemical properties of the intercalation of lithium cations and inorganic anions (Cl^-, NO_3^-) from $[LiAl_2(OH)_6]nX.qH_2O$, where X=Cl^-, NO_3^-, into gibbsite $Al(OH)_3$, to examine the structural mechanism leading to the double hydroxide lamellar intercalated compounds. The obtained phases were examined by X-Ray Diffraction (XRD), infrared spectroscopy (FTIR), thermogravimetric analysis (TG/DTA), and microscopic (SEM) techniques. The results of this paper confirm that the Li–Al LDH synthesized by this protocol can be compared with the work already published in the synthesis of double lamellar hydroxides [1, 9]. In order to have a good reinforcement between the load and the matrix (already mentioned at the beginning of the introduction), this requires interactions between the organic and inorganic phases. Such results open up a new route for the synthesis of nanocomposites using polymeric entities and layered materials [3].

II. MATERIALS AND METHODS

A. Materials

The alumina trihydrate (Gibbsite) $Al(OH)_3$ powder was supplied by DIPROCHIM in Algeria, and its chemical composition was defined by the volumetric method. This powder consisted of 61.31% Al_2O_3, 0.64% SiO_2, 2.42% CaO, 0.30% MgO, 0.16% Fe_2O_3, and up to 34% water. The average particle size of this powder was 15µm, with a density of about 3.106g/cm^3. Two fatty acids were used: palmitic acid $C_{16}H_{32}O_2$ and stearic acid $C_{18}H_{36}O_2$, which had molecular weights of 256.43g/mol and 284.49g/mol respectively.

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B. Synthesis of $[LiAl_2(OH)_6]nX.qH_2O$

The layered double hydroxide $[LiAl_2(OH)_6]nX.qH_2O$ was synthesized using the previously reported method [11, 13, 17, 19]. In a standard experiment, the intercalation was achieved by stirring a suspension of gibbsite in an aqueous solution containing a 6-fold molar excess of lithium salts (LiCl, LiBr, or $LiNO_3$) at 90°C for 15h, as shown in Figure 1. Samples were washed with 5-10ml of deionized water and then dried in an oven at 90°C for 1-2h to give samples of idealized composition.

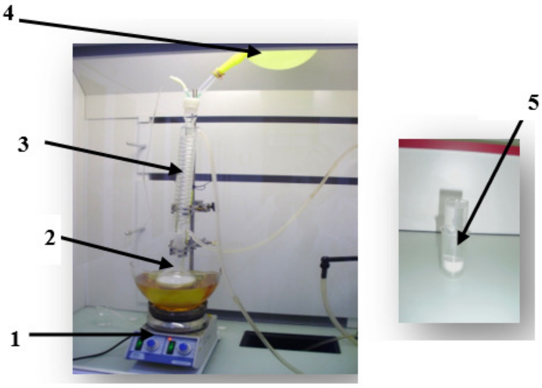

Fig. 1. Experimental setup of the gibbsite synthesis by lithium salt: 1: hotplate, 2: synthesis balloon, 3: refrigerant, 4: nitrogen gas balloon, 5: sample after filtration.

C. Anion Exchange Reactions

The intercalated fatty acids were stuffed as follows: 7 moles of $[LiAl_2(OH)_6]n_2OX.qH$ were added to 4-fold excess of stearic or palmitic acid. The mixture was stirred for 48h at room temperature in a nitrogen atmosphere. After hustle and bustle, the product was isolated by filtration, washed with deionized water, and dried in an oven at room temperature for 48h.

D. Characterization

The layered double hydroxide $[LiAl_2(OH)_6]nX.qH_2O$ was examined in a Siemens D5000 X-ray diffractometer, equipped with a graphite monochromator placed between the sample and the detector. The X-ray source was a copper anticathode ($\lambda_{CuK\alpha 1}$ = 1.5406Å), while the beam divergence was limited to 0.2°. The diffractograms were recorded between 2° and 70° (90° in some cases) 2θ, using an impact of 2° for mounting in grazing incidence. The infrared spectrum was examined using a NICOLET 5700 spectrometer, employing KBr technical dilution (1.5% w/w) on a range of 400-4000cm with a resolution of 2cm. Thermogravimetric analysis was carried out on a Setaram TG - DTA 85, from 20 to 850°C with a heating rate of 5°C/min. Microscopic studies were carried out with an E3 Electroscan SEM at 10 to 30kV, which allowed a magnification up to 30,000 times.

III. RESULTS AND DISCUSSION

A. X-ray Diffractograms of Hybrid Materials

Figure 2 shows the intensity/angle graph for raw and calcinated materials. The raw alumina spectrum has two major peaks at 19° and 21°, corresponding to the combination of gibbsite and bayerite phases. The other peaks correspond to structures and monohydrate forms. The calcinated at 300°C material has lower peaks. This is supposed to be the result of smaller crystallite domain sizes due to the stacking disorder of aluminum hydroxide layers. The diffractograms of the gibbsite products, which came from lithium salts intercalation, showed new reflections differing from those of the crystalline gibbsite. Figure 3 represents the X-ray diffractograms of the LiCl salt intercalation in the $Al(OH)_3$ structure. The possibility for gibbsite to react with lithium salts has been shown individually [20]. The components' intercalation depended on the $Al(OH)_3$ dispersion and the nature of lithium chloride, while it was also limited by the diffusion rate of a layer of the obtained lithium chloride. Among the studied lithium halides, LiCl was more reactive with $Al(OH)_3$. This halide showed intercalation between LiCl and $Al(OH)_3$. The peak at about 14° after 15h reaction indicates that gibbsite was transformed into LDH. These reflections of LDH were in agreement with those reported in [17, 21-22]. Lithium cations were located in the octahedral voids of the aluminum hydroxide layer.

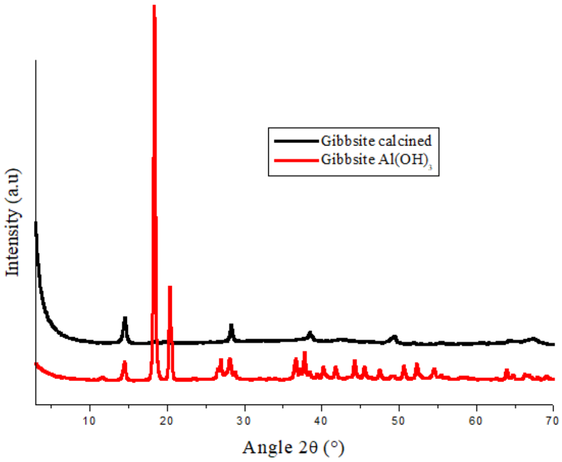

Fig. 2. X-ray diffraction (XRD) of crystalline gibbsite and gibbsite calcined at 300°C.

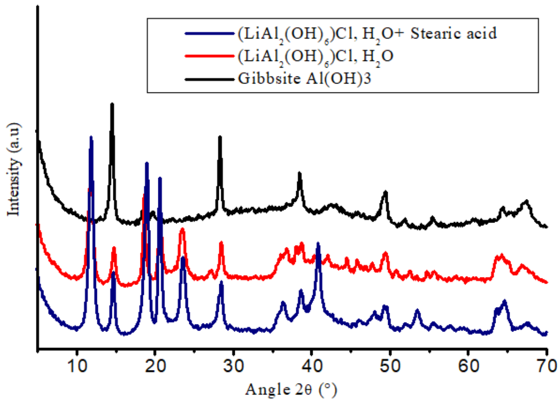

Fig. 3. X-ray diffraction (XRD) of crystalline gibbsite, gibbsite intercaled by LiCl, and anionic exchange precursor with fatty acids (stearic acid).

The chloride anions are opposite to lithium cations, at exactly the midway between the interlayer spaces, in such a way that they are partially lied in the holes of hydroxide ions of the layers. The X-ray diffractograms contained intense reflections with multiple interplanar distances, indicating that the structure of the products was lamellar. Analogous studies were performed for $[LiA1_2(OH)_6]Br^-$ and $[LiAl_2(OH)_6]NO_3^-$. Treatment results of $[LiAl_2(OH)_6]Br^-$ and $[LiAl_2(OH)_6]NO_3^-$ precursors were similar to those of $[LiAl_2(OH)_6]C1^-$.

B. Thermogravimetric Analysis

Figure 4 shows the Differential Thermal Analysis (DTA) thermogram for a gibbsite specimen. As it can be observed, the gibbsite loses most of its structural water by thermal dehydration above 279.23°C with a weight of about 30%. Furthermore, the TG-DTA curve gradually varies with increasing temperature, indicating that the gibbsite structure changes continually upon heating. This change led to the formation of several transition alumina phases that are alumina of crystallographic structure intermediates between hydrate and alumina *α* [23, 24].

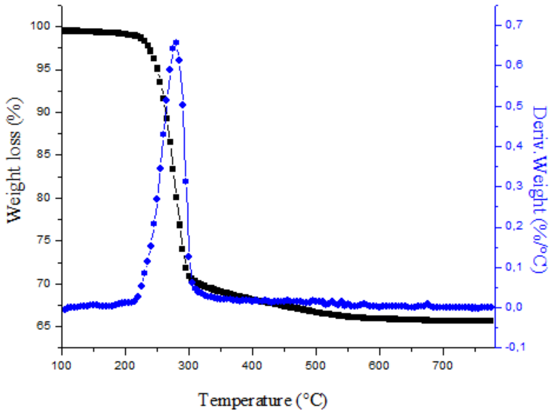

Fig. 4. TG/DTA curves of raw gibbsite.

The thermal stability of the lithium salt intercalated into gibbsite noted as compounds $[LiAl_2(OH)_6]X$ where X={Cl, Br, NO_3} was examined by TG/DTA measurements between 100-800°C, and these results are depicted in Figure 5.

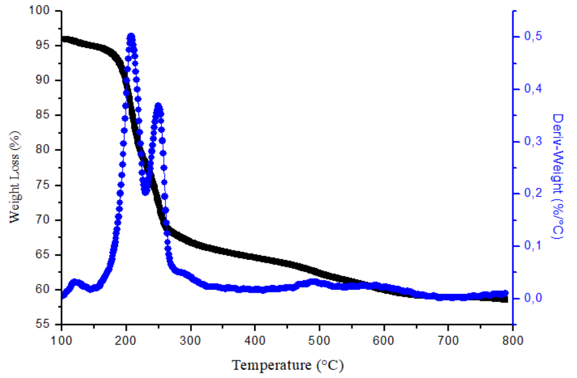

Fig. 5. TGA and DTG curves of $[LiAl_2(OH)_6]Cl.H_2O$ precursor.

The TG/DTA curves exhibit two temperature range regions at 100-300°C and 300-600°C. The TG curve shows that the major weight loss occurred below 300°C. A weight loss of 25% below 250°C happened probably due to the loss of water from the external surface. This weight loss is indicated by the two sharp endothermic peaks seen in the DTA curve at 207.78°C and 250.85°C respectively. The second loss of 15% in temperatures between 300 and 600°C was attributed to the interlamellar water molecule and dehydroxylation of metal hydroxide layers [25]. $[LiAl_2(OH)_6]Br.H2O$ and $[LiAl_2(OH)_6]NO_3.H_2O$ samples showed the same trends during the thermal analysis with an almost identical weight loss rate [26].

C. Infrared Spectroscopy (FTIR)

All reactions were carried out in a closed reaction vessel with continuous N_2 purging. Under such conditions, CO_2 likely does not dissolve into the samples. The IR spectra of the $LiX/Al(OH)_3$ LDH, as depicted in Figure 6, show no CO_3^- characteristics at ~1400cm^{-1}, indicating no contamination by dissolved carbonate from the air during its synthesis. The IR spectra show the bands of stretching vibrations of OH groups, deformation vibrations of Al-OH and water molecules, and stretching vibrations of the Al-O bond of the $[LiAl_2(OH)_6]X$ LDH [27]. The absorption bands that appear at the 500cm^{-1} range are attributed to A1-O bond deformation, and a wide strip of binding OH water appears at 3500cm^{-1}. Moreover, some bands, especially those observed around 1150cm^{-1}, are identifiable.

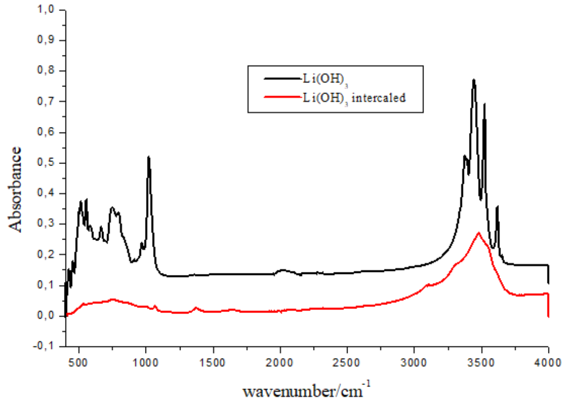

Fig. 6. IR spectra of rough gibbsite and gibbsite intercalated by LiCl salt.

Figure 7 shows a band between 3550cm^{-1} and 3300cm^{-1}, which is attributed to the OH bond elongation. A band appearing at 1650cm^{-1} corresponds to the OH bond deformation, and the one at 750cm^{-1} corresponds to the Al-OH bond deformation. Figure 8 shows the IR spectra of $LiAl_2(OH)_6]Br.H_2O$, $[LiAl_2(OH)_6]NO_3.H_2O$, and the LDHs exchanged by fatty acids, which were similar. In these spectra, the difference in the intensity decreases. Further bands were found at 2920cm^{-1} corresponding to the C—H bond with asymmetric elongation, at 2850cm^{-1} corresponding to the C—H symmetric stretching bond, and at 1720cm^{-1} and 1190cm^{-1} corresponding to the C=O and the C-O bonds. This analysis revealed the presence of all the characteristic vibration modes of the double lamellar hydroxide. Furthermore, the absorption bands observed at 3500cm^{-1} and 1600cm^{-1} were attributed to hydroxylated layers of the [Li-Al-Cl] LDH vibration modes in the IR spectrum of intercalated LDH, confirming the LiX intercalation into the gibbsite.

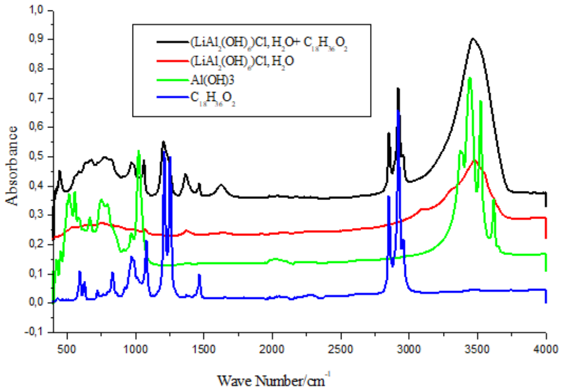

Fig. 7. IR spectra of gibbsite intercalated by salt and exchanged by stearic acid.

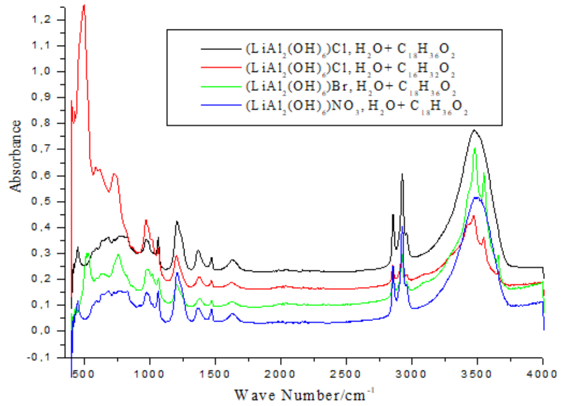

Fig. 8. IR spectra of gibbsite intercaled by Br, NO_3 salts and exchanged by stearic and palmitic acid.

D. *Scanning Electron Microscopy (SEM)*

Figure 9 shows images obtained by SEM for various raw and synthesized materials to obtain an HDL gibbsite, revealing a difference in their particle morphology. The second loss of 15% in temperatures between 300-600°C is attributed to the interlamellar water molecule and dehydroxylation of metal hydroxide layers [25]. $[LiAl_2(OH)_6]Br.H2O$ and $[LiAl_2(OH)_6]NO_3.H_2O$ samples showed the same trends during the thermal analysis with an almost identical weight loss rate [26].

IV. CONCLUSION

This study aimed at the synthesis and the characterization of a gibbsite based double lamellar hydroxide filler, using several characterization techniques (XRD, ATG/ATD, FTIR, and SEM). The FTIR spectra confirmed the penetration of molecules within these matrices. New absorption bands appeared for the investigated materials, including synthesized and exchanged samples, following the disappearance of the characteristic bands, and a decrease in the absorbance of the corresponding peaks. Moreover, the thermogravimetric analysis (TG/DTA) proved the high thermal stability of all materials. Their calcination at high temperatures resulted only in their dehydration, thus creating several transition phases. The gibbsite seems to intercalate certain lithium salts, while halogen anions intercalate within the gibbsite structure. The crystalline structure indicated that these materials showed lamellar intercalation of $[LiAl_2(OH)_6]^+$ cations. The main contribution of the current research is the elaboration of a mineral ceramic by incorporating a fatty acid between its layers, thus facilitating the ceramic-polymer interaction.

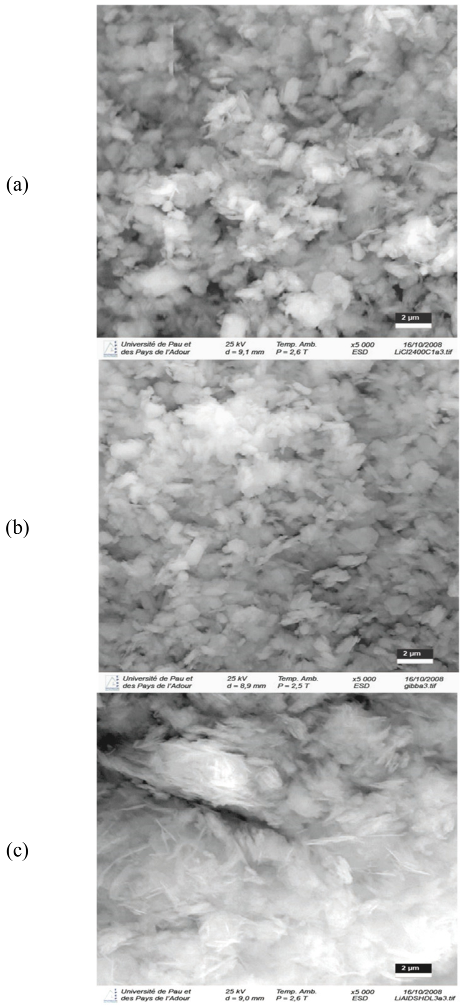

Fig. 9. SEM images of (a) gibbsite $Li(OH)_3$, (b) intercalation of the lithium salt into gibbsite, and (c) precursor+stearic acid.

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