Dynamic water vapor sorption on Mg(Ga^{3+})O mixed oxides: Analysis of the LDH thermal regeneration process

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ARTICLE INFO

ABSTRACT

The rehydration process of the calcined MgGa-layered double hydroxides (Ga-LDH) was analyzed at different temperatures and relative humidities. Results clearly showed that Ga-LDH sample presented an excellent regeneration kinetic, in comparison to the aluminum typical one. Different techniques such as X-ray diffraction, infrared spectroscopy and thermal analysis were used to elucidate the presented results.

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1. Introduction

Layered double hydroxides (LDHs) comprise a unique family of layered solids composed by positively charged brucite-like layers, which are separated by charge balancing anions. The general formula of LDHs may be described by the expression: $[M^{2+}_{(1-x)}M^{3+}_x(OH)_2]A^{n-}_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are metal cations capable of occupying the octahedral interstices of a brucite-like sheet, while A^{n-} represents organic or inorganic anions [1–3]. The bracketed term in the chemical formula represents the brucite-like layer which contains divalent cations sixfold coordinated to hydroxyl groups. The layer gains a positive charge because of isomorphic substitution of M(II) divalent cations by M(III) trivalent cations. Anionic species along with water molecules are hosted into the interlayer space. Physicochemical properties of LDHs can be tuned either by varying the composition within the layers or by varying the nature of interlayer anions. Thus, LDHs have had important applications in several fields such as catalysis, anion exchangers, chemical additives, and as drug delivery carriers, among others [1–5].

The nature of the interlayer anions may be varied via ion exchange or by taking advantage of the so-called memory or reformation effect. Thermal treatment of LDHs, at temperatures lower than 600 °C, causes the formation of mixed oxides, $M^{2+}(M^{3+})O$. Some of these oxides are able to recover the layered structure after contact with water or anionic solutions [5–10].

It is worth mentioning that the interlayer anions do not occupy rigid positions; on the contrary, they are mobile [11]. The anions' mobility in LDHs is determined mainly by the physicochemical properties (which are in turn determined by the chemical composition), and the hydration degree, which control the dynamics of intercalated compounds. In this context, it is particularly interesting to study the influence of the chemical composition of the layers and the hydration degree between the layers on the regenerability of LDHs from the corresponding $M^{2+}(M^{3+})O$ mixed oxides, where different processes may occur such as recrystallization and the spinel formation among others [5,9,12–14].

The mixed oxides derived from thermal treatment of LDHs have also found several applications, mainly as acid–base catalysts, as they are non-toxic, inexpensive, and have tunable basic properties, focusing on the final application. The carbonate-containing MgAl LDH has been the most widely used in producing mixed oxide catalysts for base-catalyzed reactions [10,11,15]. The catalytic performance of these mixed oxides is a function of their surface basic properties which in turn are determined by the chemical composition of the LDH and the activation procedure. In this context, the partial or complete hydration of mixed oxides is a crucial parameter to tune the catalytic properties, since when Brönsted basic sites are created, reactions such as aldol condensation of aldehydes and ketones and cyanoethylation of alcohols and Knoevenagel and

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Claisen–Schmidt can be performed [16–19]. Furthermore, changing the nature of the M(III) trivalent cation is an interesting alternative for the modification of physicochemical properties [20,21]. Among different M(III) trivalent cations, there have been some LDH reports describing the gallium containing synthesis and structural properties [22–27].

As mentioned above, the most used LDH is the MgAl–CO_3. Recently a complete study was reported concerning the rehydration kinetics and consequently the modulation of basic sites in the Mg(Al)O mixed oxides [28]. Besides, as mentioned above, the composition of the layers is also a variable parameter that can be conveniently tailored to manipulate the properties of mixed oxides. Thus, this work was started with the goal of elucidating the influence of the trivalent metal on the hydration kinetics of Mg(M^{3+})O mixed oxides, M^{3+} being other than aluminum, specifically, gallium.

2. Experimental

MgGa layered double hydroxide was prepared by the coprecipitation at low supersaturation method. Two separate solutions were prepared, an alkaline solution of KOH and K_2CO_3, and a metallic solution containing the metal nitrates ($Mg(NO_3)_2$ and $Ga(NO_3)_3$) in the required proportions, where the Mg/Ga nominal molar ratio was 3. Both solutions were added simultaneously at a controlled rate to a glass reactor with mechanical stirring, at a constant pH of 8. The precipitate was aged for 18 h at 80 °C, then washed abundantly with bidistilled water, and finally dried at 100 °C overnight. The sample was labeled as Ga-LDH. The LDH crystalline formation was confirmed by XRD. Then, the sample was calcined at 550 °C for 6 h for sample thermal activation, according to the TG analysis (see Section 3).

Materials were characterized by X-ray diffraction (XRD), using a diffractometer Bruker D8 Advance coupled to a copper anode X-ray tube. The presence of the LDHs or the periclase structures was confirmed by fitting the diffraction pattern with the corresponding Joint Committee Powder Diffraction Standards (JCPDS). A thermogravimetric analysis was performed on all the samples to determine the activation temperature. These experiments were performed in a Q500HR equipment from TA Instruments at 5 °C/min in dry air atmosphere.

After the thermal and structural characterization, different dynamic water vapor sorption experiments were carried out on a temperature-controlled thermobalance TA Instruments model Q5000SA, equipped with a controlled humidity chamber. The experimental variables used were temperature, time, and relative humidity (RH). The mass used in each experiment corresponds to 6 mg of each activated LDH and all the experiments were carried out using N_2 (Praxair, grade 4.0) as carrier gas and distilled water. The N_2 flow used in all the experiments was 100 mL/min, and the relative humidity percentages were controlled automatically with the Q5000SA equipment. First, water vapor sorption/desorption isotherms were generated at temperatures between 40 and 80 °C, varying the relative humidity from 0 to 85 to 0%. These experiments were performed on the three samples. Finally, isothermal experiments were performed in some of the samples at preset temperatures and RH.

After the water sorption experiments and in order to identify the hydration products, the samples were characterized by standard thermogravimetric analyses (TGA), infrared (FTIR) spectroscopy and X-ray diffraction (XRD). For the TG analyses, the experiments were performed under air atmosphere, with a heating rate of 5 °C/min in a thermobalance TA Instruments model Q500HR. For the FTIR spectroscopy, samples were analyzed on a Spectrometer NICOLET 6700 FT-IR. In the XRD case, the equipment used was the same as the one mentioned above.
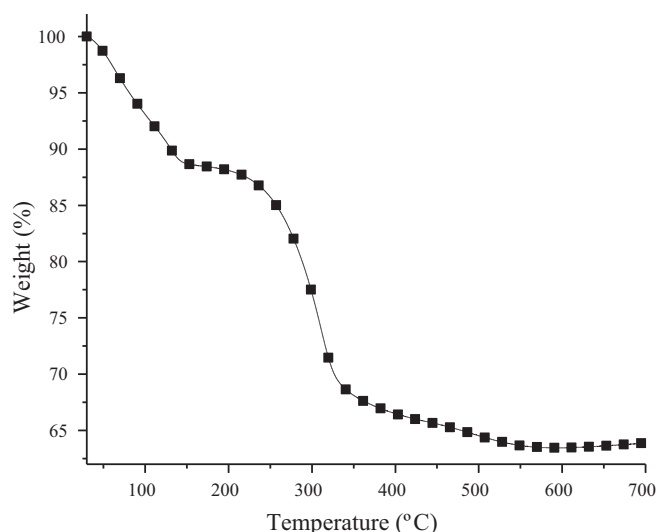

Fig. 1. Decomposition thermogram of the Ga-LDH sample. The experiment was performed at 5 °C/min into an air atmosphere.

3. Results and discussion

Initial thermogravimetric analysis was performed in the Ga-LDH sample to determine the activation temperature (Fig. 1). According to the TG and DTG curves, between room temperature and 130 °C there were two mass loss of around 11.5%, associated to superficial and interlayer water evaporation processes. Then, the sample presented the dehydroxylation process, between 220 and 370 °C, corresponding to 32.6%. Finally the Ga-LDH sample presented a final mass loss of 3.8% between 425 and 540 °C, which must correspond to the decarbonation process. Based on these results the sample was thermally activated at 550 °C for 6 h. Fig. 2 shows the XRD patterns of the sample after the thermal decomposition. As would be expected, it fitted to the periclase structure (MgO, JCPDS file 30-0794), confirming the layered structure's destruction and the formation of Mg(Ga^{3+})O mixed oxides.

After thermal activation, the sample was submitted to different relative humidity conditions for the following experiments. Fig. 3 shows the sorption/desorption isotherms of water vapor on the native and calcined Ga-LDH samples at different temperatures. The activated Ga-LDH sample was analyzed at different
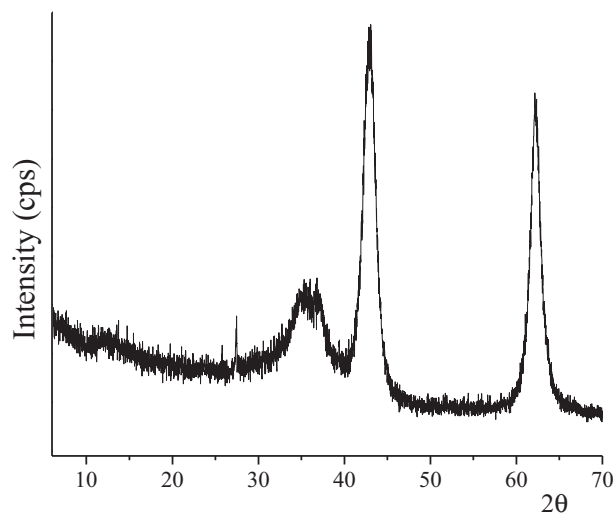

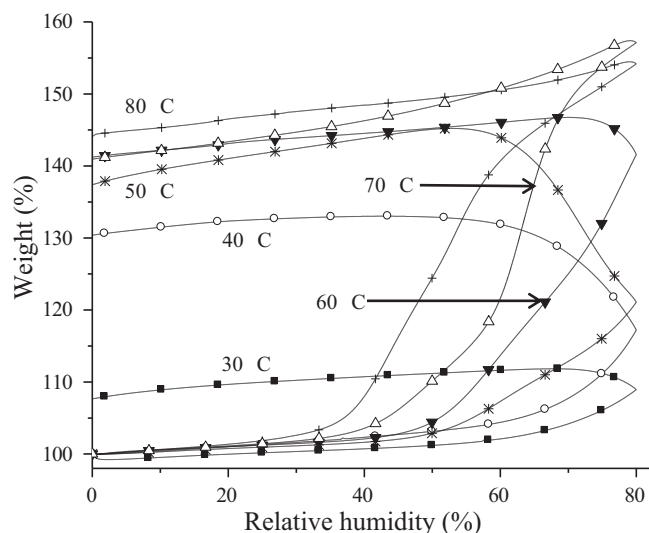**Fig. 2.** XRD pattern of the Ga-LDH sample after the thermal activation.

Fig. 3. Water sorption–desorption isotherms, at different temperatures, of the activated Ga-LDH sample.

Fig. 4. XRD pattern of the Ga-LDH rehydrated sample at 70 °C and 80% of RH.

temperatures. According to the IUPAC classification, the isotherms generated between 30 and 60 °C presented sorption curves type III, while the adsorption isotherms measured at 70 and 80 °C correspond to type V isotherms [29,30]. In vapor systems, this behavior is usually associated to condensation in pores. Additionally, it is evident that all isotherms presented hysteresis loops, and none of them closed. A similar behavior had been previously observed on different calcined Mg/Al LDH samples, although in that case all the isotherms were type III [28,31]. In those cases, the mass increments produced during the water sorption–desorption isotherms were attributed to the recovery of the lamellar structure, which implied the H_2O vapor chemisorption. Initially, there is a water adsorption process over the particle surface, and then these water molecules are chemisorbed, producing the LDH regeneration, where most of the interlayer anions must be $(OH)^{1-}$. Samples presented here have a similar general behavior. However, there are some aspects which must be pointed out. The final mass gained in these isotherms was equal to 40%, which is a lower value than that observed in the previous work. It can be simply explained in terms of the gallium mass, which is heavier than that of aluminum. Additionally, in the aluminum case [28] only the isotherm performed at 80 °C presented the type V behavior, but in this case, the type V behavior was observed since the 70 °C. These results suggest a higher water and $(OH)^{1-}$ affinity of the Ga-LDH sample, in comparison to the aluminum one.

Of course, all these results clearly indicate that not only water adsorption occurred, but a chemical process was present as well, due to the final mass increments. In fact, the mass gained may be attributed to the recovery of the lamellar structure, which implies the sample re-hydroxylation and re-hydration and the formation of $(OH)^{1-}$ as interlayer anions. Finally, it should be mentioned that the as-synthesized Ga-LDH sample was tested under the same conditions as those established for the activated sample. This sample presented sorption isothermal curves of type III (data not shown). Nevertheless, in these cases the quantities of water gained were minimal ($\sim$ 3%), and in these cases the hysteresis loops did close. Therefore, the pristine Ga-LDH only presented some superficial water adsorption, as it might be expected.

To prove the Ga-LDH regeneration some of the hydrated products, obtained during the isothermal experiments, were analyzed by XRD, FTIR and TGA. Fig. 4 shows the XRD pattern of the Ga-LDH sample regenerated at 70 °C. It is evident that this sample recovered the layered structure completely. Additionally, when the
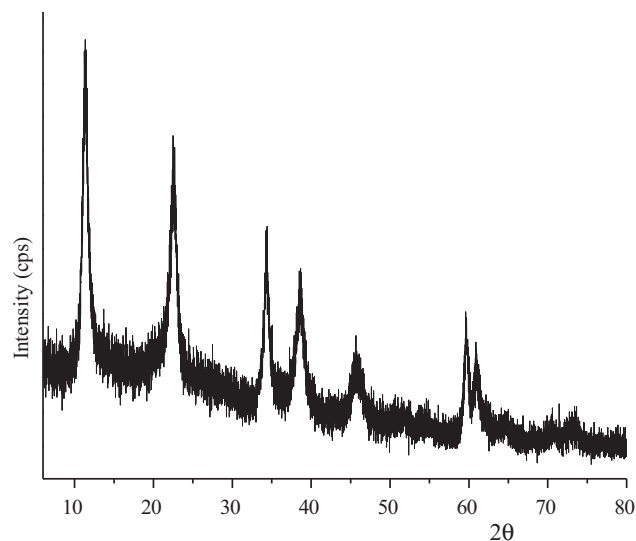
regenerated samples were analyzed by TGA–DTG, the XRD result was confirmed (Fig. 5). It is clear that the pristine and regenerated samples presented almost identical thermal behaviors. Initially, the first loss of mass (between 30 and 135 °C) which corresponds to superficial and interlayer water desorption. Then, the second loss of mass corresponds to the Ga-LDH dehydroxylation (220–480 °C) with the corresponding formation of the periclase structure. On the other hand, the activated sample presented a different behavior, as it could be expected. This sample only lost 6–7%, which may correspond to the loss of some superficial water, hydroxyls and carbonates.

To further analyze the water vapor adsorption–absorption mechanisms on Ga-LDH, different isothermal experiments (40, 50, 60 and 70 °C) were carried out at relative humidity equal to 50%, 60%, 70%, and 80% (Fig. 6). As it can be seen, qualitatively, water sorption processes (adsorption and absorption) are more dependent of temperature than RH. For example, setting up the relative humidity at 60% (Fig. 6B), the water sorption isotherms presented the following behavior: at 40 °C, the activated Ga-LDH only trapped 15.5%, but the sorption was importantly increased up to 49.2%, 52.7% and 48.6% at 50, 60, and 70 °C, respectively, in the same
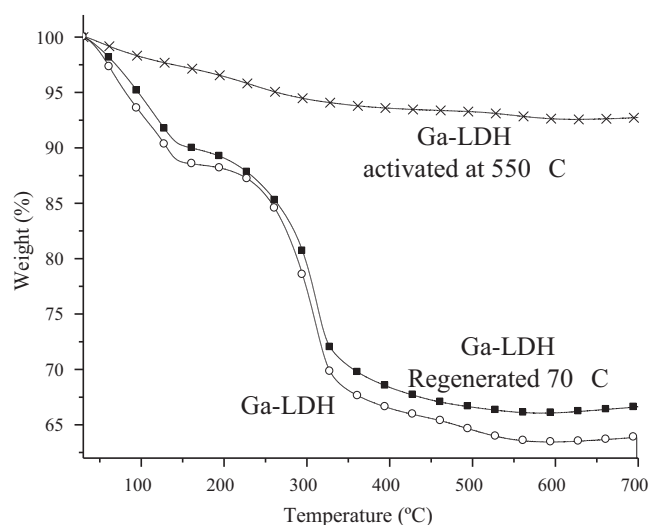

Fig. 5. Decomposition thermograms of the native, activated, and regenerated at 70 °C Ga-LDH samples after humidity treatment.
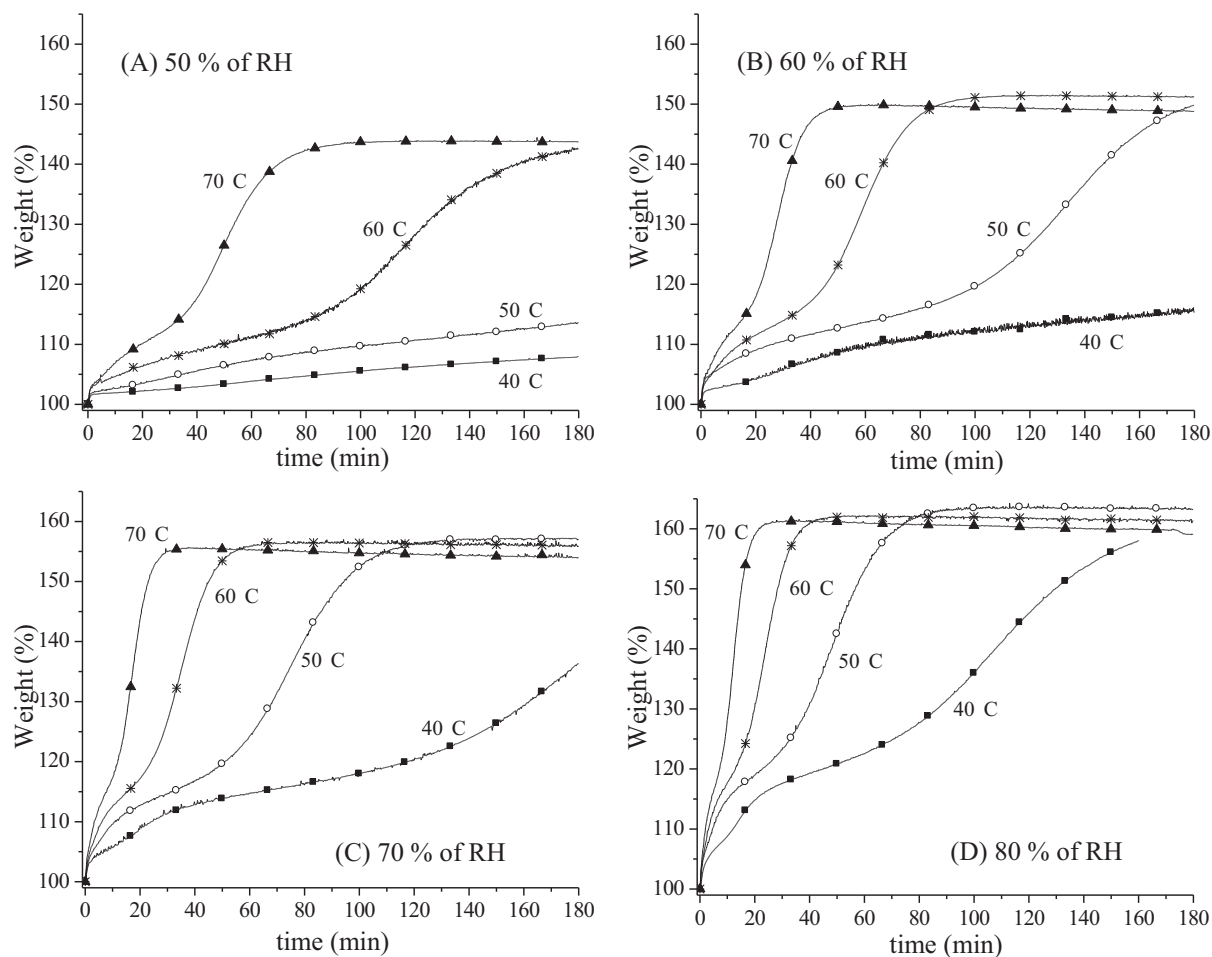
Fig. 6. Isotherms of water sorption on activated Ga-LDH at different temperatures (from 40 to 70 °C) and different relative humidity (from 50 to 80%).

period of time. Furthermore, it is evident that sorption curves are divided into two different steps, very well defined. Initially, the samples presented a mass increment of about 13%, where temperature modified the time in which this mass increment was reached. While sample treated at 50 °C finished the first process on around 1 h, the sample treated at 70 °C finished it in only 15 min. It must be mentioned that sample treated at 40 °C, apparently, only presented this initial process. This process would be associated to the water adsorption and the initial absorption over the particle surfaces. Once the first process was completed the second and most important process was developed. In this case, the second process must correspond to the Ga-LDH regeneration, layer reconstruction, which implies the structural hydroxylation, the incorporation of −OH ions as charge-balancing anions and the water adsorption. Finally, from these curves it should be mentioned that sample treated at 60 °C gained more mass than that treated at 70 °C. It must be simply the consequence of a higher H_2O evaporation rate at 70 °C.

In general, the behavior observed at a relative humidity of 60% (Fig. 6B) was similar than that observed at the other RH conditions. Perhaps the most significant difference among the curves is the final mass increment, which increased as a function of the RH. Of course, it can be attributed to higher water adsorption induced by the RH conditions.

Fig. 7 displays the FTIR spectra acquired for the Ga-LDH sample immediately after treatment under different relative humidities; also included are the spectra of native and activated samples, as a reference. The spectrum of native sample contains the absorption

bands between 3670 and 3450 cm^{-1} due to the O−H stretching, and at 1627 cm^{-1} is observed the band attributed to the bending deformation of molecular water, while the band attributed to asymmetric stretching C−O bonds in carbonate ions are observed at 1348 cm^{-1}. The bands at 1735 and 1260 cm^{-1} should be ascribed
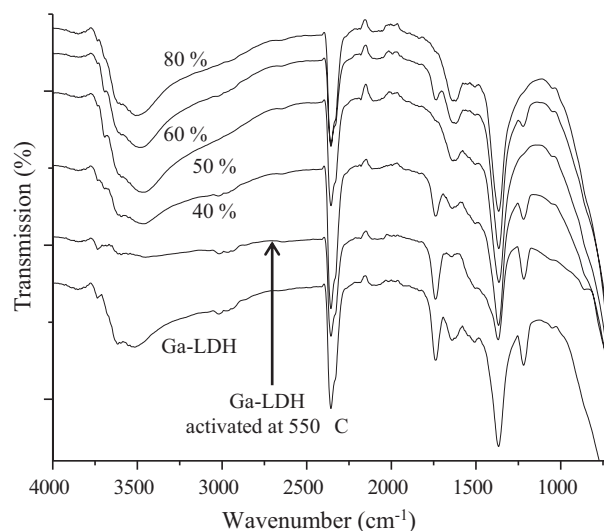

Fig. 7. FTIR spectra of native and activated Ga-LDH samples and then the activated sample rehydrated under different relative humidity.

to monodentate nitrate species coordinated to the LDH surface. These nitrate anions, commonly exhibit asymmetric and symmetric stretching vibrations at 1700–1500 cm^{-1} and 1390–1250 cm^{-1} regions, and they came from synthesis of LDH. The unusual asymmetric stretching found at 1735 cm^{-1} should be attributed to the hydrogen bonding often present between nitrate anions and water and hydroxyl groups of brucite-like layers [32]. Actually, the absorption bands correspond to nitrates with a C$_{2v}$ symmetry, indicating that most NO$_3^-$ anions are still intercalated in the native samples [33,34].

With thermal activation, the bands due to ν_{OH} and δ_{H_2O}, almost disappear but the bands due to carbonates and nitrates are still observed, revealing that even though the dehydroxylation has been completed, some nitrates remained adsorbed in surface. With rehydration, independently of the percentage of humidity, the intensity of bands ν_{OH} and δ_{H_2O} increases. No difference was observed in the position of the band due to carbonate in rehydrated and native samples, suggesting that carbonate ions interact similarly with the layers of these samples.

4. Conclusions

The Ga-LDH rehydration process was analyzed thermokinetically using different relative humidities and temperatures. The Ga-LDH sample regenerates through a similar reaction mechanism previously reported for an Al-LDH sample. Nevertheless, Ga-LDH sample presented a faster regeneration process than that observed on the Al sample. The Ga-LDH regeneration process depends on temperature and relative humidity. Therefore, these two factors may induce differences in the final microstructural properties of the LDH samples.

Acknowledgements

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