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Thermokinetic Study of the Rehydration Process of a Calcined MgAl-Layered Double Hydroxide

Heriberto Pfeiffer,[†] Enrique Lima,*[,†] Víctor Lara,[‡] and Jaime S. Valente[§]

[†]*Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito exterior s/n, Cd. Universitaria, Del. Coyoacán, CP 04510, México D.F., Mexico,* [‡]*Universidad Autónoma Metropolitana, Iztapalapa, Avenida San Rafael Atlixco No. 186, Col. Vicentina, CP 09340, México D.F., Mexico, and* [§]*Instituto Mexicano del Petróleo, Eje Central 152, CP 07730, México D.F., Mexico*

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The rehydration process of a calcined MgAl-layered double hydroxide (LDH) with a Mg/Al molar ratio of 3 was systematically analyzed at different temperatures and relative humidity. Qualitative and quantitative experiments were done. In the first set of samples, the temperature or the relative humidity was varied, fixing the second variable. Both adsorption and absorption phenomena were present; absorption process was associated to the LDH regeneration. Of course, in all cases the LDH regeneration was confirmed by other techniques such as TGA, solid state NMR, and SAXS. In the second set of experiments, a kinetic analysis was performed, the results allowed to obtain different activation enthalpies for the LDH regeneration as a function of the relative humidity. The activation enthalpies varied from 137.6 to 83.3 kJ/mol as a function of the relative humidity (50 and 80%, respectively). All these experiments showed that LDH regeneration is highly dependent on the temperature and relative humidity.

Introduction

Layered double hydroxides (LDHs), also known as Hydrotalcite-like compounds by reference to the naturally occurring hydrotalcite mineral, are a family of anionic clays that have received much attention in the past decades. Their structure is based on $M^{2+}(OH)_6$ octahedral units sharing edges to build $M(OH)_2$ brucite-like layers. A LDH is created by partial isomorphous substitution of M^{2+} cations for trivalent cations with similar ionic radius, rendering a positively charged layer. This charge is electrically compensated by anionic species located in the interlayer region, along with hydration water molecules. They are represented by the general formula: $[M^{2+}{}_{(1-x)}\, M^{3+}{}_{x}\, (OH)_2]^{x+}\, (A^{n-})_{x/n} \cdot mH_2O$, where the divalent and trivalent cations may be Mg^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Al^{3+}, Fe^{3+}, Ga^{3+}, Cr^{3+}, and so forth, A^{n-} may be nearly any organic or inorganic anion, and x is the trivalent cation substitution degree and takes values in the range $0.2 \leq x \leq 0.33$. Also, combinations of three or four cations have been reported. Therefore, a large number of materials with LDH structure and different physicochemical properties may be prepared.[1−3]

LDHs have found numerous applications in various fields, for instance, as antacids, PVC additives, flame retardants, and hybrid composites. Considerable research has been conducted with the aim of intercalating drugs, biological species, and organic compounds in order to use LDHs for controlled drug-delivery, as sensing devices, etc.[3] Also, because of their basic properties, they have attracted considerable attention in heterogeneous catalysis, particularly in the synthesis of fine chemicals.[4,5]

When an LDH is calcined, it progressively looses physisorbed water molecules, then interlamellar water molecules, and finally water corresponding to the dehydroxylation of the layers along with the charge-compensating anions, leading to the collapse of the layered structure. Temperatures at which these phenomena occur depend on the chemical composition of the original LDH; however, around 450−500 °C, a mixed oxide is formed.[1,2,6] In the case of calcined Mg−Al LDHs, which are perhaps the most widely studied of this family, X-ray diffraction reveals only an MgO phase with Al cations evenly distributed throughout the structure, creating a solid solution.[6] These Mg(Al)O mixed oxides have relatively high surface area (>200 $m^2\ g^{-1}$) and strong basic Lewis sites, O^{2-} atoms; hence, they have been successfully employed in many organic reactions catalyzed by bases.[7−9]

The oxides obtained from thermal decomposition of a LDH have the remarkable capacity of reconstituting the original layered structure upon adsorption of anions. This property is known as memory effect,[1,2] and it has been exploited for several applications of LDHs, such as adsorption of anionic contaminants from aqueous solutions[10,11] and SO_x removal.[12] Furthermore, if the calcined LDH is exposed to water or water vapor for a certain time, the layered structure is reconstructed, admitting OH^- groups as charge-compensating anions. This Mg−Al−OH LDH is commonly known as meixnerite or meixnerite-like. The hydroxyls act as Brönsted basic sites in catalytic reactions.[13−20]

*To whom correspondence should be addressed. Phone: + 52 (55) 5622-4640. Fax: +52(55) 5616 1371. E-mail: lima@iim.unam.mx.

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In this sense, a number of studies have been conducted to elucidate the mechanism by which LDHs are reconstructed. For instance, Hibino et al. studied the irreversibility of this process, which is caused by the gradual segregation of aluminum.[21] The coordinations of Mg and Al centers in as-synthesized, calcined, and reconstructed LDHs have been studied by X-ray absorption fine structure spectroscopy.[22] Kinetic data on the reconstruction of MgAl LDHs have been obtained by time-resolved energy dispersive X-ray diffraction.[23]

In base-catalyzed reactions, there exist three main parameters that determine the suitability of a catalyst for a given reaction. First, the nature of the basic site (Lewis or Brönsted) is of paramount importance. Also, fine-tuning the amount and strength of these sites is crucial for obtaining acceptable yields. In this sense, reconstructed Mg−Al−OH LDHs with Brönsted basic sites demonstrate higher catalytic activity than the corresponding Mg(Al)O mixed oxide in several reactions of industrial interest, such as aldol condensation,[13] cyanoethylation of alcohols,[14] and epoxidation of unsaturated ketones.[4] However, the most favorable amount and strength of the Brönsted basic sites must be determined experimentally for a given system, and this is usually done by varying the reconstruction time (time of exposure to water/moisture). It must be kept in mind that the sample with highest basic strength will not necessarily be the best catalyst for a particular reaction.[13,14,16−18]

Despite this, no systematic studies have been conducted on the rehydration mechanism of LDHs. Furthermore, the effect of the rehydration temperature has not been explored previously; reconstruction is always carried out at room temperature.[15] For these reasons, this study was devoted to determine the effect of relative humidity and temperature of rehydration on the water sorption by calcined Mg(Al)O mixed oxides.

Experimental Procedure

Synthesis. Mg−Al LDH with a Mg/Al molar ratio of 3 was prepared by coprecipitation at low supersaturation. An aqueous solution (1 M) was prepared by dissolving the appropriate amounts of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ in distilled water. Separately, a 2 M alkaline solution containing K_2CO_3 and KOH was prepared. Both solutions were added simultaneously to a glass reactor, maintaining the pH constant at 9.0. The precipitate was kept under vigorous stirring at 80 °C for 18 h. Then, it was washed repeatedly with hot deionized water and dried at 100 °C for 24 h. A portion of this sample was calcined at 550 °C for 4 h, prior to rehydration tests; this sample was labeled as activated LDH.

Materials obtained were characterized by X-ray diffraction (XRD), using a diffractometer Siemens D-5000 coupled to a copper anode X-ray tube. The presence of pure LDH was confirmed by fitting the diffraction pattern with the corresponding Joint Committee Powder Diffraction Standards (JCPDS).

Water Adsorption. Different dynamic water vapor sorption experiments were carried out on a temperature-controlled thermobalance TA Instruments model Q5000SA, equipped with a humid-controlled chamber. Then, the experimental variables used were temperature, time, and relative humidity (RH). The weight used in each experiment corresponds to 3 mg of 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 total flux used 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 30 and 80 °C, varying the relative humidity from 0 to 85 to 0%. Additionally, different adsorption curves were obtained maintaining the RH constant (20, 30, 40, 50, 60, 70, and 80%), but increasing the temperature from 25 to 70 °C. Finally, isothermal experiments were performed at different temperatures and RH.

Characterization. After the water sorption experiments and in order to identify the hydration products, the samples were characterized by standard thermogravimetric analyses (TGA), solid state nuclear magnetic resonance spectroscopy (NMR), and small-angle X-ray diffraction (SAXS). For the TG analyses, the experiments were performed under air atmosphere, with a heating rate of 3 °C/min in a thermobalance TA Instruments model Q500HR. ^{27}Al MAS NMR spectra were acquired with a 4 mm probe on an Avance II Bruker spectrometer at an operating frequency for ^{27}Al of 78.15 MHz. Small ^{27}Al flip angles of $\pi/12$, pulse delays of 0.5 s and a spinning speed of 10 kHz were used for the data collection. Chemical shifts are referenced to 1 M $AlCl_3$. Small angle X-ray scattering experiments were performed using a Kratky camera coupled to a copper anode X-ray tube whose Kα radiation was selected with a nickel filter. The SAXS intensity data, $I(h)$, were collected with a linear proportional counter. Then, they were processed with the ITP program.[24−27] where the angular parameter, h, is defined as $h = 4\pi \sin \theta/\lambda$; θ and λ are the scattering angle and the X-ray wavelength, respectively.

Results and Discussion

The sorption/desorption isotherms of water vapor on the native and activated LDH samples are shown in Figure 1. Initially, the activated LDH sample was analyzed at different temperatures. According with 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 corresponded to type V isotherms. These two kinds of isotherms are obtained in systems where the interactions between the adsorbate and the adsorbent are relatively weak and adsorbate−adsorbate interactions are considerable.[28,29] Additionally, it is evident that all isotherms presented hysteresis loops, and none of them closed. All the samples gained weight after the desorption processes. These results clearly indicate that not only water adsorption occurred, but a chemical process was present as well.

Different sorption behaviors were observed as a function of the temperature and relative humidity (RH) in sorption and desorption processes; during sorption stage, samples gained more weight as a function of the temperature, following the behavior described previously. This weight gained may be attributed to the recovery of the lamellar structure; water is first adsorbed over the particle surfaces and then it is absorbed. Later, the last process brings about the regeneration of the LDH lamellar structure. In fact, the global process, that is, the regeneration of hydrotalcite, can be

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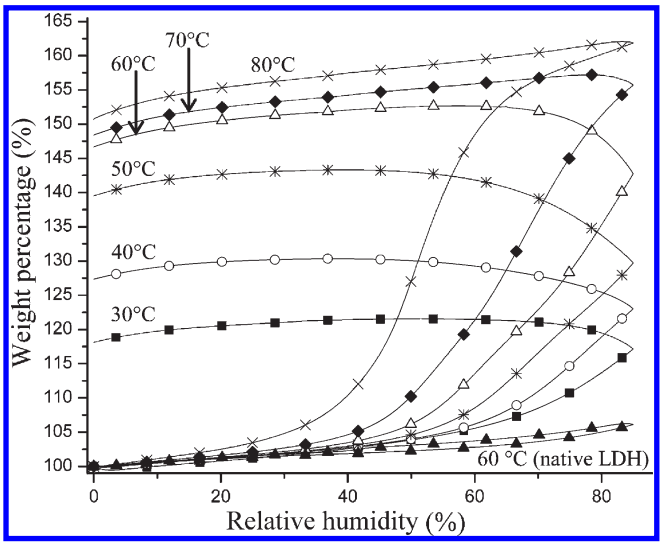

Figure 1. Water sorption−desorption isotherms of native and activated LDH at different temperatures.

deduced by desorption curves, where all the samples showed an increment of the final weight, as the hysteresis loops do not close. The final weight gained for each sample increased as a function of the temperature from 17.3 wt % at 30 °C up to 50 ± 2 wt % at the highest temperatures. In fact, if it were reasonably assumed that the LDH was totally converted into the periclase structure and later it was regenerated into a meixnerite phase, the weight gained or lost theoretically must be 47.2 wt %, which fits very well with these results (see reaction 1 in which the LDH formula corresponds to a Mg/Al molar ratio of 3 and the interlayer water is not considered). Of course, the small differences of weight can be attributed to interlayer occluded water. These results strongly support that a chemical reaction took place

$$Mg_{0.75}Al_{0.25}O_{1.125} + 1.125H_2O \leftrightarrow [Mg_{0.75}Al_{0.25}(OH)_2](OH)_{0.25} \quad (1)$$

Besides, it should be pointed out that desorption isotherms presented a continuous weight increment at the highest temperatures, which is an indicative that the sorption processes continued up to saturation at those conditions. Finally, it should be noticed that all desorption isotherms presented a small loss of weight. For example, while the sample treated at 30 °C only lost 3.5 wt %, the sample treated at 80 °C lost 12 wt %. This behavior can be simply explained as spontaneous evaporation of condensed water.

The as-synthesized LDH sample was tested under the same conditions as those established for the activated powders. Again, these samples presented sorption isothermal curves of type III. Nevertheless, in these cases the quantities of water gained were considerably smaller, and their hysteresis loops did close. Therefore, the pristine LDH only presented the adsorption water process and not the water absorption, as it could be expected. For comparison purposes, in Figure 1 it can be seen the sorption/desorption curve at 60 °C of the native LDH. From this figure, it should be pointed out that although the activated LDH sample presented the water adsorption process, both samples desorbed the same quantity of water, 6 wt %. This quantity of adsorbed water must correspond to the water adsorbed over the surface of the particles, hence both LDH samples, before and after the activation-regeneration processes, have similar external specific surface.

To further analyze the hydrated products obtained during the isothermal experiments, the regenerated samples were analyzed

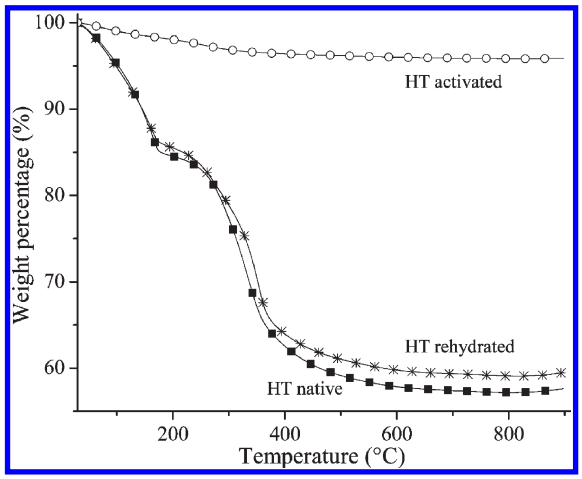

Figure 2. TGA curves of the pristine, activated, and regenerated at 60 °C LDH samples after humidity treatment.

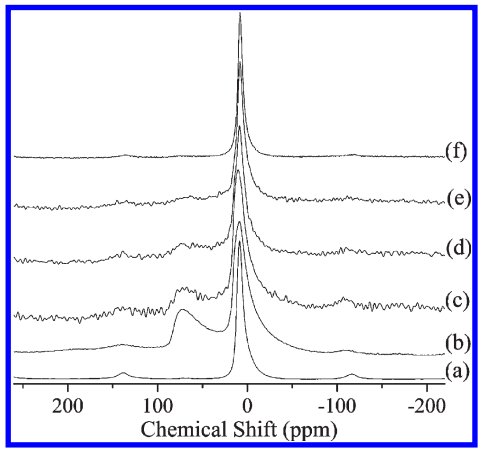

Figure 3. ^{27}Al MAS NMR spectra of native (a) and activated (b) LDH and sample activated and then rehydrated at 60 °C under variable relative humidity of 20 (c), 40 (d), 50 (e), and 70% (f).

by different techniques such as, TGA, NMR, and SAXS. Initially, some LDH samples were analyzed by TGA. Figure 2 shows the thermal behavior of the native, activated, and regenerated at 60 °C samples. It is clear that the pristine and regenerated samples presented very similar behaviors. Initially, the first loss of weight (between 30 and 150 °C) corresponds to superficial and interlayer water. Then, the second loss of weight corresponds to the LDH dehydroxylation (200−500 °C) with the corresponding formation of the periclase structure. In fact, the only evident difference was observed at the end of the thermogram, where the pristine sample lost 3% of weight more than the regenerated sample. On the other hand, the activated sample practically did not lose weight, as it could be expected, because all the water and hydroxyl ions were eliminated during the activation process performed at 550 °C.

^{27}Al MAS NMR spectra in Figure 3 show that the environment of aluminum is greatly affected as a consequence of the rehydration phenomena. Spectrum of activated sample and the rehydrated one under the lowest RH (20%) presents two well-defined isotropic NMR signals, the first one close to 8 ppm that is due to aluminum 6-fold coordinated and the second one at 71 ppm assigned to aluminum 4-fold coordinated.[30,31] With increasing of the relative humidity, tetrahedral aluminum species disappear

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Table 1. Line Width of NMR Signal of 6-Fold Coordinated Aluminum

sample	ΔH (Hz)
LDH rehydrated at 20% of RH	1234
LDH rehydrated at 40% of RH	980
LDH rehydrated at 50% of RH	696
LDH rehydrated at 70% of RH	565

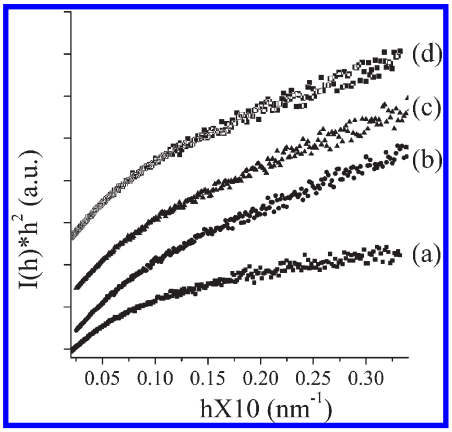

Figure 4. Kratky plots of rehydrated LDH samples at constant temperature (60 °C), varying the relative humidity, 20 (a), 40 (b), 50 (c), and 70% (d).

and they are no longer present in the sample rehydrated under the highest RH (70%). The spectrum of this completely rehydrated sample is very close that of the native sample. Besides, data in Table 1 indicates that the broadness of peak due to octahedral aluminum species is also a function of the RH: the higher the RH, the narrower the peak. These results support that the coordination sphere of aluminum is completed from 4-fold to 6-fold with water molecules. Rehydration under low relative humidity is, however, not enough to complete the coordination of the tetrahedral aluminum species and to compensate the gradients in electric field on octahedral aluminum species which indeed could be at the origin of the broadness of the NMR signals.

It is important to notice that, of course, an evolution in the texture of the surface as a consequence of the rehydration process is expected. In this context, SAXS results are relevant as they show that hydration occurs in a way such that the shape of the particles is maintained (Figure 4). Actually, independently of the RH, all the scattering profiles of samples display a region at moderate angles where the intensity is related to h^{-2}, and at higher scattering vector the scattering intensity tends to be proportional to h^{-1}. This behavior fits to bidimensional objects; that is, the scattered heterogeneities are platelets-like. Samples, however, can be differentiated through the fractal dimension value, as determined by the SAXS data and under the Porod law.[32,33] Table 2 shows that fractal dimension decreases as the RH increases. Fractal dimension should be understood here as a parameter that measures the irregularities at the surface of the material. Irregularities have two contributions, the first one due to the distribution of functional groups and the second one arising from networking effects which in turn are produced by interconnection of pores with different sizes and shapes. In our case, it seems that the surface functional groups are determinant for the roughness of the surface. Indeed, the sample hydrated under the lowest RH has

Table 2. Fractal Dimension Value As Determined from SAXS Data

sample	fractal dimension[a]
LDH rehydrated at 20% of RH	2.31
LDH rehydrated at 40% of RH	2.09
LDH rehydrated at 50% of RH	2.10
LDH rehydrated at 70% of RH	2.28

[a] Error associated to these values is 5%.

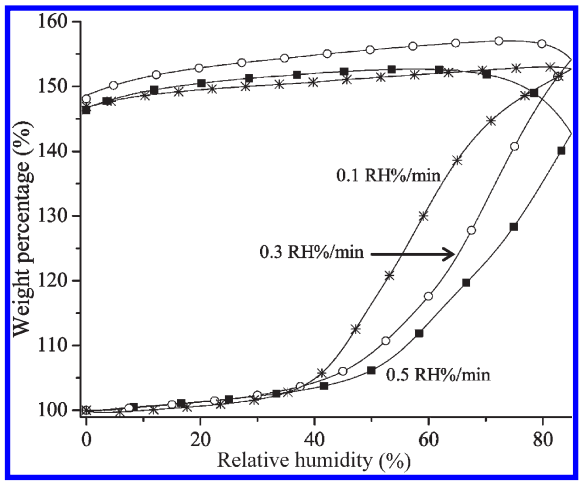

Figure 5. Sorption/desorption isotherms of the activated LDH. These experiments were performed at 60 °C using different rates of relative humidity increment (0.1, 0.3, and 0.5 RH %/min).

the highest fractal dimension that could be due to the high density of tetrahedral species at the surface. With rehydration under moderated RH, a relatively stable and roughened surface with unsaturated coordinated aluminum is obtained, and under high RH denser particles are formed with a lower surface/volume ratio.[34,35] These results are relevant as they support that rehydration can be used to manipulate the surface of LDHs. Often, catalytic sites appear as defects at surface.

Once the different processes between the activated LDH and water vapor were identified and characterized, three different kinds of experiments were performed. (1) The relative humidity increment was performed at different rates; (2) the RH was fixed and the temperature was increased continuously; and (3) different isothermal experiments were performed. All these experiments were performed in order to obtain information about the LDH regeneration mechanism and kinetics.

Figure 5 shows the sorption/desorption isotherms of the activated LDH at 60 °C, but using different rates on the relative humidity increment (0.1, 0.3, and 0.5 RH%/min). It is clearly evident that diminishing the rate increment of relative humidity produces changes in the obtained isothermal from type III to type V. While at 0.5 RH%/min only adsorbate−adsorbent interactions were observed, when the rate was decreased adsorbate−adsorbate interactions were detected as well, in other words the formation of water multilayers was evidenced. However, all the samples regenerated, and therefore absorbed the same quantity of water, 47−48 wt %. Additionally, this figure establishes that LDH dehydration is a process kinetically controlled.

A different set of samples was analyzed fixing the relative humidity and varying the temperature. In this case, the relative humidity was fixed (20, 30, 40, 50, 60, 70, and 80% RH) and

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temperature was varied from 25 to 70 at 0.5 °C/min (Figure 6). In these curves, two different processes could be evidenced. At the very beginning of the experiments, all the samples increased their weight exponentially. This effect could be attributed to the water adsorption. As it could be expected, the quantity of water adsorbed increased as a function of the RH. While the samples with a relative humidity of 20 and 30% only adsorbed 0.3 wt %, the samples with 70 and 80% RH adsorbed between 4 and 5 wt %.

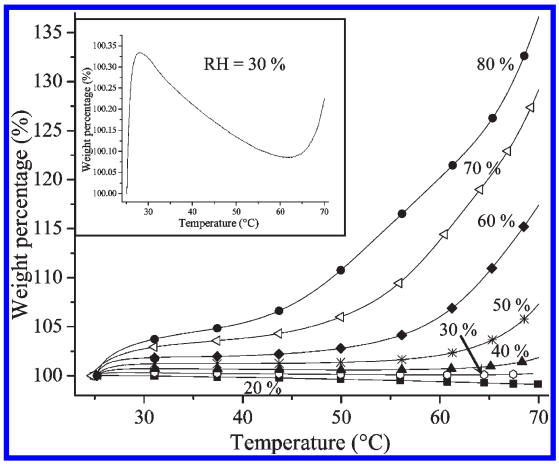

Figure 6. Activation temperatures of adsorption and absorption processes on the activated LDH, using different relative humidity (20, 30, 40, 50, 60, 70, and 80%).

Later, most of the samples evidenced a second process as a function of the temperature. The second weight increment must be associated to water absorption, in other words to the LDH regeneration. Again, the quantity of water absorbed increased as a function of the relative humidity established for each experiment. In these cases, the absorption process was activated at lower temperatures when the relative humidity was increased. For example the activation temperature varied from 63 to 50 to 41 °C at 30, 60, and 80% of relative humidity, respectively. Something else has to be pointed out; the experimental curves at lowest RH (20, 30, and 40% of relative humidity) depicted a different trend. In these cases, after the initial weight increment associated to the water adsorption, the samples clearly showed a decrement of weight, which ranged between 29 and 62 °C (Inset of Figure 6). This process has to be associated to water desorption. In other words, after the sudden water adsorption observed at the very beginning of the experiments, an adsorption−desorption equilibrium is established, where desorption process is favored with temperature. This desorption process is finally stopped when water adsorption is activated, beginning then the LDH regeneration. This final absorption process produces again an increment of weight.

To further understand the water vapor adsorption-absorption mechanisms on LDH, different isothermal experiments (30, 50, 60, 70, and 80 °C) were carried out at relative humidity equal to 50, 60, 70, and 80% (Figure 7). As it could be expected, qualitatively, water sorption processes (adsorption and absorption) increased as a function of temperature and relative humidity.

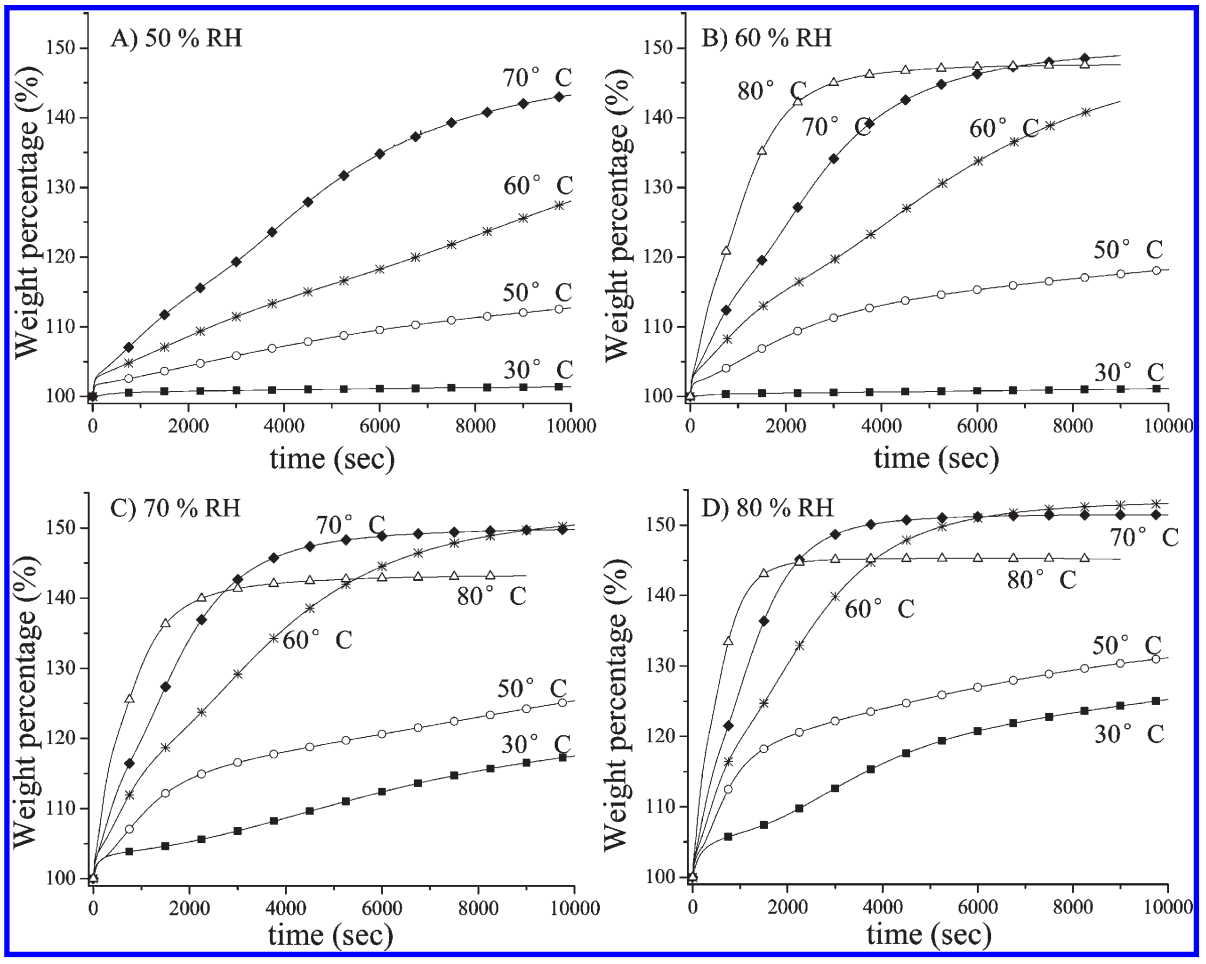

Figure 7. Isotherms of water sorption/desorption on activated LDH at different temperatures (from 30 to 80 °C) and different relative humidity (from 50 to 80%).

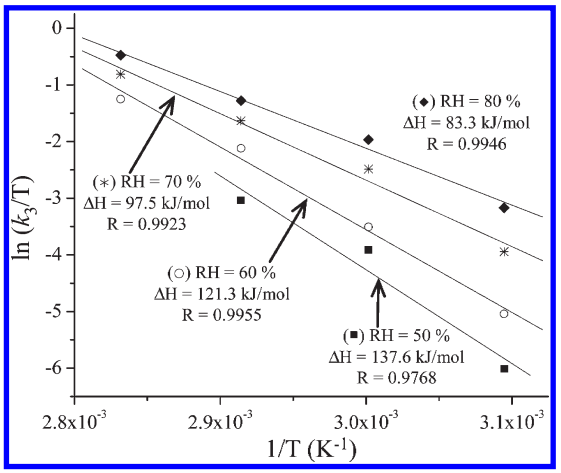

Figure 8. Eyring's plots for the rate constants of water absorption (k_3) at different relative humidity.

Setting up the relative humidity at 50%, the water sorption isotherms presented the following behavior. Although the activated LDH practically did not adsorb and/or absorb water at 30 °C (1.4 wt %), the sorption was importantly increased up to 12.7, 28.1, and 43.2 wt % at 50, 60, and 70 °C, respectively, in the same period of time (Figure 7A). In these graphs, it is evident that in the first seconds all the samples presented an increment of weight of about 1−3 wt %. This process must be associated to the initial water adsorption over the particle surfaces. Then, at longer times, isotherms presented exponential behaviors, which should be a combination effect of different processes such as water adsorption and LDH regeneration. In fact, the LDH regeneration implies two different processes, the formation and incorporation of −OH to the LDH structure and the formation and incorporation of −OH ions as charge-balancing anions. Of course, as the absorption process progresses, the quantity of water adsorbed must increase as well, because it should be water molecules adsorbed in the new LDH interlayer spaces regenerated.

In general, the behavior observed at a relative humidity of 60% (Figure 7B) was similar than that observed previously. While the activated LDH, heat-treated at 30 °C, only trapped 1.2 wt %, the total water adsorbed/absorbed increased as a function of temperature up to 47.6 wt % at 80 °C. In the first half-hour, it is evident that sorption process increased as a function of the temperature. Nevertheless, at long times the sample heat-treated at 70 °C trapped more water than the sample treated at 80 °C. In addition, although the sample heat-treated at 80 °C reached the plateau, the sample treated at 70 °C did not. In other words, sample treated at 70 °C has not finished the adsorption−absorption processes. It seems that at 80 °C the water adsorption must be limited through water evaporation. Then, the final quantity of water adsorbed decreases as a function of the temperature. The same behaviors, but more drastic, were observed at 70 and 80% of relative humidity (Figure 7C,D). In these two cases, the adsorption−absorption processes increased as a function of temperature during the first period of time, as the previous case. However, at long times, the samples heat-treated at 80 °C trapped less water than those at 70 °C, and subsequently they trapped even less water than the samples treated at 60 °C. These results confirm that temperature plays a very important role on the absorption and adsorption processes, limiting the adsorption at high temperatures.

All these isotherms were fitted to the following exponential model (eq 2), which is divided in two parts. The first part of the equation corresponds to the water adsorption−desorption processes, which had been already determined qualitatively. The second part of this equation corresponds to the LDH regeneration, in other words to water absorption

$$y = (k_1/(k_1 - k_2))\exp^{(-k_1 x)} + A\exp^{(-k_3 x)} + B \qquad (2)$$

where y represents the weight percentage of the total water trapped, x is the time, k_1, k_2, and k_3 are the water adsorption, desorption, and absorption exponential constants respectively, and A and B are the pre-exponential factors. k_1 and k_2 values did not seem to show any kind of tendency, although k_3 showed progressively an increment as a function of temperature and relative humidity. Therefore, if these data follow linear trends, as a function of temperature, then the gradients of these best fit lines should fit the Eyring's model, as it can be used on solid−gas reaction system. These results are illustrated in Figure 8. It is clear that plots of $\ln(k/T)$ versus $1/T$ describe linear trends, fitting Eyring's model. Therefore, the activation enthalpies (ΔH) for the water absorption process on an activated LDH could be determined as a function of the relative humidity. The ΔH values obtained were 137.6, 121.3, 97.5, and 83.3 kJ/mol, varying the relative humidity from 50 to 80%. These results clearly show that the absorption process is more dependent on temperature when the relative humidity is lower, as it could be expected.

In other words, when the relative humid is increased, the absorption process occurs at lower temperatures.

Conclusions

Rehydration of a calcined Mg−Al layered double hydroxide occurs through both water adsorption and absorption processes. Two phenomena are determinants to manipulate the physicochemical properties at surface of material. Relative humidity and temperature are variables that can be used adequately to produce rehydrated LDHs with different grade of roughness and different amount of tetrahedral aluminum species. The activation enthalpies (ΔH) for the water absorption process on an activated LDH were determined for different relative humidity. The absorption process is more dependent on temperature when the relative humidity is lower.

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