Influence of Mg/Al Ratio on the Thermokinetic Rehydration of Calcined Mg−Al Layered Double Hydroxides

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The rehydration process of calcined MgAl-layered double hydroxides (LDHs), with different Mg/Al molar ratios (2.0, 2.5, 3.0, 3.5, and 4.0), was analyzed at different temperatures and relative humidities. Kinetic results clearly showed that LDHs with Mg/Al molar ratios of 2.5 and 3.0 have the fastest H_2O absorption. This behavior was attributed to the cations' structural ordering and to thermodynamic factors. In addition, results allowed obtaining the activation enthalpies for the LDH regeneration of the different samples as a function of the relative humidity. The different activation enthalpies, for each LDH and independently of the Mg/Al molar ratio, showed that the H_2O absorption process is more dependent on temperature if the relative humidity is low. Finally, when we analyzed the activation enthalpies as a function of the Mg/Al molar ratio at a defined temperature, their values did not behave linearly. The water absorption process proved to be more dependent on temperature for the LDHs with molar ratios equal to 2.5 and 3.0.

Introduction

Layered double hydroxides (LDHs) represent a class of ionic lamellar materials with positively charged layers and exchangeable hydrated gallery anions.[1] LDHs contain a combination of at least one divalent (Mg^{2+}, Zn^{2+}, Co^{2+}, etc.) and one trivalent (Al^{3+}, Ga^{3+}, Fe^{3+}, etc.) cation. These cations are 6-fold-coordinated in an oxygen (hydroxyl) environment, sharing edges to form brucite-like layers. LDHs can be chemically expressed by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{II} represents a divalent metal cation; M^{III}, a trivalent metal cation; and A^{n-}, an anion (inorganic or organic).[2−4] LDHs are usually prepared by coprecipitation,[5] but several alternate methods have been reported, such as urea hydrolysis,[6] sol−gel,[7,8] and an environmentally friendly method for large-scale production.[9]

The layered structure of LDHs collapses when they are heated at temperatures between 250 and 650 °C due to dehydration, dehydroxylation, and loss of interlayer anions. The obtained mixed oxides are usually solid solutions with a periclase-like structure, which are able to recover the layered structure if in contact with an anion in aqueous solution or in a moist environment.[10−12] The recrystallization of LDHs from periclase-like mixed oxides is referred to in the literature as "memory effect", and it can be exploited to tune the physicochemical properties of LDHs, which in turn determine their potential applications as adsorbents or catalysts.[13−16]

In Meixnerite-like compounds (Mg−Al−OH LDH), which are usually obtained by calcination of Mg−Al LDH and subsequent reconstruction with water or water vapor in an inert atmosphere, hydroxyl anions play the role of Brönsted basic centers. These are claimed to be the active sites in many base-catalyzed reactions. Actually, in basic catalysts, the nature, strength, and number of sites are parameters that determine their catalytic efficiency.[17,18] For instance, an increase in catalytic activity is reported in reactions such as aldol condensation, cyanoethylation of alcohols, and epoxidation of unsaturated ketones when Mg−Al−OH LDHs (hydrated catalyst) are used instead of the corresponding Mg(Al)O mixed oxide.[19,20] Rehydration of the mixed oxide, however, implies evolution of basicity regarding not only the basic sites' nature, but also their amount and strength.[21] The structural modifications that occur during calcination and reconstruction, such as changes in Al coordination, particle size and crystallinity, have also been the object of several studies.[10,22]

Recently, it was reported that the conditions (relative humidity and temperature) of rehydration are crucial parameters driving the kinetics of the reconstruction by memory effect of a Mg(Al)O mixed oxide with a Mg/Al ratio close to 3.[23] When the Mg/Al molar ratio is varied in the interval 2−4, several structural changes take place, which must affect their reconstruction behavior. First, the charge of layers is controlled by the degree of isomorphous substitution of Mg^{2+} by Al^{3+} cations; in addition, the charge density distribution is controlled by the distribution of Al^{3+} ions in the octahedral sheets.[24,25] Thus, the Mg/Al ratio of mixed oxides Mg(Al)O can be appropriately manipulated in combination with hydration conditions to modulate the surface properties of Mg−Al−OH LDHs. This work was then started with the goal of studying the effect of the Mg/Al ratio of mixed oxides on their rehydration process under controlled conditions of humidity and temperature.

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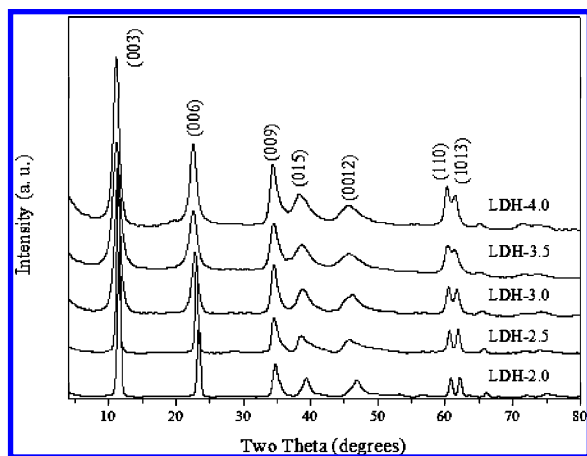⊥ Instituto Mexicano del Petróleo.

Figure 1. XRD patterns of LDH samples prepared with different Mg−Al molar ratios.

TABLE 1: Chemical Composition of LDH Samples

sample	chemical formula	Mg/Al ratio
LDH-2.0	$[Mg_{0.675}Al_{0.324}(OH)_2](CO_3)_{0.162} \cdot 0.77H_2O$	2.08
LDH-2.5	$[Mg_{0.733}Al_{0.267}(OH)_2](CO_3)_{0.133} \cdot 0.69H_2O$	2.75
LDH-3.0	$[Mg_{0.745}Al_{0.255}(OH)_2](CO_3)_{0.127} \cdot 0.85H_2O$	2.93
LDH-3.5	$[Mg_{0.773}Al_{0.227}(OH)_2](CO_3)_{0.114} \cdot 0.89H_2O$	3.40
LDH-4.0	$[Mg_{0.790}Al_{0.210}(OH)_2](CO_3)_{0.105} \cdot 0.95H_2O$	3.78

by sharp and intense lines at low 2θ angles that correspond to basal (001) reflections. Apparently, upon increasing the Mg/Al ratio, there is a tiny decrease in crystallinity, as observed by the increasingly wider peaks, and the overlap of the 110 and 1013 reflections in the LDH-3.5 and LDH-4.0 samples. In addition, once the LDH structure was confirmed in all the samples, their chemical composition was obtained (Table 1). As can be seen, the Mg/Al molar ratios are close to the nominal values, within experimental error.

On the basis of a previous report,[23] which presented a thermokinetic analysis of the LDH regeneration on a sample with a Mg/Al molar ratio of 3.0, similar isothermal experiments were performed for the LDH calcined samples, but varying the Mg/Al molar ratios to 2.0, 2.5, 3.5, and 4.0. Figure 2 displays ^{27}Al MAS NMR spectra of activated sorbents prior to water sorption. It is clear that mixed oxides, produced by thermal activation, contain aluminum 6-fold coordinated (signal close to 8 ppm) and also 4-fold coordinated (signal in the range 65−73 ppm). Note that signal due to tetrahedral aluminum is shifted to stronger fields as the Mg/Al ratio increases, suggesting that the chemical environment of unsaturated aluminum species is significantly different due to the composition of samples. Because the first aluminum neighbors should be oxygen ions, it seems that the second neighboring (aluminum or magnesium ions) are determinant to fix the chemical environment of tetrahedral aluminum. Actually, these tetrahedral aluminum species are claimed to be present at the surface of the material;[26] that is, the surface of activated LDH-4.0 has more unsaturated coordinated aluminum if compared with other samples.

Isothermal water sorption of activated samples are presented on Figures 3, 4, 5 and 6, which correspond to the isothermal experiments at different temperatures and RH of the samples with Mg/Al molar ratios of 2.0, 2.5, 3.5 and 4.0, respectively.

As could be expected, qualitatively, the water sorption processes (adsorption and absorption) seem to increase as a
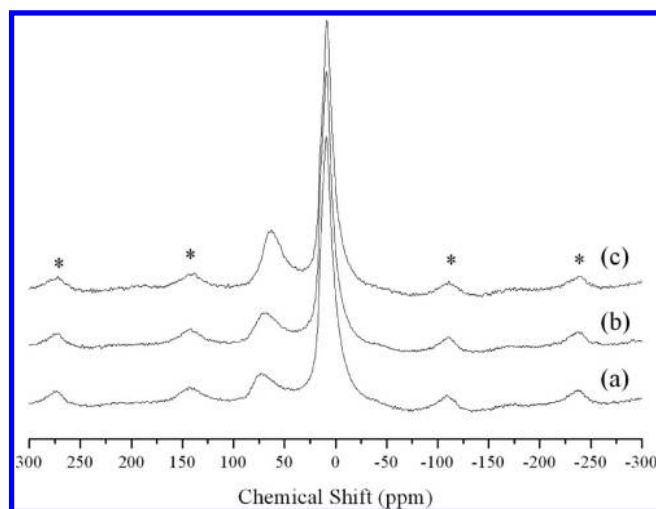
Experimental Procedure

Synthesis. Mg−Al LDH samples with nominal Mg/Al molar ratios of 2, 2.5, 3.0, 3.5, and 4 were prepared by coprecipitation at low supersaturation. Initially, 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 simultaneously added 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 washed repeatedly with hot deionized water and dried at 100 °C for 24 h. Samples were labeled as LDH-*X*, where *X* corresponds to the Mg/Al molar ratio. For example, LDH-2.5 corresponds to the thermally activated LDH, or mixed oxide, with a Mg/Al molar ratio of 2.5. Dried products were characterized by X-ray diffraction (XRD) using a diffractometer Siemens D-5000 coupled to a copper anode X-ray tube. The chemical composition of solids was determined in a Perkin-Elmer model Optima 3200 Dual Vision by inductively coupled plasma atomic emission spectrometry.

Water Sorption. Different dynamic water vapor sorption experiments were carried out on a temperature-controlled thermobalance TA Instruments model Q5000SA equipped with a humidity-controlled chamber containing distilled water. Portions of the LDH samples were calcined at 550 °C for 4 h prior to rehydration tests. The weight used in each experiment corresponds to ∼3 mg of the LDH samples, and all the experiments were performed using N_2 (Praxair, grade 4.8) as flow gas. The N_2 total flow used was 100 mL min^{-1}, and the relative humidity (RH) percentages were controlled automatically with the Q5000SA equipment. Different isothermal sorption curves were obtained maintaining the RH constant (50, 60, 70, and 80%) at the following temperatures: 30, 50, 60, 70, and 80 °C.

Characterization. Activated samples, as well as some products after the water sorption experiments, were characterized by solid state nuclear magnetic resonance spectroscopy (NMR). ^{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$_3$.

Results and Discussion

Figure 1 presents the X-ray diffraction patterns of the dried samples, all of which present pure LDH phase, characterized

Figure 2. ^{27}Al MAS NMR spectra of activated LDHs at 550 °C: (a) LDH-2.5, (b) LDH-3.5, and (c) LDH-4.0. An asterisk (*) indicates spinning side bands (10 kHz).
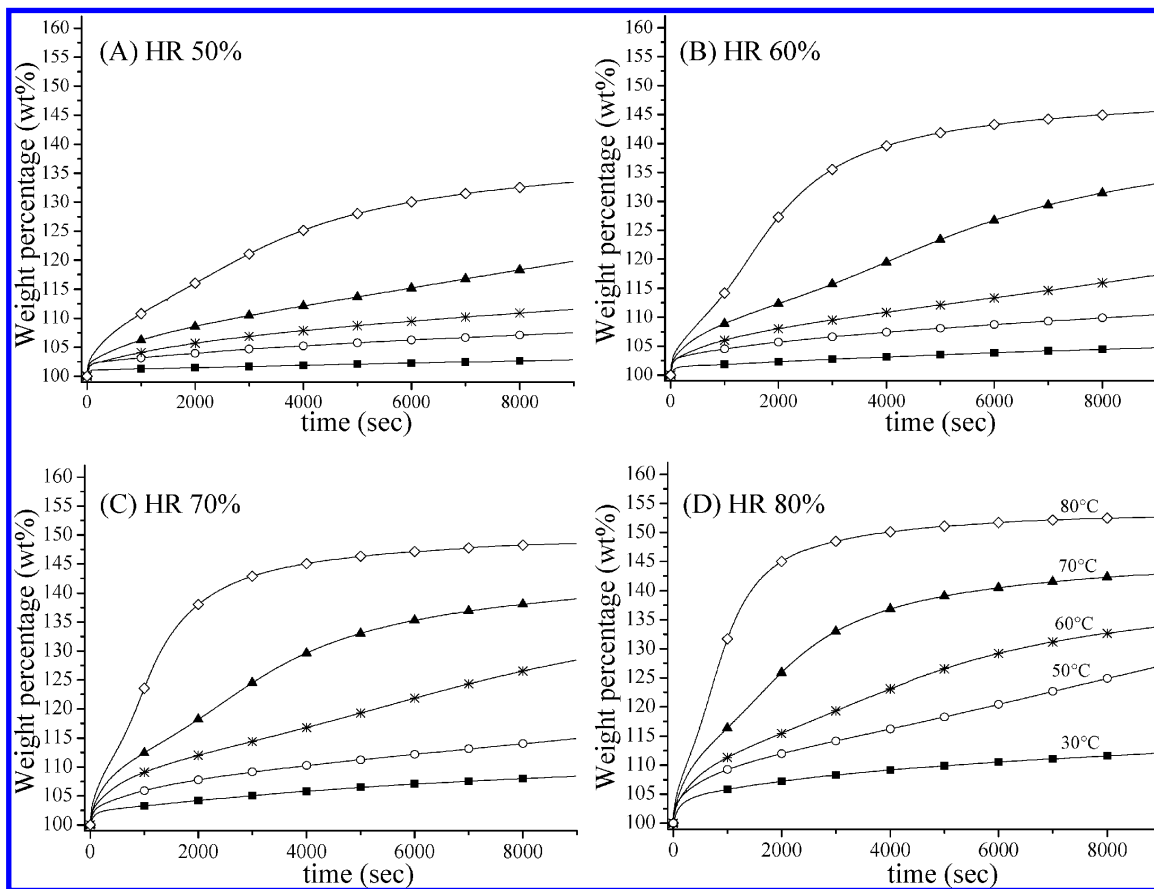
Figure 3. Isotherms of water sorption/desorption on the LDH-2.0 sample varying the temperature (from 30 to 80 °C) and relative humidity (from 50 to 80%).
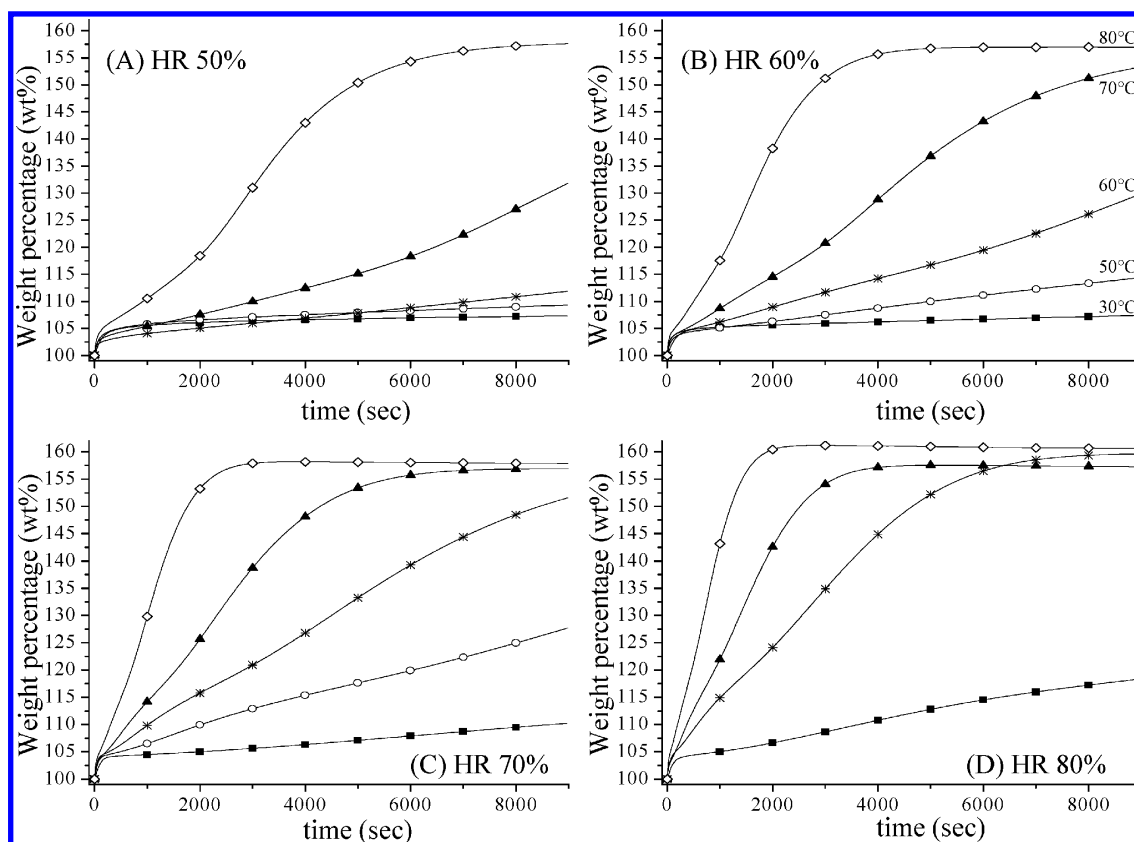

Figure 4. Isotherms of water sorption/desorption on the LDH-2.5 sample varying temperature (from 30 to 80 °C) and relative humidity (from 50 to 80%).
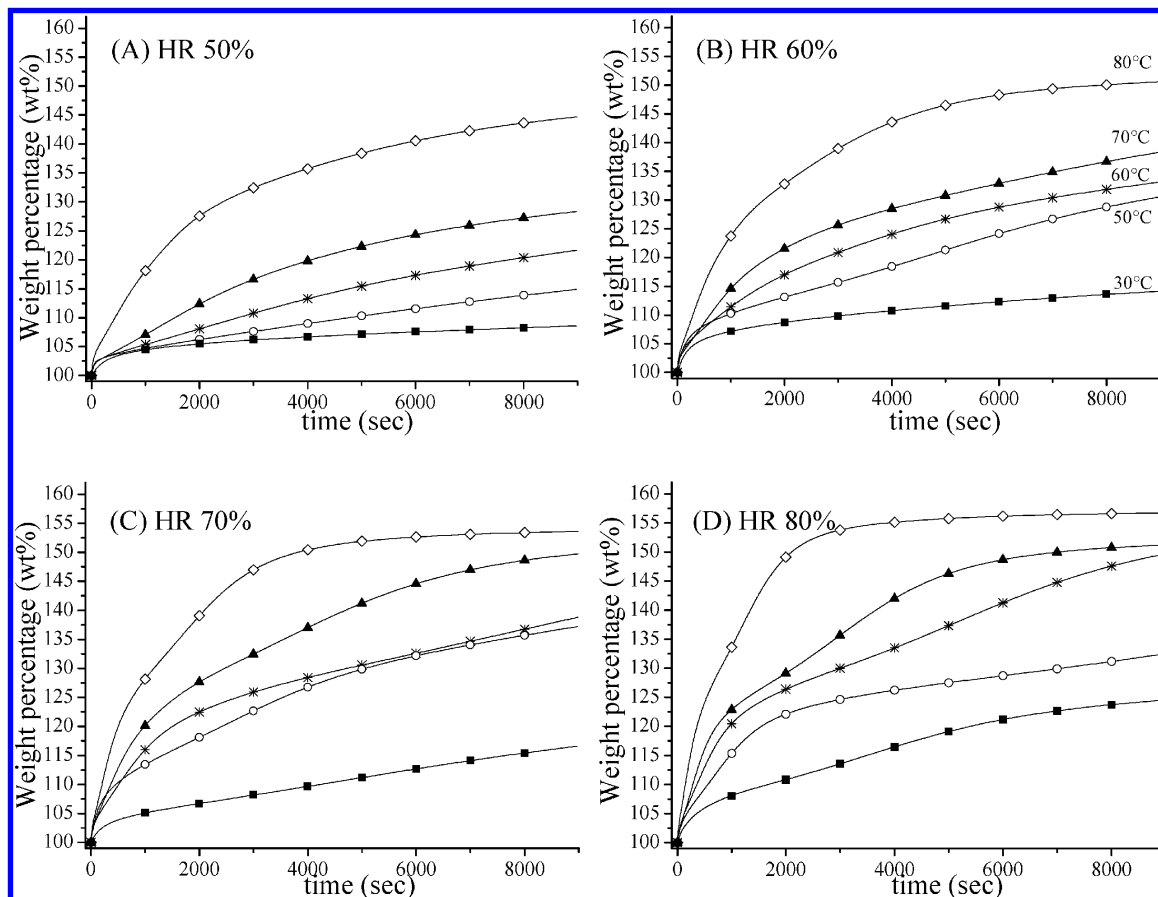
Figure 5. Isotherms of water sorption/desorption on the LDH-3.5 sample varying temperature (from 30 to 80 °C) and relative humidity (from 50 to 80%).

function of temperature and relative humidity in all the samples. For example, on the LDH sample with a Mg/Al molar ratio of 2.0, when the relative humidity was fixed at 50%, the water sorption isotherms presented the following behavior. Although the activated LDH practically did not adsorb or absorb water at 30 °C (2.8 wt %), the sorption was importantly increased up to 7.5, 11.5, 19.6, and 33.3 wt % at 50, 60, 70, and 80 °C, respectively, in the same period of time (Figure 3A). In this sample, if the RH was increased, the total water trapped increased, as well. For example, at 80 °C, the final weight increased as follows: 33.3, 45.2, 48.8, and 52.5 wt % at 50, 60, 70, and 80% of RH, respectively (Figures 3A, B, C, and D, respectively). Furthermore, in all these graphs, it is evident that in the first seconds, all the samples presented an increase of weight of ~1−5 wt %. This process must be associated with the initial water adsorption over the activated LDH particle surfaces. Then, at longer times, isotherms presented exponential behaviors, which should be a combination effect of different processes, such as water adsorption and absorption, where the water absorption corresponds to the LDH regeneration. LDH regeneration implies the formation of two different kinds of −OH radicals: the first ones are incorporated on the LDH layer structure and the second ones are incorporated as charge-balancing anions. Finally, once the water absorption is produced, some other water molecules must be adsorbed in the regenerated LDH interlayer spaces and over the particle surfaces. Actually, recovering of the layered structure with rehydration is supported by ^{27}Al NMR spectra, Figure 7. Although the signal/noise is low because of the low amount of sample characterized (3 mg), it is clear that aluminum is only 6-fold coordinated, as in a hydrotalcite-like structure fully hydrated.

In general, the behavior observed on the other LDH samples with Mg/Al molar ratios of 2.5, 3.5, and 4.0 (Figures 4, 5 and 6) were similar to those observed previously, but with the following differences. The LDH sample with a molar ratio of 2.5 (Figure 4) presented the same exponential behavior as that observed in the previous sample. However, the LDH-2.5 trapped more water under all the experimental conditions, in comparison to the LDH-2.0 sample. In addition, whereas in the LDH-2 sample, none of the isotherms reached the *plateau*, in the LDH-2.5, at least, all isotherms performed at 80 °C reached it. Finally, on this sample, the isotherm performed at 60 °C with 80% of RH captured more water than the isotherm performed at 70 °C with the same RH (Figure 4D), and it has not finished the sorption processes. Hence, these results suggest that although water absorption is enhanced as a function of the temperature, water adsorption (which is limited through water evaporation) is not favored at high temperatures, or in other words, it must be favored at low temperatures. These results are totally in agreement with the previously published results for the LDH sample with a Mg/Al molar ratio of 3.0 (here labeled as LDH-3.0),[23] in which a similar but more drastic behavior was observed. If the LDH-2.0 and LDH-2.5 are compared with the LDH-3.0 already published, something else has to be pointed out. In the first two samples, the maximum adsorbed water during the first moments of the reaction (roughly 1000 s) was around 5 wt %, but for the LDH-3.0, the maximum adsorbed water decreased to 3.0 wt %. This can be explained because an increase in the Mg/Al ratio implies a decrease in the anion exchange capacity of LDH. In addition, aluminum is incorporated into brucite-like layers, generating surfaces with a
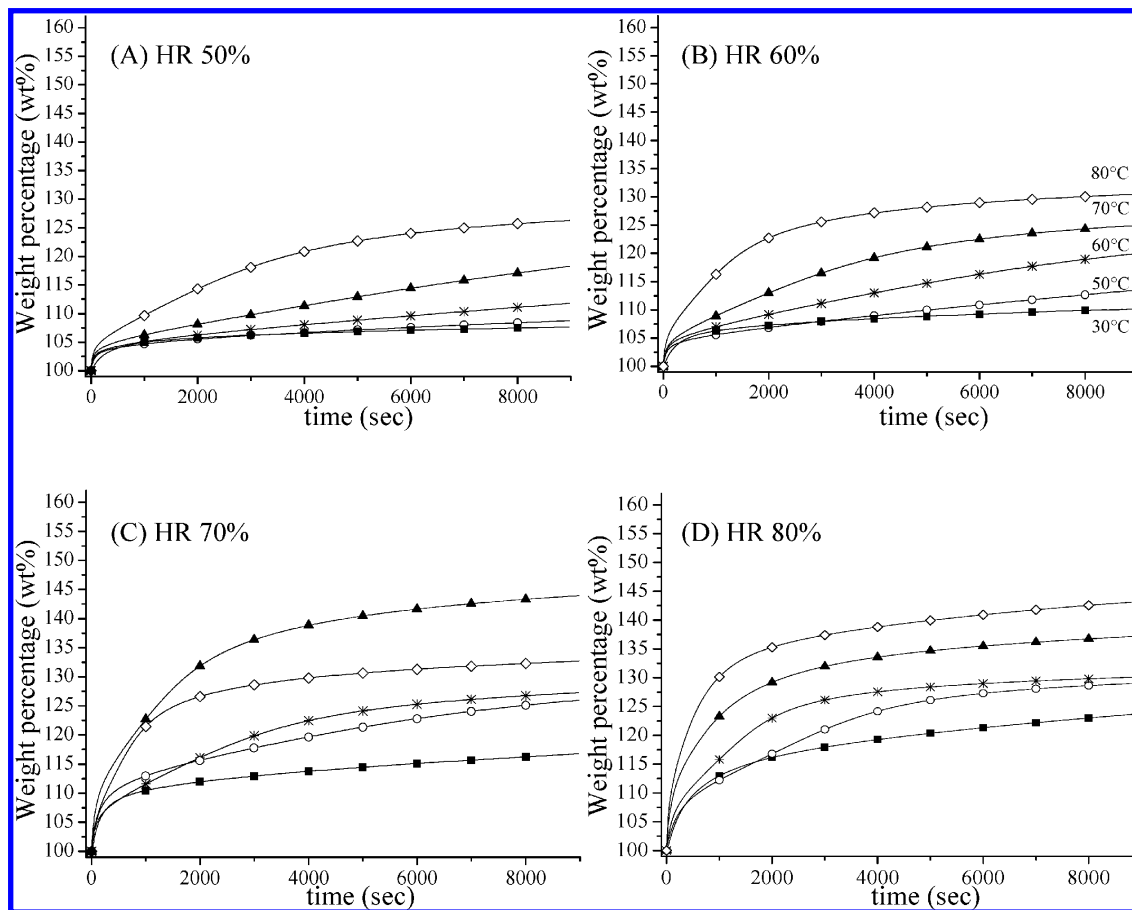
Influence of Mg/Al Ratio

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Figure 6. Isotherms of water sorption/desorption on the LDH-4.0 sample varying temperature (from 30 to 80 °C) and relative humidity (from 50 to 80%).
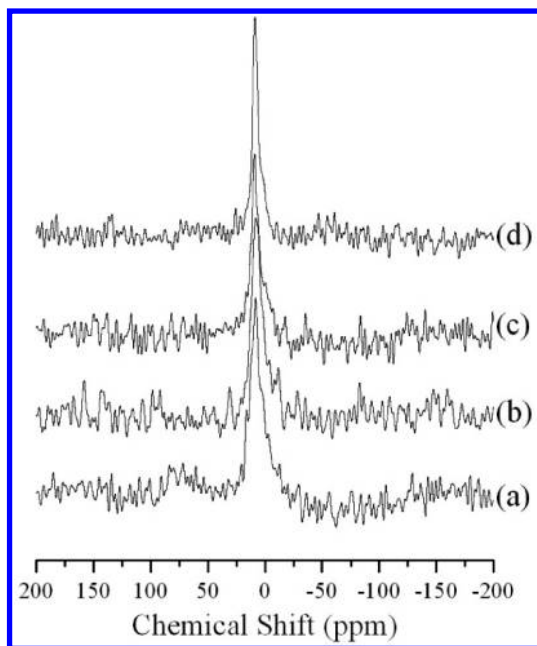

Figure 7. ^{27}Al NMR spectra of sample LDH-2.0, rehydrated at 50% of relative humidity and different temperatures: (a) 30, (b) 50, (c) 60, and (d) 70 °C.

Figures 5 and 6 show the isothermal experiments performed with the LDH-3.5 and LDH-4.0, respectively. As a general description, in these graphs, the following features are detected. The total amount of water captured decreased as a function of the Mg/Al molar ratio for all the temperature and RH experimental conditions. The maximum water adsorption produced during the first moments of the experiments follow the same tendency already observed. Although the LDH-2.0 and LDH-2.5 adsorbed up to 5 wt %, the LDH samples with Mg/Al molar ratios of 3.0 or higher adsorbed only 3 wt % at low RH. However, at a RH of 70 and 80%, LDH samples with Mg/Al molar ratios of 3.5 and 4.0 adsorbed up to 10 wt %. Therefore, the initially adsorbed water may be related to the formation of basic and reactive sites, since the most reactive sites are the first to take up OH groups. Finally, this assumption is qualitatively supported by the fact that isotherms did not overlap each other, which implies that in none of the cases has the adsorption−desorption equilibrium been reached. At a given temperature and RH, the shapes of the isotherms are also different for the different molar ratios. For instance, at 70% RH and 80 °C, samples LDH-2.0 and, especially, LDH-2.5 show a sharp increase in the first 2000 s and remain nearly stable afterward. In contrast, samples LDH-3.5 and LDH-4.0 show a slower, continuous process. This might be indicative of the degree of heterogeneity of the whole sorption process.

These results confirm that the Mg/Al molar ratio plays a very important role in the water absorption and adsorption processes, which may be correlated to catalytic phenomena. For this reason,
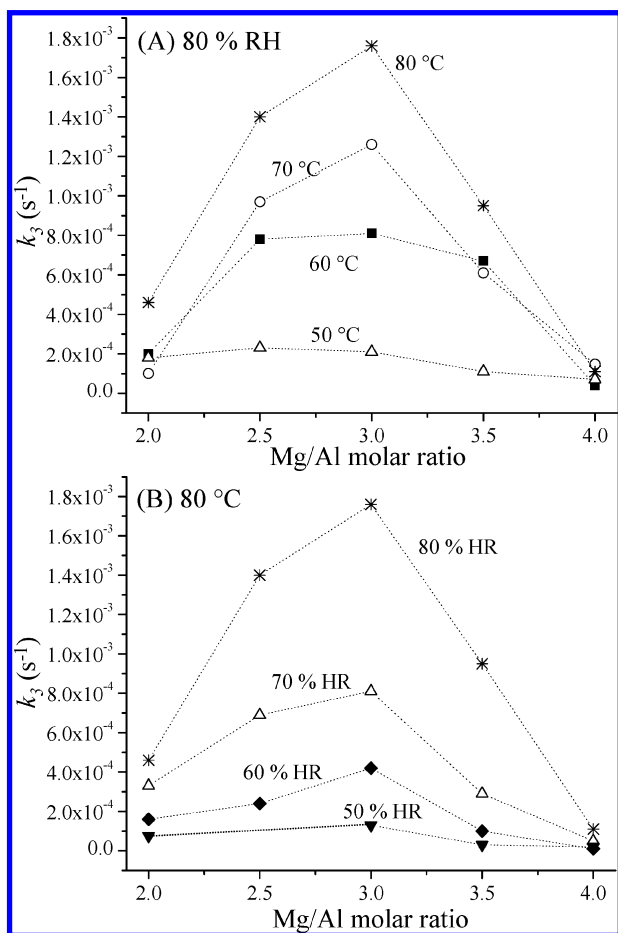
heterogeneous charge density distribution. These two phenomena are the origin of the different capacity of samples to capture water.

Figure 8. k_3 constant values at different temperatures and relative humidities.

to further analyze the Mg/Al molar ratio effect on the LDH regeneration, all these isotherms were fitted to the following exponential model:

$$y = (k_1/k_1 - k_2) \exp(-k_1 x) + A \exp(-k_3 x) + B \quad (1)$$

This model is divided into two parts: the first part of the equation corresponds to the water adsorption−desorption processes, and the second part corresponds to water absorption. 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 preexponential and y-intercept factors. k_3 was the only parameter that presented variations as a function of the temperature and RH. k_1 and k_2, constants related to the water adsorption−desorption process, did not present significant variation among the different samples, which may be explained by the physicochemical interaction between water and LDH sample. Water adsorption is produced through hydrogen bonding between the water protons and oxygen atoms located at the activated LDH surfaces. For the different LDH samples, the Mg/Al molar ratio varied, but the oxygen concentration practically must not have varied significantly.

Figure 8 shows the k_3 variations for the different LDH-Xs as a function of the temperature and RH. It is clearly evident that LDH-2.5 and LDH-3.0 (data obtained from ref 23) possess the fastest k_3 constants values, independent of the temperature or RH. This apparently indicates that there is

an optimum molar ratio, between 2.5 and 3.0, in which the reconstruction of the layered structure is easier. The estimated standard molar Gibbs free energies of reaction for Mg−Al LDHs synthesized at 25 °C have larger negative values (easier formation) at lower Mg/Al ratios.[27] Furthermore, the degree of ordering of cations in the brucite-like layers is dependent on the molar ratio. It has been shown that, with a Mg/Al ratio of 2, the cations are arranged in a honeycomb-like structure, with each Al octahedra surrounded by six Mg, whereas each Mg center is surrounded by 3 Al and 3 Mg. The degree of ordering is inversely proportional to the Mg/Al ratio, but the distribution remains nonrandom.[28] Upon calcination, the layered structure collapses, and the arrangement of the cations in the solid solution surely changes. Therefore, reconstruction is more favored in a certain interval; it is not linearly related to the molar ratio. In agreement with the results presented here, in a previous report, the best catalytic performance of meixnerite-like compounds in aldol condensation was obtained with a Mg/Al ratio of 2.5.[18] This might be so because the optimal catalytic activity is attained sooner at this molar ratio.

Independently of the qualitative tendency observed, all data were fitted to Eyring's model to obtain the activation enthalpies (ΔH) (Figure 9). It is clear that the different plots of $\ln (k_3/T)$ versus $1/T$ describe linear trends, fitting the model for all the temperatures and RHs. Therefore, the ΔH values for the water absorption process on the different activated LDHs were determined as a function of the temperature and relative humidity. The different ΔH values, obtained for each LDH sample, independently of the Mg/Al molar ratio, clearly show that the absorption process is more dependent on temperature when the relative humidity is lower (Figure 10). It means that, when the relative humidity is increased, the absorption process occurs at lower temperatures. In addition, an interesting behavior is observed when the ΔH values are analyzed as a function of the Mg/Al molar ratio at a specific RH; for example, 60%. In this case, the ΔH values were 85, 114.9, 121.3, 58.3, and 56.8 kJ/mol for the LDH-2.0, -2.5, -3.0, -3.5, and -4.0, respectively. It is worth noticing that ΔH values are not a linear function of the Mg/Al ratio. The water absorption process is more dependent on the temperature for the LDH-2.5 and LDH-3.0 samples, which, of course, is totally associated with the fact that these samples presented the highest variation in the k_3 constant values.

Conclusions

Different LDH samples (varying the Mg/Al molar ratio, 2.0, 2.5, 3.0, 3.5 and 4.0) were synthesized and activated at 550 °C. Then their rehydration processes were analyzed thermokinetically. Each sample was analyzed isothermally using different relative humidities and temperatures. The isothermal results were fitted to a specific model, which involves three different processes, identified during the LDH rehydration, H_2O adsorption, and absorption as well as H_2O desorption. The kinetic results showed that LDH-2.5 and LDH-3.0 samples absorb water faster than the other samples, independently of the temperature and relative humidity. These results were explained in terms of the thermodynamic data and chemical structure of the LDH samples. On a LDH sample with a Mg/Al ratio of 2, the cations are arranged in a honeycomb-like structure, and the degree of ordering is inversely proportional to the Mg/Al ratio, although the distribution remains nonrandom. These results were corroborated by a NMR analysis produced over the hydrated products.
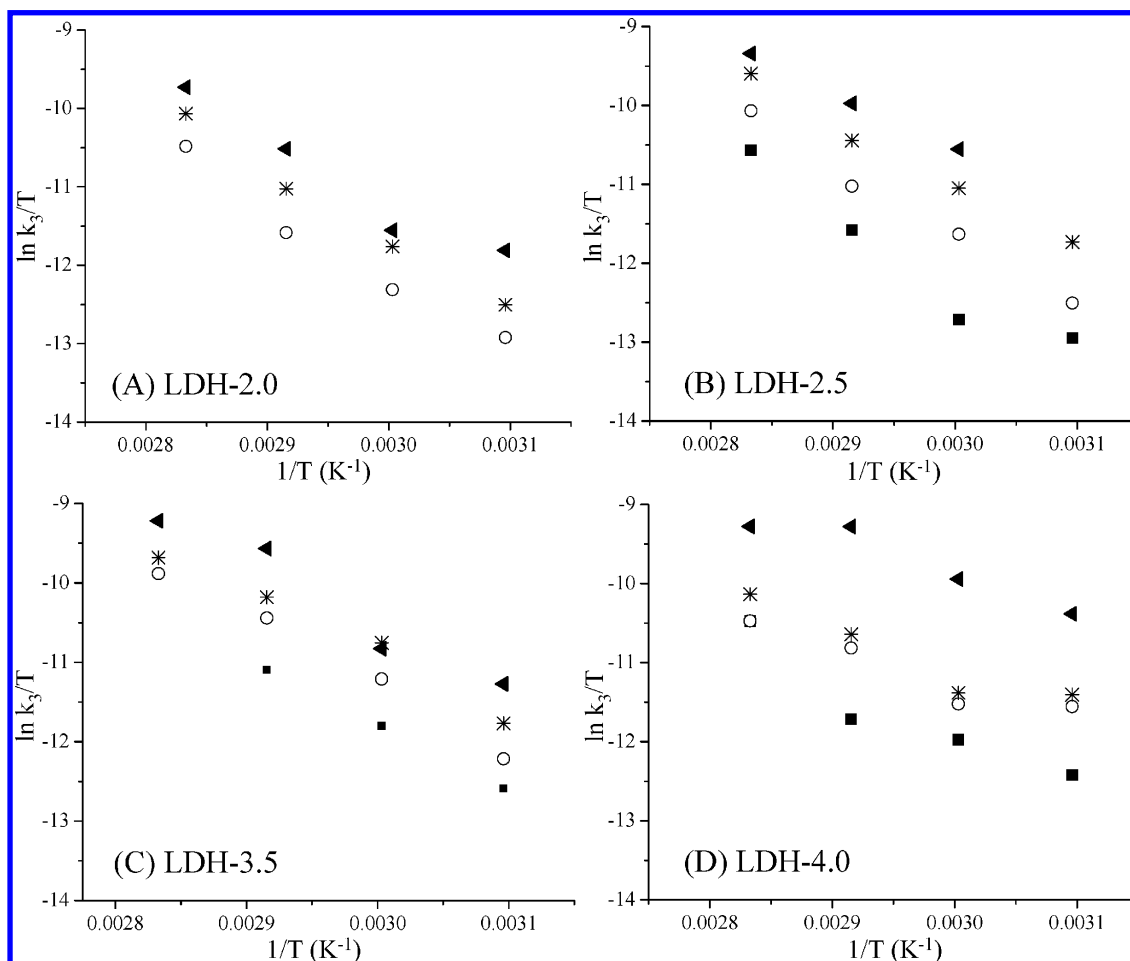
Figure 9. Eyring's plots for the different LDH samples, at different relative humidities: (solid square) 50%, (circle) 60%, (asterisk) 70%, and (solid triangle) 80%.
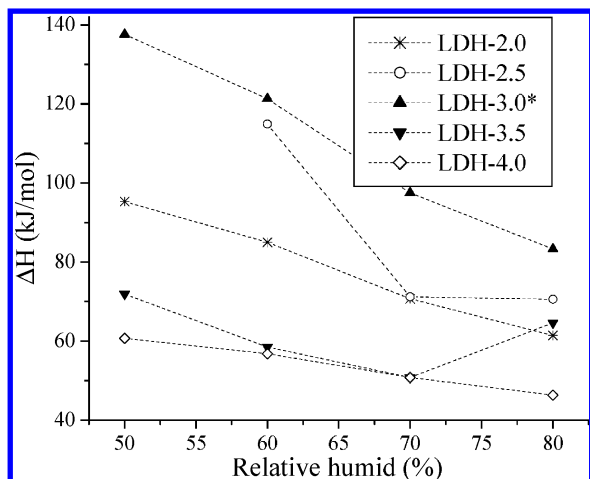

Figure 10. ΔH values obtained from the Eyring's plots for the different LDH samples. (*) data were obtained from ref 23.

The formation of the LDH is thermodynamically favored when the Mg−Al molar ratio decreases. Finally, the activation enthalpies for the LDH regeneration of the different samples were obtained as a function of the relative humidity. These results showed that the H_2O absorption process is more dependent on temperature if the relative humidity is low. In addition, if the activation enthalpies are compared as a function of the Mg/Al molar ratio at a defined temperature, their values do not behave linearly, as would be expected. The water absorption process proved to be more dependent

on the temperature for the LDH with molar ratios equal to the 2.5 and 3.0 samples.

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