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REHYDRATION OF Zn-Al LAYERED DOUBLE HYDROXIDES

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Abstract—Rehydration is shown to be straightforward for the reconstruction of polyoxometallate-pillared layered double hydroxides. Zn-Al hydrotalcite-like minerals were prepared with Zn/Al ratios of 1 to 5 by coprecipitation at pH 7. Good crystallinity was obtained for samples with Zn/Al ratios above 2. Thermal decomposition was achieved by calcining the samples at 300 to 900 °C. The calcined samples were exposed to decarbonated water, with or without hydrothermal treatment to evaluate reconstruction of the hydrotalcite-like minerals by rehydration. Restoration of the hydrotalcite-like structure was found to be independent of the Zn/Al ratios for samples calcined between 300 and 400 °C; however, a second phase, aluminum hydroxide or zinc oxide, was generally detected. A spinel phase, formed during the calcination of samples at temperatures above 600 °C, inhibited reconstruction of the hydrotalcite-like phase. The rehydrated hydrotalcite-like minerals had Zn/Al ratios close to 2, irrespective of the chemistry of the starting material.

Key Words—Hydrotalcite, Hydrothermal Treatment, Layered Double Hydroxide, Reconstruction.

INTRODUCTION

There is considerable interest in the synthesis and application of layered double hydroxides (LDHs), also called hydrotalcite-like compounds (HTLCs) (Cavani et al. 1991; de Roy et al. 1992). They consist of positively charged brucite-like sheets with intercalated anions and water molecules, and can be represented by the general formula:

$$[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[A^{m-}_{x/m}\cdot nH_2O]^{x-} \quad [1]$$

short noted $[M^{II}_R - M^{III} - A]$ with $R = (1-x)/x$ and where M^{II} can be Mg, Zn, Ni, Cu or Co and M^{III} Al, Cr or Fe. M^{II}/M^{III} molar ratios (noted R) between 1 and 5 are possible (Miyata 1975; Reichle 1985). Such LDHs have have attracted attention as adsorbents (Miyata 1983; Kopka et al. 1988), catalysts (Martin and Pinnavaia 1986; Suzuki et al. 1989) and precursors for catalysis (Clause et al. 1992). Their calcination yields a mixture of oxides (Sato et al. 1986) that show catalytic behavior for many basic reactions (Cavani et al. 1991).

The high affinity of HTLC for carbonate anions precludes reversible exchange, thus making it unsuitable as an anion-exchange material. However, carbonate can be removed by thermal decomposition and the oxides obtained will sorb anions when suspended in solution to restore the hydrotalcite structure. Some calcined HTLCs reconstruct the original hydrotalcite structure on exposure to aqueous solution (Miyata 1980; Sato et al. 1987). However, other oxides need hydrothermal treatment between 80 and 250 °C (Sato et al. 1988; Kooli et al. 1994) to reproduce the hydrotalcite structure. This property has also been used as an effective route to a variety of materials, the method being applied to intercalate both organic and inorganic anions (Chibwe and Jones 1989; Chibwe and Pinnavaia 1993; Kooli et al. 1994).

In earlier work, we focused on Zn-Al and Zn-Cr HTLCs as anion-exchangers and proton conductors (Dupuis et al. 1990; de Roy and Besse 1991; de Roy et al. 1992). To the best of our knowledge, no work has ever been published concerning the rehydration of Zn-Al LDHs. This paper describes the reconstruction properties of Zn-Al LDHs. Numerous parameters were studied to characterize the nature of the products obtained, including Zn/Al ratios, calcination temperatures of precursors, temperature of hydrothermal treatment and pH of the suspension. Powder X-ray diffraction (PXRD), Fourier transform infrared (FTIR) spectroscopy and chemical analysis by inductive coupled plasma atomic emission spectroscopy (ICP-AES) were performed to identify samples. Extended X-ray absorption fine structure (EXAFS) was used to investigate the change in the nature of the Zn environment during rehydration.

EXPERIMENTAL

The synthesis method used for the Zn-Al HTLC was similar to that described by de Roy et al. (1992). A solution containing zinc and aluminum chloride salts with Zn/Al ratios ranging from 1 to 5 was added to decarbonated water with vigorous stirring at constant pH = 7. The white slurry was aged overnight. The precipitate was centrifuged, washed several times with decarbonated water and then dried at room temperature.

The precipitates were calcined overnight under air atmosphere at temperatures in the 300 to 900 °C range.

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Table 1. Determination of Zn/Al ratios by chemical analyses and of *a* and *c* parameters for the original precipitate, the rehydrated phases without hydrothermal treatment and the rehydrated phases with hydrothermal treatment.

Samples	Zn/Al ratio		Original precipitate		Rehydrated sample		Rehydrated sample (hydrothermal)	
	calc.†	obs.‡	*a* (Å)	*c* (Å)	*a* (Å)	*c* (Å)	*a* (Å)	*c* (Å)
[Zn_1-Al-Cl]	1.00	0.98	3.0631(3)	23.2216(2)	3.0774(1)	22.7641(4)	3.0749(6)	22.8269(2)
[Zn_2-Al-Cl]	2.00	1.93	3.0738(5)	23.3037(1)	3.0726(4)	22.9322(5)	3.0741(1)	23.2417(0)
[Zn_3-Al-Cl]	3.00	2.86	3.0887(7)	23.5303(0)	3.0740(6)	22.9319(2)	3.0745(2)	23.2133(5)
[Zn_4-Al-Cl]	4.00	3.80	3.0890(2)	23.5966(7)	3.0728(2)	23.0425(3)	3.0726(4)	23.1571(3)
[Zn_5-Al-Cl]	5.00	4.87	3.1077(0)	23.5605(3)	3.0706(7)	22.7456(0)	3.0713(8)	22.8822(7)

† Calculated from charged material.
‡ Observed for the precipitation.

The calcined oxides thus obtained were suspended in 100 mL of decarbonated water, at room temperature (25 °C). After being stirred for 1 h, some of the suspension was hydrothermally treated in a Teflon cell, at autogenous pressure and at several temperatures in the range 50 to 160 °C, overnight. The rest was kept in suspension and stirred for 18 h, without the hydrothermal treatment. The rehydrated oxides were centrifuged, washed with decarbonated water and then dried at room temperature.

To examine the effect of the pH on rehydration, the pH of a suspension of calcined oxide and decarbonated water was adjusted to 4.5 by adding hydrochloric acid solution and to 10 by adding sodium hydroxide solution, before the hydrothermal treatment at 120 °C.

Zn and Al in the products were assayed by ICP-AES, using a JY 70 II spectrometer. The PXRD patterns were recorded on a Siemens D501 apparatus fitted with a graphite back monochromator using Cu*K*α radiation. The calculation of the lattice parameters was performed using least-square refinement. The FTIR spectra were obtained with a Perkin-Elmer 16PC spectrophotometer (single beam) using the KBr pellet technique. The TGA diagrams were recorded with a Setaram TG-DTA92 analysis unit, at a heating rate of 5 °C min^{-1} under air atmosphere. X-ray adsorption spectra at the *K* edge of Zn were obtained at the French Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (L.U.R.E.) synchrotron radiation facility. The EXAFS analyses were carried out using programs written by Michalowicz (1991).

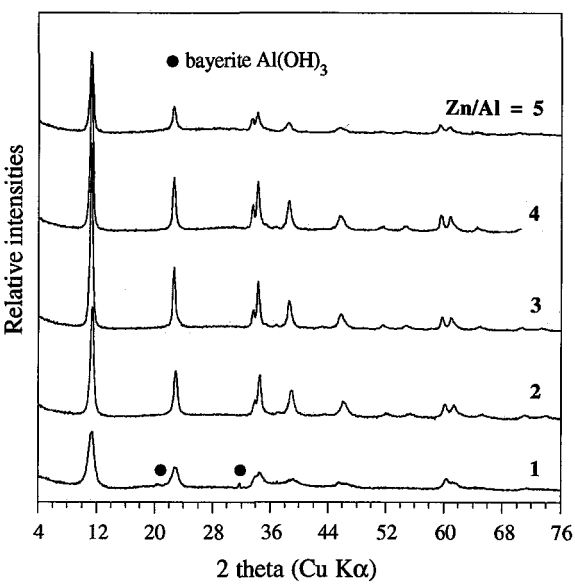


Figure 1. PXRD patterns of original precipitates with different Zn/Al ratios: 1, 2, 3, 4 and 5.

RESULTS AND DISCUSSION

Characterization of the Precipitate

The Zn/Al ratios in the precipitates are given in Table 1. There was a slight discrepancy between calculated and observed ratios, indicating that almost all Zn and Al ions were precipitated during synthesis.

The PXRD patterns of the samples (Figure 1) show that only an HTLC is detected, at different Zn/Al ratios, except for a trace of bayerite phase ($Al(OH)_3$), also observed at Zn/Al = 1. The crystallinity of the HTLC was improved when the Zn/Al ratio was higher than 2. The peaks are indexed in a hexagonal cell with rhombohedral symmetry, where the *c* parameter corresponds to 3 times the distance between adjacent brucite-like layers, and the *a* parameter is almost the same as that of brucite (3.10 Å). The interlayer distance, *d*, is approximately 7.9 Å. This value is in the literature range (Miyata 1983; de Roy et al. 1992). The *a* parameter increased as the Zn/Al ratio increased (Table 1) due to substitution of the Zn cation (r = 0.745 Å) by the smaller Al cation (r = 0.53 Å) (Shannon and Prewitt 1969). The *c* parameter also increased with the substitution rate, due to the increase in the electrostatic interactions between the chloride anions and the positively charged layers (Brindley and Kikkawa 1979).

FTIR spectra are shown in Figure 2. Irrespective of the Zn/Al ratio, all of the samples showed a strong broad absorption band at 3400 to 3500 cm^{-1}, corresponding to the ν(OH) vibration. There was also participation of water molecules whose δ(HOH) mode is

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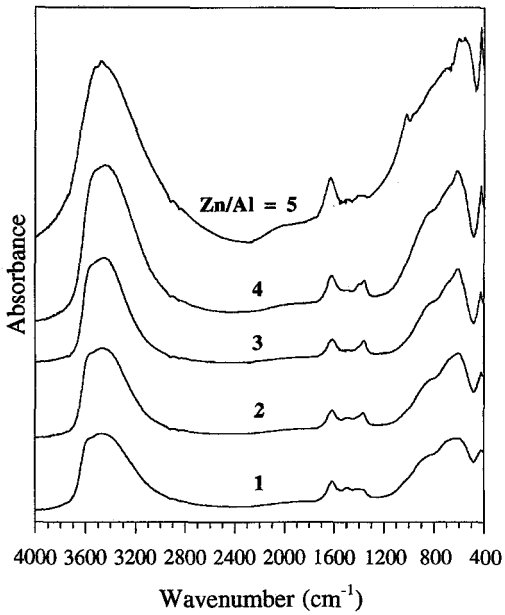


Figure 2. FTIR spectra of original precipitates with different Zn/Al ratios: 1, 2, 3, 4 and 5.

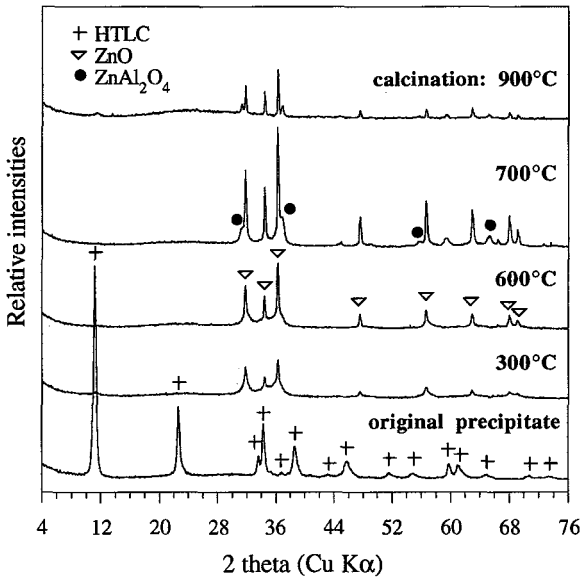


Figure 3. PXRD patterns of samples in [Zn_3-Al-Cl] series. Original precipitate and calcined oxides obtained at different temperatures: 300, 600, 700 and 900 °C.

recorded at 1640 cm^{-1}. The position of this band was shifted to relatively high frequencies as the Al content decreased in the brucite-like layer, consistent with the studies of Hernandez-Moreno et al. (1985) and Kooli et al. (1993). The peaks at frequencies below 800 cm^{-1} can be attributed to metal-oxygen vibrations ν(M-O) and δ(O-M-O) (Gastuche et al. 1967; Bish and Brindley 1977). However, at Zn/Al ratio = 1, a shoulder band and a broad band appeared at 1026 and 800 cm^{-1}, indicating the presence of a second phase already detected by PXRD as $Al(OH)_3$. The weak band in the region 1500 to 1400 cm^{-1} can be attributed to carbonate anions adsorbed during the synthesis. FTIR data agree closely with those of XRD analysis, and confirm that the crystallinity is improved at ratios higher than 1, the bands at low frequencies becoming sharper.

There was no difference in the TGA curves for products with different Zn/Al ratios. The TG curves showed 2 main weight losses in the ranges 20 to 280 and 450 to 800 °C. The first weight loss occurred in 2 stages. The first stage is attributed to the loss of physisorbed and interlayer water between 25 and 180 °C. The second stage occurred continuously up to above 300 °C and corresponds to the elimination of structural hydroxyl groups in the basic layer (Martin and Pinnavaia 1986; El Malki 1991). At higher temperatures (450 to 700 °C), there was total dehydroxylation and elimination of interlayer chloride. De Roy et al. (1992) have reported that the loss of Cl^- is accompanied by the release of gaseous HCl during this step under air atmosphere.

THERMAL STABILITY. The PXRD patterns of the phase with Zn/Al = 3, the original precipitate and the oxides obtained by the calcination at different temperatures in the range of 300 to 900 °C, are shown in Figure 3.

For the samples heated to 300 °C, the diffraction pattern of HTLC disappeared and only the zinc-aluminum oxide phase was detected. The *a* parameter of this phase (3.225 Å) was lower than that of pure zinc oxide (JCPDS value 3.249 Å), as a result of the incorporation of Al inside the zinc oxide particles, in agreement with previous studies (Miyata 1980). At 600 °C, only a zinc oxide phase was detected with a spinel phase beginning to appear around 700 °C. Calcination at higher temperature (for example, 900 °C) caused sintering of the mixed oxides, with segregation and formation of ZnO and $ZnAl_2O_4$ phases with sharp peaks of the spinel phase. We then used the calcined compounds to study the reconstruction properties.

Rehydration Properties

WITHOUT HYDROTHERMAL TREATMENT. *Influence of Zn/Al Ratio.* The reconstruction properties were investigated using the [Zn_3-Al-Cl] oxides calcined at 300 °C, and suspended in decarbonated water.

Figure 4 shows that all the oxides regenerated the original hydrotalcite structure after the 18-h rehydration, irrespective of the Zn/Al ratio. However, the $Al(OH)_3$ phase was also detected in the [Zn_1-Al-Cl] series and as traces for the other compounds. A certain amount of zinc oxide phase was also observed, in addition to the HTLC. The proportion of zinc oxide increased at high Zn/Al ratios between 4 and 5.

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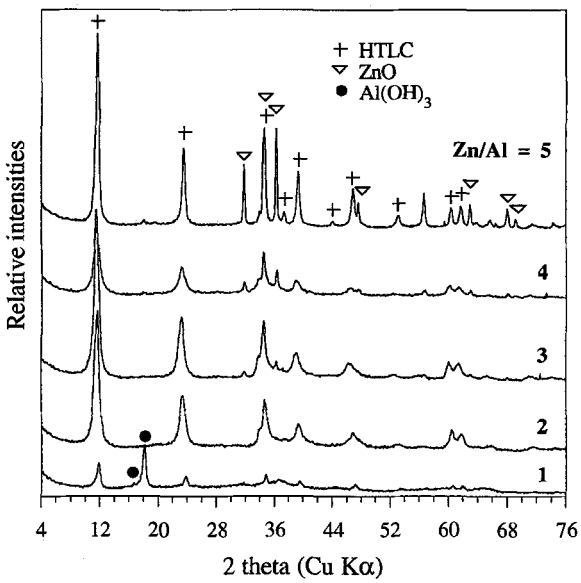


Figure 4. PXRD patterns of rehydrated samples prepared with calcined oxide obtained at 300 °C. Values are Zn/Al ratios of original precipitates.

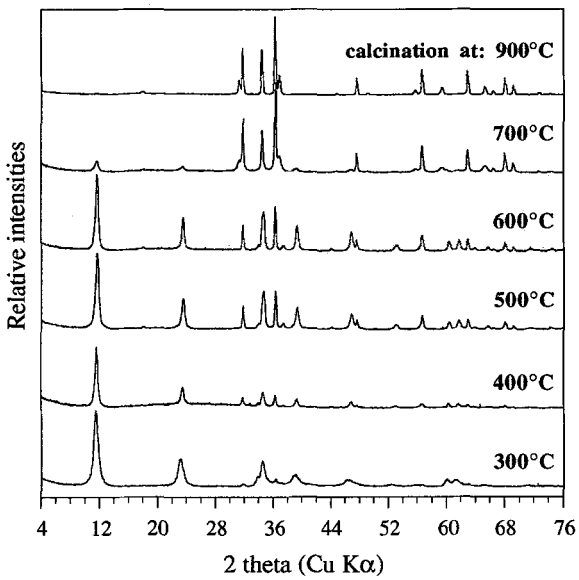


Figure 5. PXRD patterns of rehydrated samples of [Zn_3-Al-Cl] series derived from calcined oxide obtained at different temperatures: 300, 400, 500, 600, 700 and 900 °C.

The *a* parameters of the rehydrated HTLCs (Table 1) were usually lower than those of the original precipitates, except in the case of Zn/Al = 1, where it was higher. This suggests that not all Al ions participate in the reconstruction process. Aluminum hydroxide was detected within the rehydrated product. The formation of aluminum hydroxide suggests that the calcined oxides are rich in Al on the surface, with formation of an amorphous alumina phase that cannot be detected by PXRD (Rebours et al. 1994).

For the other cases, a decrease in this parameter may be due to the behavior of the Zn ion. The zinc-aluminum oxides were not totally rehydrated, and so some Zn ions could form an oxide phase (ZnO), or an amorphous zinc hydroxide phase undetectable by PXRD.

The *c* parameters of rehydrated samples were always lower than those of the original ones, due to the presence of carbonate anions in the interlayer space, and to the interactions between the positively charged layers and the anions.

Effect of Calcination Temperatures. The ability to restore the original structure was examined for the oxides calcined at different temperatures between 300 and 900 °C. The results are summarized in Table 2.

Figure 5 indicates that the calcined oxides could be rehydrated if the temperature of calcination was no higher than 600 °C. In addition to the HTLC, the presence of zinc oxide was also detected, and its PXRD intensity increased with calcination temperature. The rehydration was not achieved for the sample calcined at temperatures higher than 700 °C; only traces of HTLC were detected with the spinel and zinc oxide phases. The formation of spinel-type phases makes the reconstruction process more difficult (Kooli et al. 1994).

The *a* and *c* parameters decreased with an increase in calcination temperature of the precipitates, and were

Table 2. Comparison of *a* and *c* parameters for [Zn_3-Al-Cl] phase calcined at different temperatures between 300 and 600 °C and rehydrated without hydrothermal treatment or with hydrothermal treatment between 50 and 160 °C.

Rehydrated without hydrothermal treatment			Rehydrated with hydrothermal treatment†		
Calcination temperature (°C)	*a* (Å)	*c* (Å)	Hydrothermal temperature (°C)	*a* (Å)	*c* (Å)
300	3.0740(2)	22.9320(3)	50	3.0742(4)	22.9610(1)
400	3.0670(5)	22.7393(1)	80	3.0740(7)	22.9663(2)
500	3.0657(1)	22.6880(7)	120	3.0740(5)	22.9319(6)
600	3.0654(8)	22.6027(4)	160	—‡	—‡

† Calcination was carried out at 300 °C before the hydrothermal rehydration.
‡ No HTLC is regenerated.

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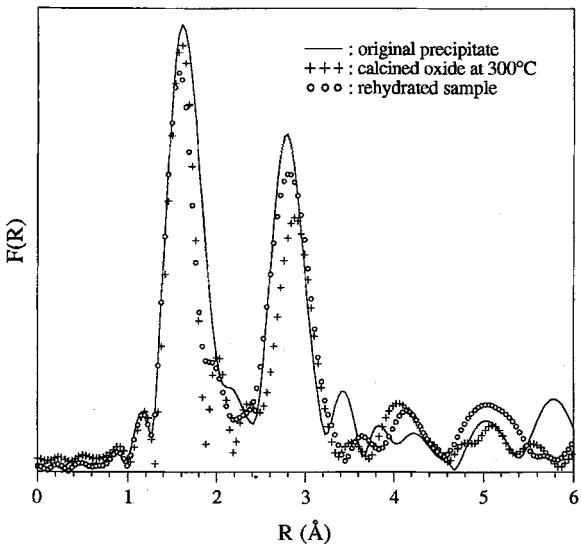


Figure 6. Fourier transform of k^3 weighted EXAFS spectra at K edge of Zn of [Zn_3-Al-Cl] series:—original precipitate, ++ calcined oxide at 300 °C and oo rehydrated sample from calcined oxide at 300 °C (no phase correction).

always lower than those of the original precipitates. The decrease in the a parameter may be related to partial reactivity of Zn before rehydration, causing it to participate as a zinc oxide phase. The possibility of partly restoring the original hydrotalcite-like structure by rehydration of samples calcined at 600 °C excludes alumina (Al_2O_3) segregation during thermal treatment of Zn-Al LDHs, consistent with the results of Rey et al. (1992).

The FTIR spectrum of the oxide obtained after calcination at 300 °C shows that the hydrotalcite structure was lost. M-O vibration bands almost disappeared and broadened. After rehydration, a typical FTIR spectrum of Zn-Al HTLC with a strong band of the ν_3 mode of the carbonate anion at 1370 cm^{-1} (Brindley and Kikkawa 1979) was obtained. The strong broad band at 3540 cm^{-1} is due to the OH stretching mode and a shoulder centered on 3000 cm^{-1} suggests the presence of hydrogen-bonded water molecules and carbonate anions (Hernandez-Moreno et al. 1985). As the calcination temperature increased, there was no significant change in the FTIR spectrum. The intensity of the carbonate band decreased, meaning that the amount of HTLC within the rehydrated powders was lower. Conversely, the intensity of the band at 800 cm^{-1} increased and a new band appeared at 1100 cm^{-1}, a result of the presence of zinc oxide within the samples, compared to the FTIR spectrum of the starting precipitate.

These FTIR data confirm the results obtained by PXRD analysis and are also in close agreement with an EXAFS study conducted at the K edge of zinc on calcined and rehydrated samples. On Figure 6, the radial distribution of Zn is represented in the case of the [Zn_3-Al-Cl] sample. The 3 major maxima of radial electron density observed for these compounds are easily assigned to the first 3 shells arising from O atoms for the first and third peaks and Zn or Al atoms for the second peak. For the [Zn_3-Al-Cl] original precipitate (synthesized at room temperature), the first peak is characteristic of an octahedral environment: the Zn^{2+} cation is surrounded by 6 oxygen atoms. When this phase was calcined at 300 °C, we could observe a shift of this peak to the shorter distances and a decrease in its intensity. This modification confirms the presence of zinc oxide at this temperature. In zinc oxide, the Zn atom is in a tetrahedral environment. The surface area of the peak therefore decreases and the Zn-O distance shortens. In the case of the second peak, we observed a marked collapse for the HTLC calcined at 300 °C. The lamellar structure was destroyed and the distance obtained was close to the pure zinc oxide phase. As for the rehydrated phase, the second peak was located between that of the original precipitate and that of the HTLC calcined at 300 °C, meaning that 2 phases are formed after the reconstruction process, a phase with the hydrotalcite structure along with the remaining zinc oxide.

WITH HYDROTHERMAL TREATMENT. Previous studies have reported that some calcined oxides revert to the original structure of the precipitates with hydrothermal conditions (Sato et al. 1988; Kooli et al. 1994; Courty and Marcilly 1983). This was attempted here.

Effect of Zn/Al Ratio. Different precipitates with variable Zn/Al ratios were calcined at 300 °C and the hydrothermal treatment was carried out at 120 °C as described before. After the rehydration, the hydrotalcite structure was obtained irrespective of the Zn/Al ratio, although the zinc oxide phase was also detected in the rehydrated powders. The intensity of reflections of the zinc oxide phase was higher than that obtained in the rehydrated product without hydrothermal treatment. For Zn/Al = 2, no significant amount of zinc oxide phase was detected. As mentioned previously, after the rehydration, the a parameter of the HTLC is always lower than for the starting precipitate. This value was around 3.074 Å, corresponding to a chemical composition of HTLC with Zn/Al ratio = 2.

Effect of Calcination Temperature. As described above, the calcination temperature affects the reconstruction properties without hydrothermal treatment. We also investigated the influence of this factor. The temperature of the hydrothermal treatment was set at 120 °C and the calcination temperature varied from 300 to 900 °C. The Zn/Al ratio was 3.

At 300 °C, the HTLC was the major phase, compared to zinc oxide. It was difficult for samples calcined at temperatures in the range of 400 to 600 °C to rehydrate and reconstruct the hydrotalcite structure.

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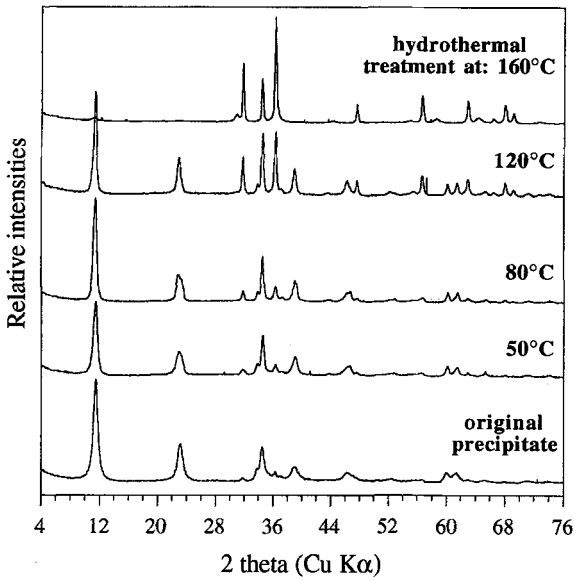


Figure 7. PXRD patterns of samples of [Zn_3-Al-Cl] series hydrothermally rehydrated at different temperatures: 50, 80, 120 and 160 °C. That for the calcined oxide at 300 °C, which is used for the hydrothermal rehydration experiments, is given for comparison.

Only traces of the hydrotalcite structure were detected, and zinc oxide was present as the main compound in the product. Only the spinel and zinc oxide phases were detected as a mixture in the rehydrated powders when the precipitates were calcined between 700 and 900 °C.

Influence of Hydrothermal Temperature. The Zn-Al oxide regenerated the hydrotalcite structure at 120 °C, accompanied by the formation of zinc oxide. Accordingly, to make the reaction more complete, we studied the influence of the hydrothermal temperature on the rehydration rate, for the range 50 to 160 °C.

The PXRD patterns (Figure 7) of the samples hydrothermally rehydrated between 25 and 80 °C showed the typical pattern of the hydrotalcite structure, with that of a trace amount of zinc oxide phase. The intensity of PXRD of zinc oxide increased with the hydrothermal temperature. This treatment favored the crystallization of zinc oxide which was initially amorphous in the precipitation. At 160 °C, only the zinc oxide phase was present and no reconstruction occurred, suggesting that the rehydration of zinc oxide is not favored at relatively high hydrothermal temperatures; only an improvement in the crystallinity of the zinc oxide phase (sharper PXRD peaks) was observed. For this case, we can suppose that, during the rehydration, amorphous alumina on the surface was rehydrated as $Al(OH)_3$, and amorphous zinc hydroxide was formed, during the early stage of rehydration. Some of the amorphous zinc hydroxide then decomposed to ZnO in the range 120 to 160 °C.

Influence of pH Medium. Kooli et al. (1995) reported that Ni-Al oxide was not rehydrated in water when calcination temperature varied from 400 to 600 °C. However, the reconstruction was achieved in an acid medium by exposure to decavanadate solution; the pH therefore played an important role in this case.

The hydrotalcite structure was found to be slightly reconstructed from the Zn-Al oxide calcined at 400 °C, by the hydrothermal treatment at 120 °C. The pH of the suspension was 6.9. When this pH was decreased to 4.5 by adding hydrochloric acid solution, the hydrothermal treatment at 120 °C rehydrated the Zn-Al oxide to reconstruct the hydrotalcite structure. This time, the HTLC was the main phase accompanying zinc oxide and zinc hydroxide. However, at higher pH values of the suspension (around 10), only the oxide phase was obtained. The pH conditions affected the reconstruction process and the lower pH favored the rehydration of the Zn-Al oxides. In the acid medium, all the amorphous phases around the calcined oxides were dissolved and there was a complete reconstruction of the oxide, without secondary reactions. The dissolution of some zinc ion was shown by the decrease in the *a* parameter, which varied from 3.088 to 3.064 Å.

CONCLUSION

We have shown that the [Zn_R-Al-Cl] HTLCs were obtained irrespective of the Zn/Al ratio, at pH 7. The hydrotalcite structure was collapsed by calcination at 300 °C, and zinc oxide doped with Al crystallized, but the formation of amorphous alumina and zinc aluminates was not excluded on the surface of the zinc oxide particles. Similar phases have been previously reported in the Mg-Al and Ni-Al hydrotalcite compounds. At higher temperatures, only sintered spinel ($ZnAl_2O_4$) and zinc oxide phases were detected in the calcined samples. The reconstruction was fully obtained by simple exposure to a solution of decarbonated water of the Zn-Al oxides calcined below 400 °C. At higher calcination temperatures, this process was difficult to achieve, whatever the Zn/Al ratio and whether or not hydrothermal treatment was applied. However, zinc oxide spread as the hydrothermal temperature increased. In general, the rehydrated phase had the hydrotalcite structure and chemical composition with Zn/Al = 2, irrespective of the initial composition. It was difficult to regenerate the original hydrotalcite structure when the spinel-like phase was formed. It thus seemed to be an inhibitor for the rehydration process. Possibly, during the reconstruction process, there is a preliminary reaction of rehydration at an early stage of reconstruction of amorphous phases and then a rehydration of the Zn-Al oxides.

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