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Reconstruction of layered double hydroxides from calcined precursors: a powder XRD and ^{27}Al MAS NMR study

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The reconstruction of layered double hydroxides with the hydrotalcite-like structure from material previously calcined at increasing temperatures has been studied. Both the calcination temperature and the time the samples spent equilibrating with a controlled water vapour pressure have been considered. The crystallinity of the samples and the crystalline phases formed have been assessed by powder X-ray diffraction, while the local environment of the Al ions has been probed by ^{27}Al MAS NMR. It has been found that reconstruction is complete when the sample has been calcined at or below 550 °C, after 24 h rehydration, while equilibration for 3 days is adequate to reconstruct samples previously calcined at 750 °C. Only partial reconstruction is observed after calcination at 1000 °C. However, the NMR results indicate that, in all cases, some of the Al ions remain in tetrahedral sites.

Introduction

Layered double hydroxides (LDHs) with the hydrotalcite (HT) structure, are a family of well known materials which have received much attention in recent years.[1,2] Their general formula can be written $[\mathrm{M^{II}}_{1-x}\mathrm{M^{III}}_x(\mathrm{OH})_2](\mathrm{A}^{n-})_{x/n}\cdot m\mathrm{H_2O}$, and the structure corresponds to that of brucite, with partial $\mathrm{M^{II}/M^{III}}$ substitution. The interlayer space contains water molecules and the balancing anions (A^{n-}). Exchange of the intercalated anions is, in general, easy but for carbonate it is rather difficult.[3] Intercalation is achieved by direct synthesis, anionic exchange, or by reconstruction of the layered structure when contacting the material calcined at 300–500 °C with solutions of anions.[4,5] Reconstruction of the structure is, however, very difficult if the material has been calcined at too high a temperature.[6]

Monitoring structural changes during calcination has been the aim of numerous studies. For a Mg,Al-carbonate hydrotalcite (the temperature ranges vary depending on the nature of the layer cations) the layered structure is maintained up to *ca.* 200 °C, then a mostly amorphous phase is formed, and crystallization of MgO starts. Location of $\mathrm{Al^{III}}$ cations has not been fully resolved, and formation of amorphous Al oxides, or of a solid solution in the MgO structure, has been claimed.[1,4] Finally, above 800 °C, formation of MgO and of $\mathrm{MgAl_2O_4}$ spinel is observed.

In the present paper, we report on the changes, mainly affecting $\mathrm{Al^{III}}$ ions, taking place during the thermal decomposition of a Mg,Al-carbonate hydrotalcite, and during the controlled reconstruction of the layered structure. ^{27}Al magic-angle spinning NMR spectroscopy is a powerful tool to probe the local Al environment and all HT materials have been studied by this technique. Some selected samples have been studied by two-dimensional triple-quantum ^{27}Al MAS NMR spectroscopy, a recently introduced technique which allows spectra of half-integer quadrupole nuclei to be recorded with unprecedented resolution.[7,8]

Experimental

Sample preparation

All chemicals were from Fluka p. a. (Switzerland). A solution containing $\mathrm{Na_2CO_3}$ (1 M) and NaOH (2 M) was added to 500 ml of distilled water until pH = 10. Another solution containing $\mathrm{Mg(NO_3)_2\cdot 6H_2O}$ (2 M) and $\mathrm{Al(NO_3)_3\cdot 9H_2O}$ (1 M) was prepared, and added dropwise to the pH 10 solution at 40 °C with continuous magnetic stirring. Once addition was completed, the slurry was magnetically stirred at 70 °C for 70 h. The solid was filtered off and washed with distilled water, until a negative assay for nitrate was observed in the washing liquids. This parent sample is denoted C2. In order to assess the destruction–reconstruction process of the layered structure, the sample was calcined in air for 2 h progressively at 150, 250, 350, 450, 550, 650, 750 and 1000 °C (samples C2-*T*, where *T* is the calcination temperature, °C). For preparation of the reconstructed samples, the calcined samples were put in a vacuum desiccator with a saturated solution of ammonium chloride at 25 °C (water vapour pressure 18.6 mmHg[9]) for 24 h (samples C2-*T*R). In some cases, reconstruction was extended to 72 or 96 h.

Techniques

Elemental chemical analyses for Mg and Al were carried out at Servicio General de Análisis Químico (University of Salamanca, Spain) by atomic absorption in a Mark 2 ELL-240 instrument after dissolving the samples in nitric acid. Powder X-ray diffraction patterns (PXRD) were collected on a Siemens D-500 diffractometer using Cu-Kα radiation ($\lambda = 1.54050$ Å). Differential thermal analysis (DTA) and thermogravimetry (TG) were performed on Perkin-Elmer DTA7 and TGA7 instruments, respectively. FTIR spectra were collected in a Perkin-Elmer FT1730 instrument using the KBr pellet technique; 100 scans were averaged to improve the signal-to-noise ratio at a nominal resolution of 4 cm^{-1}. ^{27}Al MAS NMR spectra were recorded at 104.3 MHz on a (9.4 T) Bruker MSL 400P spectrometer. Single-quantum ('conventional') ^{27}Al MAS NMR spectra were measured using short and powerful radiofrequency pulses (0.6 μs, equivalent to 10° pulse angle), a spinning rate of 15 kHz and a recycle delay of 500 ms. Chemical shifts (δ_{Al}) are quoted in ppm from $[\mathrm{Al(H_2O)_6}]^{3+}$. The triple-quantum (3Q) ^{27}Al MAS NMR spectra[7,8,10] were recorded with radiofrequency magnetic field amplitudes of *ca.* 150 kHz. 256 data points were acquired in the t_1 dimension in increments of 7 μs. To produce pure-absorption lineshapes in the 3Q MAS spectra the optimum conditions for excitation and transfer of the ($\pm$3Q) coherences using a simple two-pulse sequence were used. The phase cycling was composed of six phases for the selection of 3Q coherences. This phase cycling was combined with a classic overall four-phase cycle in order to minimise phase and amplitude missettings of the receiver. The ppm scale was referenced to ν_0 frequency in the ν_2 domain and to $3\nu_0$ in the ν_1 domain [reference $Al(H_2O)_6^{3+}$].

Results and discussion

Parent sample

Elemental chemical analysis data (16.41% Mg, 10.45% Al, by weight) indicate a Mg/Al ratio of 1.74, slightly lower than the value in the parent solutions (Mg/Al = 2.0). The DTA curve shows two endothermic peaks, ascribed to removal of interlayer water, and to decarbonation and dehydroxylation. The interlayer water content was calculated from the TG results, and the presence of interlayer carbonate was concluded from FTIR (carbonate ν_3 at 1435 cm^{-1}, ν_1 at 1050 cm^{-1}) and ^{1}H–^{13}C cross-polarisation MAS NMR spectra (single peak at δ 171). The calculated formula for the hydrotalcite materials was $[Mg_{0.64}Al_{0.36}(OH)_2](CO_3)_{0.18}\cdot0.78H_2O$.

The PXRD pattern for the original sample (Fig. 1) shows diffraction maxima corresponding to diffraction by basal planes at 7.6, 3.8 and 2.6 Å, similar to those previously reported in the literature and corresponding to a well crystallised hydrotalcite-like structure. Assuming a 3R stacking of the layers[11,12] and from the positions of the peaks due to planes (003) and (110), the lattice parameters were calculated as $c = 22.79$ Å and $a = 3.05$ Å. The former corresponds to three times the layer-to-layer distance, while the latter corresponds to the average metal–metal distance within the layers. The interlayer space, assuming 4.8 Å for the width of the brucite-like layer,[13] was 2.8 Å, in accord with location of the carbonate anions with their molecular plane parallel to the brucite-like layers.

The ^{27}Al MAS NMR spectrum of the parent sample (Fig. 2) contains a sharp (full-width at half-maximum, FWHM, *ca.* 370 Hz) peak at δ 9.1 with a relatively broad low-frequency shoulder, assigned to octahedral Al. The sheared 3Q ^{27}Al MAS NMR spectrum (Fig. 3) clearly shows that sample C2 contains two types of Al sites (overlapping resonances S1 and S2). The peak S1, at δ ca. 11 (F1) [δ ca. 9 (F2)], displays a distribution of isotropic chemical shifts. We speculate that this may be due to the presence of a range of slightly different local Al environments generated by the random insertion of Al in the layers. The low-frequency F2 shoulder (S2) is essentially undistributed but it has an average quadrupole coupling constant much larger than S1, A more detailed discussion of the multiple-quantum NMR spectrum will be given elsewhere.

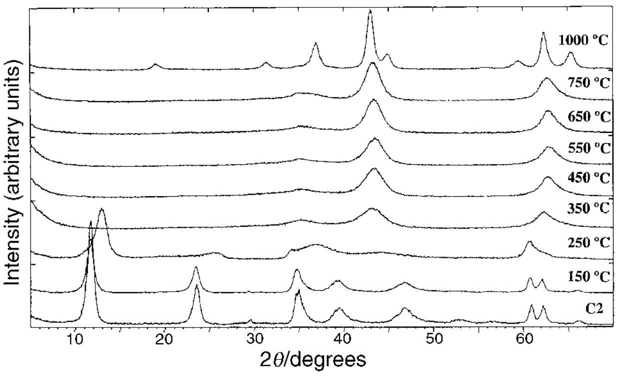

Fig. 1 PXRD patterns of the original C2 sample and materials calcined at the temperatures indicated.

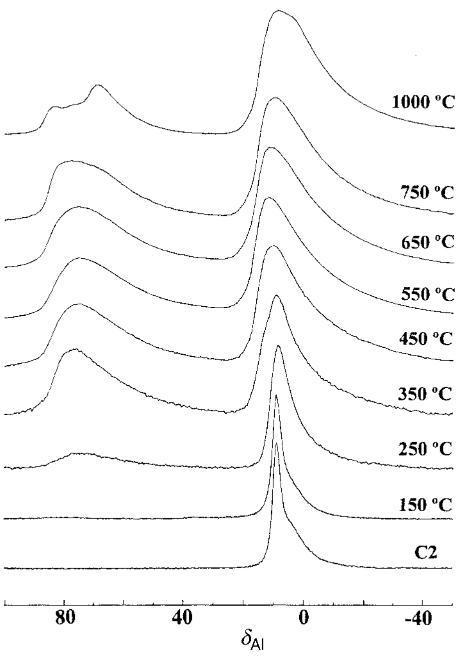

Fig. 2 ^{27}Al MAS NMR spectra of the original C2 sample and materials calcined at the temperatures indicated.

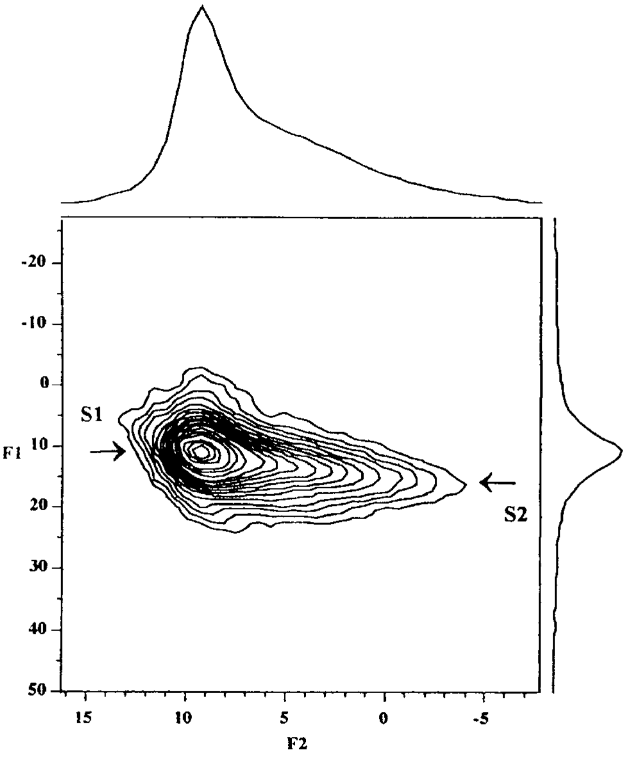

Fig. 3 Sheared 3Q ^{27}Al MAS NMR spectrum of the parent C2 sample.

Calcined samples

Fig. 1 shows the PXRD patterns for the calcined samples. The results are similar to those previously reported by other authors.[1,2,14,15] On calcination at 150 °C no appreciable change is observed in the PXRD patterns, which are almost identical (relative intensities and positions of the peaks). In accord with this, the ^{27}Al MAS NMR spectra of this sample and C2 (Fig. 2) are very similar. When the sample is calcined at 250 °C the PXRD peaks are slightly weaker and broader, and the peak corresponding to diffraction by planes (003) shifts from 7.60 to 6.84 Å. It is of note that the intensity of the second harmonic, planes (006), decreases much more than that of the peak for planes (003). The definition of the doublet close to $2\theta = 60°$ is also slightly worse, but overall it can be concluded that the sample partially retains a layered structure, with similar metal–metal distances in the layer as in the parent sample. These results are in accord with those previously reported by Tichit *et al.*,[16] who suggested that the peak broadening and spacing decrease upon calcination at 200 °C is due to a disordered structure, which remains mostly layered. This suggestion is consistent with the ^{27}Al MAS NMR spectrum (Fig. 2) of the sample calcined at 250 °C which displays a much broader (FWHM = 860 Hz) six coordinate Al peak at δ *ca.* 8.8. Based on XAS data, Belloto *et al.*[17] indicate that, when the sample is calcined at 200 °C, *ca.* 10% of Al^{III} ions migrate from octahedral to tetrahedral coordination, through three oxygens from the hydroxy layer and one apical oxygen from the interlayer, giving rise to cation vacancies in the layer. This migration is consistent with our results since the ^{27}Al MAS NMR spectrum of the sample calcined at 250 °C reveals the presence of about 25% four-coordinate Al (peak at δ *ca.* 76). Kanezaki[14] has reported a detailed high temperature PXRD analysis of Mg,Al-carbonate decomposition, concluding that at *ca.* 200 °C a new phase is formed, with a basal spacing of 6.6 Å, which is attributed to removal of interlayer carbonate and formation of a hydroxy-containing layered material. However, previous studies[18,19] have shown that CO_2 evolution coincides with the second endothermic effect in the DTA curve, clearly above 250 °C.

Calcination at 350 °C gives rise to distinct differences in the PXRD patterns. Only three broad, ill defined peaks are recorded, with positions which roughly coincide with those of MgO (periclase). The shift from the positions reported in JCPDS files has been attributed[16] to the formation of a non-stoichiometric spinel containing Al^{III} ions. ^{27}Al MAS NMR spectroscopy also shows that at 350 °C the structure undergoes major changes (Fig. 2). The four-coordinate Al peak at δ 76 accounts for *ca.* 47% of the total area. The six-coordinate Al resonance is quite broad (FWHM 1400 Hz) and shifts slightly to δ 9.9. At 450 °C both the four- and the six-coordinate Al peaks broaden further (for the latter FWHM = 2000 Hz) and shift slightly to δ 72 and 12. The unsheared 3Q ^{27}Al MAS NMR spectrum of this sample is shown in Fig. 4. In the four-coordinate Al region the spectrum contains a single peak (S3), while in the six-coordinate Al region two overlapping peaks (S1 and S2) are present.

No major changes are observed as the calcination temperature is increased up to 750 °C, when it is observed that the PXRD peak at 2θ *ca.* 35° broadens, with a noticeable shoulder at $2\theta = 37°$. At 750 °C the ^{27}Al MAS NMR spectrum changes only slightly: the four-coordinate Al peak sharpens, shifts to δ *ca.* 76 (with a broad shoulder at δ *ca.* 67) and accounts for less than 40% of the total area.

When the sample is finally calcined at 1000 °C, sharper PXRD peaks are recorded, the positions of which coincide with those of periclase (MgO) and ($MgAl_2O_4$) spinel. This sample gives a completely different ^{27}Al MAS NMR spectrum (Fig. 2) with several peaks present. Its unsheared 3Q ^{27}Al MAS NMR spectrum (Fig. 5) contains a faint (S5) and two strong (S4 and S3) four-coordinate Al peaks and probably two six-coordinate (S2 and S1) Al resonances.

Rehydrated samples

Fig. 6 shows the PXRD profiles for rehydrated (from gaseous water vapour) samples for 24 h under the experimental conditions described above. It is observed that the layered structure, coincident with that of the parent uncalcined sample, is recovered for all rehydrated samples, if previous calcination has been performed at or below 550 °C. Sample C2-550R displays peaks which are even sharper than those of sample C2-150. For these samples, only diffraction maxima due to the LDH are recorded. ^{27}Al MAS NMR spectroscopy (Fig. 7) confirms that, up to 550 °C, the samples may be regenerated. A detailed analysis of the spectra suggests that the regeneration is not always entirely reversible. Firstly, all regenerated samples contain small amounts of four-coordinate Al, typically $< 5\%$, but as much as *ca.* 14% for the sample calcined at 250 °C. The samples calcined at 350, 450 and 550 °C give six-coordinate ^{27}Al NMR resonances which are sharper (for the latter FWHM = 290 Hz) than the parent C2 sample and do not exhibit a low-frequency tail. The local Al environment in these samples may be less disordered than in the starting material.

Rehydration of sample C2-650, however, does not fully recover the layered structure. Although diffraction maxima due to basal planes are recorded, intense peaks due to MgO are also recorded and the situation is rather similar for sample C2-750R. The ^{27}Al MAS NMR spectra of these samples (Fig. 7) are similar and indicate the presence of up to 20% of four-coordinate Al. In the six-coordinate Al region a broad peak is seen along with a relatively sharp resonance from the rehydrated material.

Finally, for sample C2-1000R the diffraction diagram shows peaks due to the Mg,Al-carbonate LDH, MgO (periclase) and $MgAl_2O_4$ (spinel). In the region of four-coordinate Al the ^{27}Al MAS NMR spectrum of this sample (Fig. 7) displays three

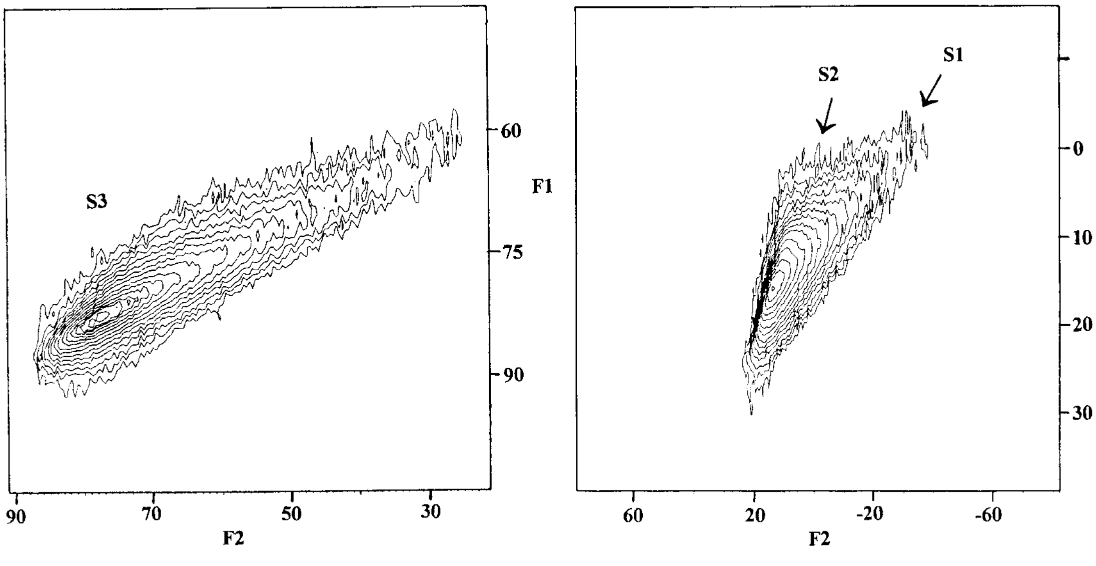

Fig. 4 Unsheared 3Q ^{27}Al MAS NMR spectrum of sample C2 calcined at 550 °C.

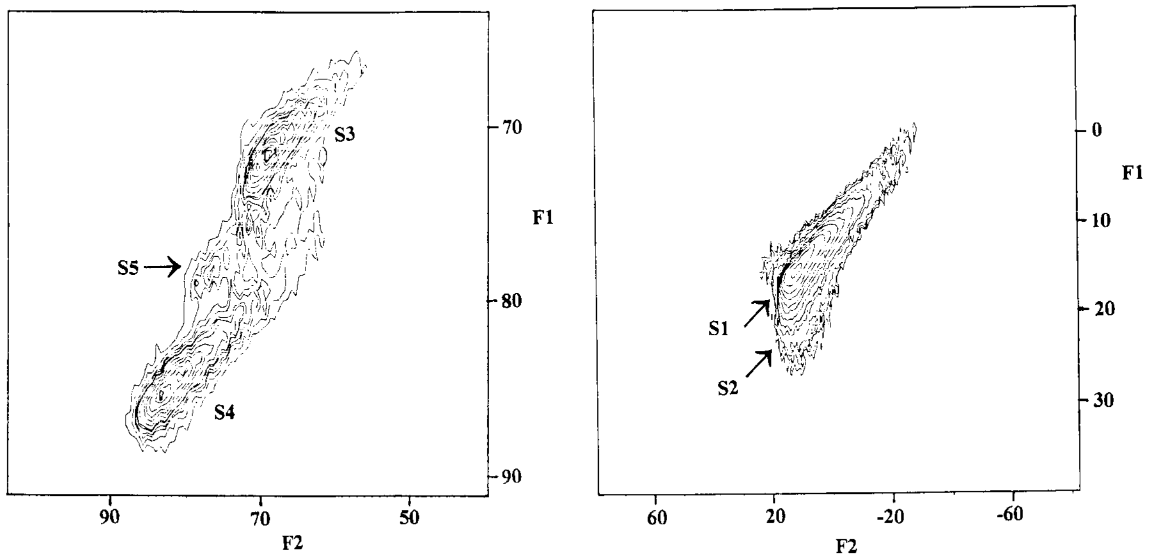

Fig. 5 Unsheared 3Q ^{27}Al MAS NMR spectrum of sample C2 calcined at 1000 °C.

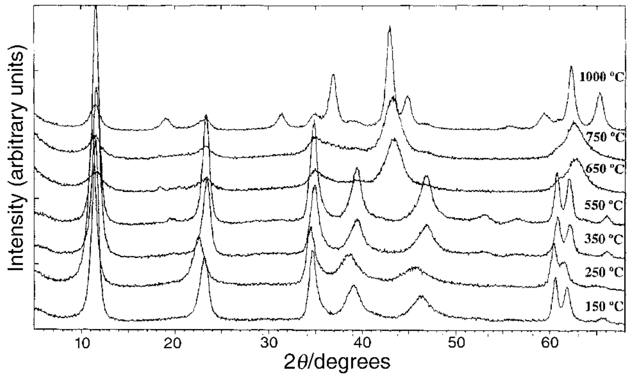

Fig. 6 PXRD patterns of the original C2 sample and materials calcined at the temperatures indicated and reconstructed for 24 h.

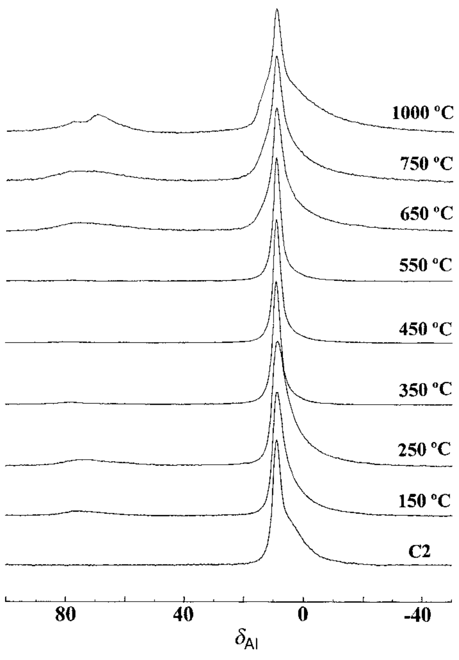

Fig. 7 ^{27}Al MAS NMR spectra of the original C2 sample and materials calcined at the temperatures indicated and reconstructed for 24 h.

peaks at similar positions as seen in the spectrum of the non-regenerated sample. The six-coordinate Al regions of the calcined and regenerated samples are, however, quite different. Similarly to parent C2, the regenerated sample shows a peak at δ *ca.* 9.1 with a low-frequency tail. This indicates that a certain amount of hydrotalcite has been regenerated.

The effect of the duration of the rehydration process has been also studied for samples calcined at high temperatures, where recovering of the layered structure was not complete after 24 h rehydration. The results are shown in Fig. 8. The behaviour shown by samples previously calcined at 650 and 750 °C was rather similar. Although the layered structure was not completely recovered after rehydration for 24 h, when rehydration was extended to 72 h, recovery of the layered structure was complete, with PXRD maxima corresponding exclusively to the LDH structure. However, when the sample had been previously calcined at 1000 °C, even after four days rehydration, diffraction maxima due to the spinel structure were still recorded. Fig. 9 shows PXRD diagrams corresponding to samples calcined at 1000 °C and rehydrated for one, three or four days. Reconstruction starts, as with samples calcined at lower temperatures, even after rehydration, but diffraction maxima due to MgO and $MgAl_2O_4$ are also recorded. When the rehydration time is increased, the intensities of the peaks due to the LDH phase increase. In addition, changes in the relative intensities of peaks due to MgO and the spinel can be observed. This is clearly shown in the inset in Fig. 9. The maximum at 2θ *ca.* 45° is due to planes (400) of the $MgAl_2O_4$ spinel, while the maximum at 2θ *ca.* 43° is

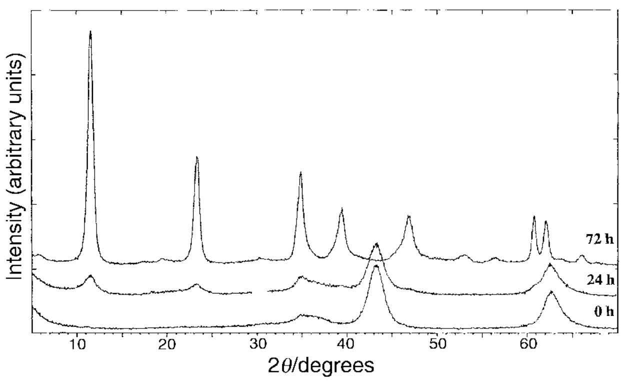

Fig. 8 PXRD patterns of the C2 sample calcined at 750 °C and reconstructed for the periods of time indicated.

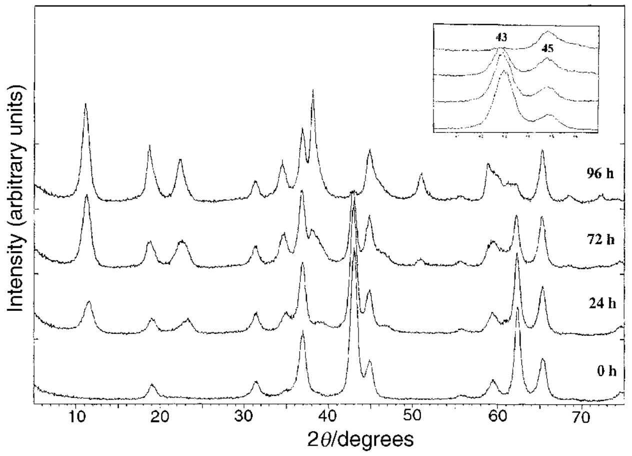

Fig. 9 PXRD patterns of sample C2 calcined at 1000 °C and reconstructed for the periods of time indicated. The inset depicts a 40–47° 2θ expansion of the patterns.

originated by planes (200) of MgO. As this inset shows, the peak due to the spinel remains unchanged during rehydration, while the peak due to MgO is progressively removed, probably because MgO is required to build the reconstructed LDH crystallites.

Conclusions

Calcination of hydrotalcite at increasing temperatures leads to migration of Al ions to tetrahedral sites, while the crystalline structure is progressively destroyed. When crystallization of MgO and spinel occurs, tetrahedral Al still remains in the solid. Upon rehydration with water vapour, the layered hydrotalcite structure is recovered, depending on the previous calcination temperature, as well as on the rehydration time at 25 °C. However, tetrahedral Al still exists in the solids for which PXRD shows a complete recovery of the hydrotalcite structure.

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