

SYNTHESIS AND SPECTROSCOPIC CHARACTERISATION OF DEUTERATED HYDROTALCITE

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Partly deuterated hydrotalcite, $Mg_6Al_2(CO_3)_3(OD, OH)_{16}.n(D_2O, H_2O)$ was prepared under carefully controlled conditions and characterised by infrared and Raman spectroscopy in order to come to a detailed assignment of the low wavenumber bands associated with M-O and M-OH/OD vibrational modes.

Layered double hydroxides, also known as hydrotalcites or anionic clays, play an important role in a number of industrial applications such as antacids, stabilisers in plastics, smoke and fire retardants, UV-stabilisers, filler, chloride scavenger, anion adsorbents and as catalyst or catalyst precursors [1]. Spectroscopic techniques including infrared and more rarely Raman spectroscopy have been regularly used to characterise these compounds. However, the assignment of the bands in the low wavenumber range is still a matter of debate. Especially the distinction between metal-hydroxyl and metal-oxygen bands is unclear. The way to solve this problem is to replace the hydrogen atoms by deuterium atoms resulting in a significant shift of all bands associated with the hydroxyl modes. Therefore this paper describes for the first time the synthesis of deuterated hydrotalcites and the characterisation of this material by infrared spectroscopy in comparison to normal hydrotalcites.

The hydrotalcite with theoretical composition of $Mg_6Al_2(OD)_{16}CO_3.nD_2O$ was synthesised according to the method described before by Kloprogge and Frost [2-4] for the normal hydrotalcite $Mg_6Al_2(OH)_{16}CO_3.nH_2O$. This method comprises the slow simultaneous addition of a mixed aluminium nitrate (0.25M)-magnesium nitrate (0.75M), aluminium nitrate (0.25M)-solutions in D_2O and a mixed NaOH (2.00M)- Na_2CO_3 (0.125M) solution in D_2O under vigorous stirring buffering the pH at approximately 10 and under a dry nitrogen atmosphere. The product was washed with D_2O to eliminate excess salt and dried at room temperature still under a dry nitrogen atmosphere. During this whole process extreme care was taken to exclude water from the system. Due to the fact that NaOH was used only partial deuteration has been achieved, but this is enough to enable one to identify the changes in the vibrational spectra.

In order to get a useful interpretation of the vibrational spectra of the layered double hydroxides it is necessary to apply factor group analysis. The vibrational modes of the hydroxyl groups in the LDH layers can be interpreted on the basis of the brucite ($Mg(OH)_2$) structure from which the LDH structure is derived by partial replacement of the Mg^{2+} cation by Al^{3+} . Both have a hexagonal symmetry with one formula unit per primitive cell. This leads to a space group of D_{3d} with $z=3/8$ [5] [6].

The whole vibrational representation including optically active modes will then be: $\Gamma_v = 10 A_{1g} + 5 A_{2g} + 15 E_g + 5 A_{1u} + 10 A_{2u} + 15 E_u$. The infrared active modes are thus represented by $\Gamma_{\text{vIR}} = 10 A_{2u} + 15 E_u$ and the Raman active modes by $\Gamma_{\text{vR}} = 10 A_{1g} + 15 E_g$. The remaining modes are not infrared or Raman active. The mode A_{1g} and A_{2u} represent the OH-stretching modes, E_g and E_u the corresponding librational modes and $A_{1g(T)}$, $A_{2u(T)}$, $E_{g(T)}$ and $E_{u(T)}$ the translational lattice modes. Based on the crystal structure of LDHs one can expect various OH-modes as each OH-group in the LDH layer is bonded to three metal cations. Therefore, theoretically one can expect an overlap of bands belonging to $3\text{Mg}^{2+}\text{-OH}$, $2\text{Mg}^{2+}\text{Al}^{3+}\text{-OH}$, $\text{Mg}^{2+}2\text{Al}^{3+}\text{-OH}$ and $3\text{Al}^{3+}\text{-OH}$, resulting in one broad band. However, based on the applied $\text{Mg}^{2+}\text{-Al}^{3+}$ substitution the last band will not be observed and the $\text{Mg}^{2+}2\text{Al}^{3+}\text{-OH}$ will be very weak or not observed at all [3].

The hydrotalcite samples were combined with oven dried spectroscopic grade KBr (containing approximately 1 wt% sample) and pressed into a disc under vacuum. No prior grinding was applied in order to prevent exchange of the deuterium due to exposure to moist in the atmosphere. The spectrum of the sample was recorded in triplicate by accumulating 512 scans at 4 cm^{-1} resolution between 400 cm^{-1} and 4000 cm^{-1} using the Perkin-Elmer 1600 series Fourier transform infrared spectrometer equipped with a LITA detector. For the Raman spectroscopic measurements the hydrotalcite samples were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objective lenses. No sample preparation was needed. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD as the detector. Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser (633 nm) at a resolution of 2 cm^{-1} in the range between 500 and 1500 cm^{-1} . Repeated acquisition using the highest magnification were accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. Spectral manipulation such as baseline adjustment, smoothing and normalisation of both the infrared and Raman spectra were performed using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

Fig. 1 shows the infrared spectra of both the normal and the partially deuterated hydrotalcites. Due to the fact that metal nitrates were used as starting materials during the synthesis a small amount of the interlayer carbonate has been replaced by nitrate. The presence of the nitrate is more pronounced in the IR spectrum of the deuterated sample as indicated in Table 1. Although not earlier reported in the literature the OH- or OD-groups in the hydroxide layers have a small effect on the interlayer anions in terms of spectroscopy.

Clearly visible is also the effect of partial deuteration on the OH-stretching bands in the region between 3600 and 3000 cm^{-1} , which are slightly shifted towards lower wavenumbers. A complex set of OD-stretching bands become visible in the range from 2300 to 2700 cm^{-1} . However, no bands of free D_2O are observed around 2671 , 1178 and 2788 cm^{-1} . Instead bands recognised at 2455 and 1633 cm^{-1} have to be ascribed to $\text{CO}_3^{2-}\text{-HOD}$ bridging and HOD bending modes due to partial exchange of

the hydrogen and deuterium in the interlayer water. Band component analysis indicate the presence of both three M-OH and three M-OD stretching bands which are ascribed to $\text{Mg}_3\text{-O(H,D)}$, $\text{Mg}_2\text{Al-O(H,D)}$ and $\text{MgAl}_2\text{-O(H,D)}$ with decreasing wavenumbers and decreasing intensity.

Till now the assignment of bands in the low wavenumber region has been a matter of debate. With the use of deuteration experiments a more detailed assignment can be achieved. In earlier work it has been shown that the replacement of OH by OD results in a significant shift to lower wavenumbers with on average a $\nu\text{OH}/\nu\text{OD}$ ratio in the range of 1.3-1.35 [7, 8]. Similar ratios are observed here for the deuteration of hydrotalcite. The M-OH deformation modes at 939 and 870 cm^{-1} are shifted to 711 and 627 cm^{-1} upon deuteration (ratios of 1.32 and 1.38). Interestingly a band remains visible at slightly higher wavenumber at 957 cm^{-1} , which has been interpreted as being due to incomplete deuteration, leaving an M-OH mode influenced by nearby OD-groups. The M-OH translation mode at 759 cm^{-1} shifted to 556 cm^{-1} upon deuteration (ratio of 1.36). The bands observed at 653 and 553 cm^{-1} overlap after deuteration with the bands associated with the M-OD deformation and translational modes. However, earlier work on lithium aluminate hydroxides and the deuteration of this compound indicates that these bands can be ascribed to M-O stretching modes [9]. The remaining band around 450 cm^{-1} can be ascribed to the corresponding O-M-O bending mode.

With the Raman spectra shown in Fig. 2 a comparison can be made between the partially deuterated hydrotalcites at 298 K and the normal hydrotalcites at 298 and 77 K. The band at 551 cm^{-1} visible in the normal hydrotalcites spectra has disappeared in the deuterated hydrotalcites spectrum suggesting that this band is associated with a hydroxyl mode. The 725 cm^{-1} band, which is split in two bands around 721 and 725 cm^{-1} at 77 K, is not affected by the deuteration and must therefore be associated with two overlapping metal-oxygen modes. The strong sharp band around 1068 cm^{-1} represents the ν_1 mode of the interlayer carbonate and is therefore not affected by the deuteration. The small band on the lower wavenumber site around 1044 cm^{-1} however shifts to 1060 cm^{-1} upon deuteration. In earlier work [3] this band was associated with a second type of carbonate probably on the outer surface. In that case interaction with adsorbed D_2O can explain the shift of 16 cm^{-1} . No clear OH- or OD-bands could be observed in the OH/OD-stretching region.

Acknowledgments

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References

1. M. K. TITULAER, J. B. H. JANSSEN and J. W. GEUS, *Clays Clay Miner.* **42** (1994) 249.
2. J. T. KLOPPROGGE and R. L. FROST, *Applied Catalysis A* **184** (1999) 61.
3. J. T. KLOPPROGGE and R. L. FROST, *Journal of Solid State Chemistry* **146** (1999) 506.
4. J. T. KLOPPROGGE and R. L. FROST, *Physical Chemistry, Chemical Physics* **1** (1999) 1641.

5. W. KAGUNYA, R. BADDOUR-HADJEAN, F. KOOLI and W. JONES, *Chemical Physics* **236** (1998) 225.
6. T. N. MOROZ and D. K. ARKHIPENKO, *Soviet Geology and Geophysics* **32** (1991) 52.
7. J. D. F. V. C. RUSSELL and B. VELDE, *Mineral. Mag* **37** (1970) 869.
8. U. JOHANSSON, A. HOLMGREN, W. FORSLING and R. FROST, *Analyst* **123** (1998) 641.
9. P. K. DUTTA and M. PURI, *Journal of Physical Chemistry* **93** (1989) 376.

Table 1 Infrared band positions (cm⁻¹) of normal and partially deuterated hydrotalcites

Normal hydrotalcite	Partially deuterated hydrotalcite	Assignment
3597	3565	"Mg ₃ "-OH stretching mode
3467	3436	"Mg ₂ Al"-OH stretching mode
3318	3245	"MgAl ₂ "-OH stretching mode
3063	2968	CO ₃ ²⁻ -H ₂ O bridging mode
	2561	"Mg ₃ "-OD stretching mode
	2535	"Mg ₂ Al"-OD stretching mode
	2500	"MgAl ₂ "-OD stretching mode
	2455	CO ₃ ²⁻ -HOD bridging mode
	1764	Combination mode?
1642	1645	H ₂ O OH bending mode
	1633	HOD OH bending mode
1401	1385	ν_{3a} CO ₃ ²⁻
1365	1384	ν_3 CO ₃ ²⁻ and minor ν_3 NO ₃ ⁻
	1326	minor ν_3 NO ₃ ⁻
1012	1048	ν_1 CO ₃ ²⁻ and minor ν_1 NO ₃ ⁻
	957	M-OH deformation mode*
939		M-OH deformation mode
870	864	M-OH def and ν_2 CO ₃ ²⁻
	833	ν_2 CO ₃ ²⁻
	825	ν_2 NO ₃ ⁻
759		M-OH translation mode
	711	M-OD deformation mode
667		ν_4 NO ₃ ⁻
653		ν_4 CO ₃ ²⁻
635		M-O stretching mode
	627	M-OD deformation mode
553		M-O stretching mode
	556	M-OD translation mode
450	464	O-M-O bending mode

* M = Mg or Al

Figure Captions,

Figure 1. Infrared spectra of normal Mg/Al-hydrotalcite (bottom) and its partially deuterated equivalent (top)

Figure 2. Raman spectra in the region between 500 and 1125 cm^{-1} of normal Mg/Al-hydrotalcite at 293 K (top), at 77 K (middle) and after partial deuteration (bottom).

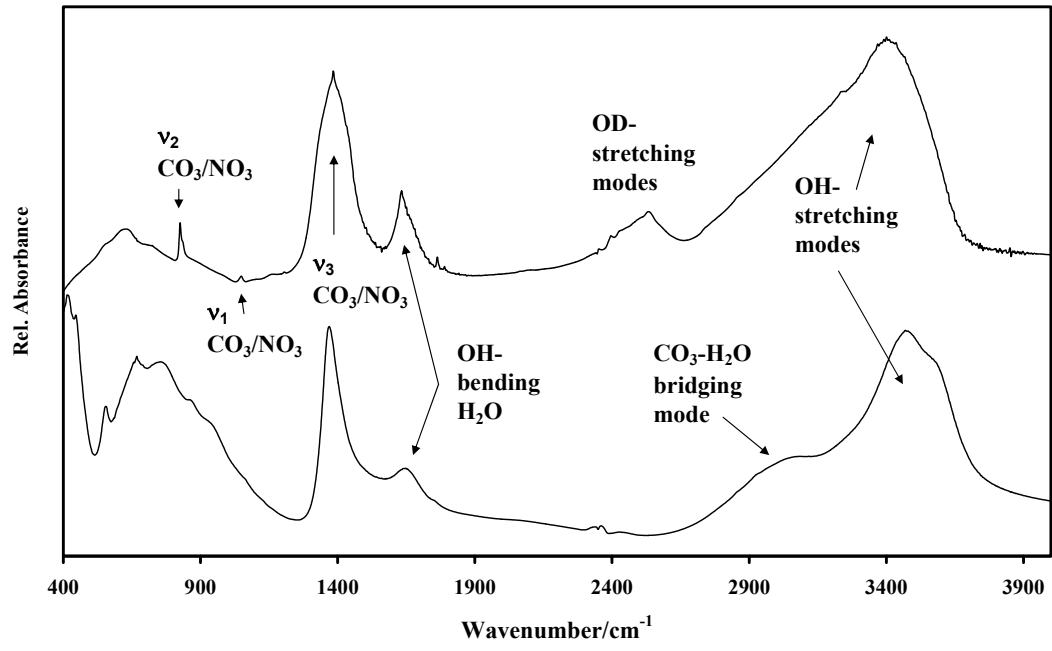


Fig. 1

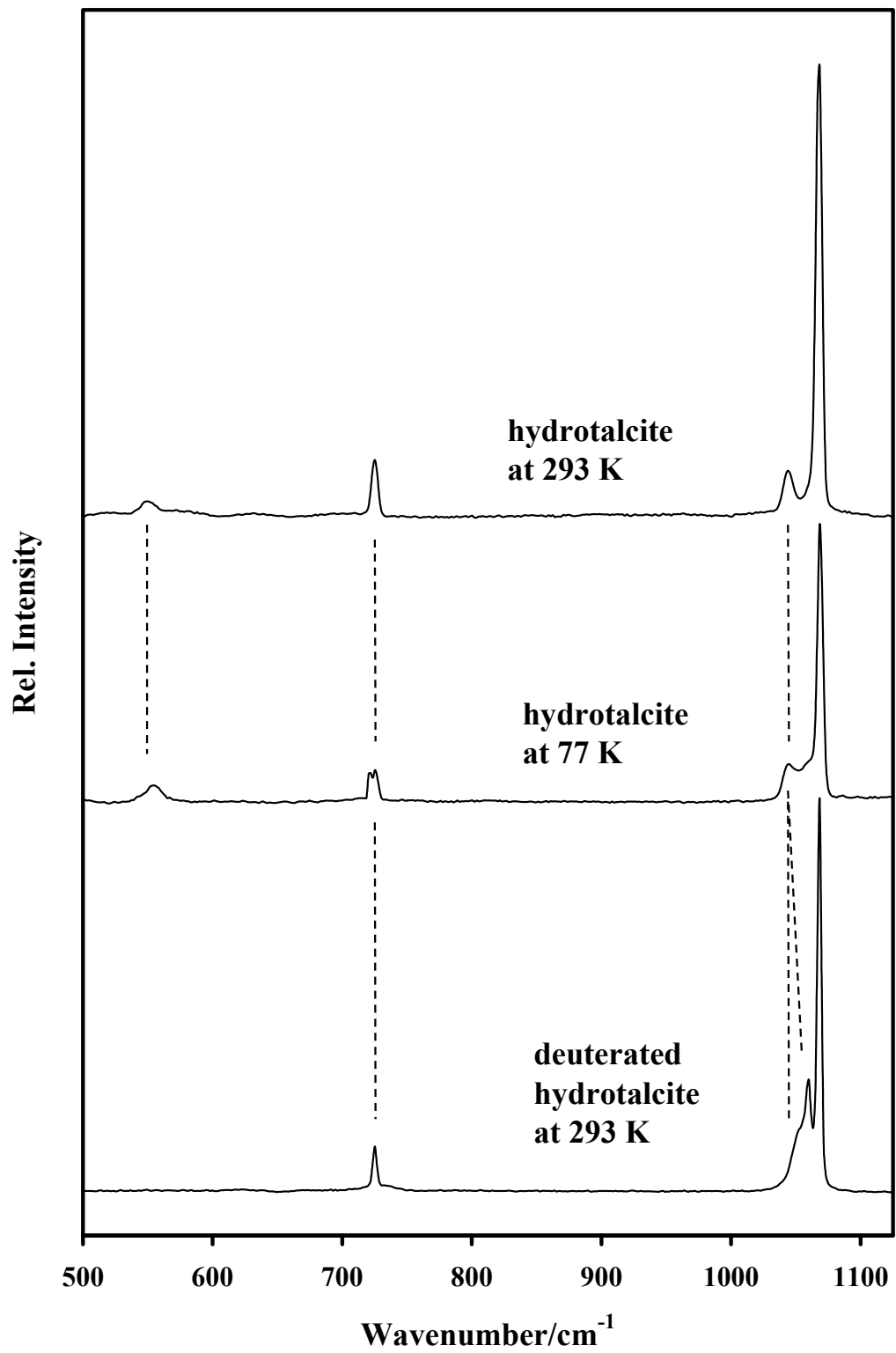


Fig. 2