

New Synthetic Routes to Hydrotalcite-Like Compounds – Characterisation and Properties of the Obtained Materials

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Hydrotalcite-like anionic clays of general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[CO_3^{2-}]_{x/2}^{x-} \cdot m H_2O$ with $M(III) = Al$ and $M(II) = Mg, Ni, Zn$ have been prepared by precipitation of the hydroxycarbonates from the “homogeneous” solution after the thermally induced hydrolysis of urea. The effect of the temperature of precipitation, of the total metal cations concentration, of the molar fraction $M(III)/M(III) + M(II)$ and of the molar fraction urea/ $M(II) + M(III)$ in solution on the composition and on the crystallinity degree of the samples has been investigated. The optimum conditions are reported to obtain micro-crystalline powders with a narrow distribution of particle size in a short time with a simple procedure. The compounds obtained have been characterised for chemical composition, thermal behaviour, particle-size distribution and

BET-surface area. In addition, the crystal structure of $Mg_{0.67}Al_{0.33}(OH)_2(CO_3)_{0.165} \cdot 0.4 H_2O$ has been refined by X-ray diffraction powder methods. The carbonate form has been converted into the chloride form by letting gaseous HCl flow over the hydrotalcite-like compounds, heated at 150 °C. The exchange of Cl^- anions with some alkoxide anions in the presence of the respective alkanols has been investigated. The exchange reaction was driven by the segregation of NaCl crystals poorly soluble in alkanols and led to the co-intercalation of the alkoxide ions together with the alkanol with the formation of a bi-layer of extended alkyl chain in the interlayer region of the Mg-Al hydrotalcite. The intercalation compound, washed with water, produces a hydrotalcite with Cl^- and OH^- as balancing anions.

Hydrotalcite-like compounds (HTlc) form, at present, a large class of inorganic materials, extensively studied as catalysts, precursors and supports of catalysts, anionic exchangers, sorbents, additives^{[1][2][3][4][5]}. Furthermore, the HTlc are, practically, the only known family of layered solids with positively charged layers and interlayered charge balancing anions that may be replaced by ion-exchange processes. The structure of HTlc originates from the packing of layers built up in a manner similar to that found in brucite, the naturally occurring $Mg(OH)_2$. In this mineral, the Mg atoms are octahedrally co-ordinated by six oxygen atoms belonging to six OH groups; each OH group is, in turn, shared by three octahedral cations and points to the interlayer space^[6]. When some of the Mg(II) cations are isomorphously replaced by Al(III) cations, carbonate anions are inserted between the metal hydroxide sheets to maintain the electroneutrality and the mineral hydrotalcite, with ideal formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, is obtained^[7]. Hydrotalcite and hydrotalcite-like minerals are rare in nature but it is relatively simple and cheap to prepare these compounds on a laboratory scale.

The general formula of synthetic HTlc is often written as $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A^{n-}]_{x/n}^{x-} \cdot m S$, where $M(II)$ may be Mg, Zn, Co, Ni, Mn, etc.; $M(III)$ may be Al, Cr, Fe, V, Co, etc.; A^{n-} is the charged compensating anion (CO_3^{2-} , SO_4^{2-} , Cl^- , NO_3^- , organic anions, etc.); m the number of mols of co-intercalated solvent (S), generally water, per for-

mula weight of compound. The number of mols x of $M(III)$ cation per formula weight of compound, generally ranges between 0.2 and 0.33, and its value determines the charge density of the layer^{[3][4]}.

Most of the synthetic HTlc are prepared by co-precipitation of the chosen $M(II)$ and $M(III)$ hydroxides with diluted NaOH and/or $NaHCO_3$ or Na_2CO_3 solutions. Poorly crystalline samples are generally obtained, unless a low degree of supersaturation and a relatively high temperature are maintained during precipitation. However, to obtain well-crystallised samples a hydrothermal treatment, i.e. digestion of the gel at 180–200 °C under pressure, is often required^{[1][4]}. In an attempt to prepare HTlc with a good degree of crystallinity using simpler methods, we turned our attention to methods known as precipitation from “homogeneous” solutions and found that the hydrolysis of urea in the presence of a mixture of $M(II)$ and $M(III)$ salts leads to the formation of HTlc with good crystallinity degree and a narrow distribution of particle size. This result is rather surprising since research papers and quantitative analysis textbooks^{[8][9]} recommend the urea method for precipitating aluminium in the presence of magnesium.

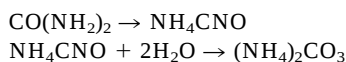
This paper describes the preparative conditions of some HTlc anionic clays by the urea method, the physico-chemical characterisation of the products thereby obtained, and the preparation of some intercalation compounds with alkoxides. In addition, a novel method to convert the carbon-

ate form of HTlc into the chloride form, by gas-solid reaction is reported.

Results

Preparation of the Hydrotalcite-Like Compounds

Urea has a number of properties that makes its use as an agent for precipitation from "homogeneous" solution very attractive and it has long been used in gravimetric analysis to precipitate several metal ions as hydroxides or as insoluble salts when in the presence of a suitable anion^[9]. Urea is a very weak Brønsted base ($pK_b = 13.8$), highly soluble in water, and its hydrolysis rate may be easily controlled by controlling the temperature of the reaction. According to Shaw and Bordeaux^[10] the mechanism of hydrolysis consists of the formation of ammonium cyanate, as the rate-determining step, and the fast hydrolysis of the cyanate to ammonium carbonate, i.e.:



The rate constant increases by about 200 times when the temperature is increased from 60 to 100°C. The hydrolysis of ammonium to ammonia and carbonate to hydrogen carbonate gives a pH of about 9, depending on the temperature. This pH is suitable for precipitating a large number of metal hydroxides.

After some preliminary positive tests, a wider investigation was undertaken to find the optimal conditions to produce, with a simple procedure, HTlc microcrystals of uniform size, well crystallised, and with the required stoichiometry. The following couples of cations, as chlorides, were considered: Mg(II)-Al(III); Zn(II)-Al(III); Ni(II)-Al(III). In the case of Zn(II), a weighed amount of ZnO was dissolved in a stoichiometric amount of 6 mol/dm³ HCl solution.

Solid urea was added to 0.5 mol/dm³ metal chloride solutions, having molar fraction $M(\text{III})/M(\text{III}) + M(\text{II})$ equal to 0.33, until the molar ratio $\text{urea}/M(\text{II}) + M(\text{III})$ reached the value 3.3. The clear solutions were heated, under stirring, at temperatures between 60 and 100°C. As expected, longer precipitation times were observed for the lower temperatures. However, all the materials showed XRPD patterns typical of hydrotalcite-like compounds. A preliminary rough analysis of the variation of the crystallinity degree as a function of the precipitation temperature was made on the basis of the quality of the X-ray diffraction patterns of the samples, that is the number of reflections, their intensity and width at half-height. The results shown in Table 1 (see also Figure 1) indicate that hydrotalcite-like compounds with a good crystallinity degree were obtained in the 90–100°C temperature range after 24–36 h of precipitation.

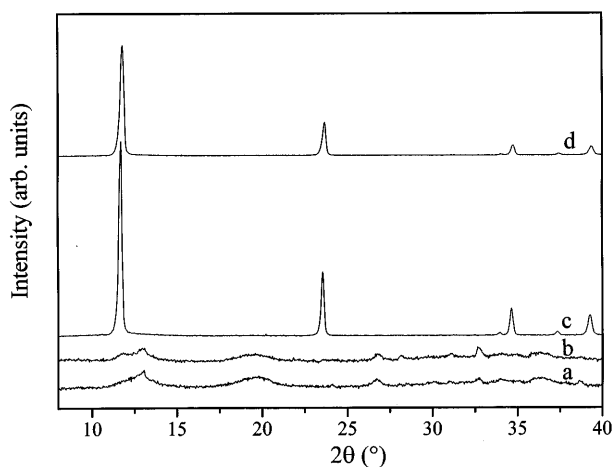
Further characterisation was performed taking into account the preparation of the Mg-Al HTlc, maintaining the temperature at 100°C and the precipitation time at 36 h. Table 2 reports the composition, expressed as a molar fraction in the solid, $X_{\text{sol}} = \text{Al}(\text{III})/[\text{Al}(\text{III}) + \text{Mg}(\text{II})]$, and the crystallinity degree of several samples, as a function of the

Table 1. Effect of the temperature and time of precipitation on the crystallinity degree of the indicated HTlc's; conditions of precipitation: total metal ion concentration: 0.5 mol/dm³; molar fraction $M(\text{III})/M(\text{II}) + M(\text{III}) = 0.33$; molar fraction $\text{urea}/M(\text{II}) + M(\text{III}) = 3.3$

Precipitation		Crystallinity degree of the indicated HTlc ^[a]		
<i>T</i> [°C]	<i>t</i> [h]	Al-Mg	Al-Zn	Al-Ni
60	360	vl	vl	l
75	72	l	l	g
90	48	vg	vg	g
100	36	g	g	g

^[a] g = good; l = low; v = very.

Figure 1. XRPD patterns of the Zn-Al-HTlc precipitated by urea hydrolysis at (a) 60°C, (b) 75°C, (c) 90°C, and (d) 100°C; the time of digestion is reported in Table 1



total concentration of the cations, of their molar fraction in solution and of the urea/Al(III) + Mg(II) molar fraction. The data of Table 2 show that the variation of the indicated parameters does not markedly affect the crystallinity degree of the samples, even though the most crystalline samples were obtained at values of the urea/Al(III) + Mg(II) fraction close to 4 and at a value of the total metal ion concentration of 0.5 mol/dm³. Temperature seems to be the most important parameter to control in order to produce well crystallised samples.

It is interesting to note that the molar fraction $\text{Al}(\text{III})/[\text{Al}(\text{III}) + \text{Mg}(\text{II})]$ of the solids reaches values near to 0.32 even when the corresponding values in solution are as low as 0.2. As already discussed, the precipitation of the HTlc occurs at pH values of 8.5–9.0 (the hydrolysis pH of ammonium carbonate) and at these pH values the solubility of magnesium hydroxide is much higher than that of aluminium hydroxide. Therefore almost all the aluminium is co-precipitated with the magnesium ions to obtain a solid with the stoichiometry of two Mg(II) for each Al(III). This corresponds to an ideal disposition in the brucite-like sheet of each aluminium atom surrounded by six magnesium atoms. In general, the Al(III) molar fraction in the solid is higher than that in solution and it is possible to reach val-

Table 2. Effect of the total metal ion concentration, of the molar fractions Al(III)/Al(III) + Mg(II) and urea/Al(III) + Mg(II) on the crystallinity degree and of the composition of Mg-Al-HTlc; temperature and precipitation time were 100 °C and 36 h, respectively

Metal ion conc. [mol/dm ³]	Solution			Solid	
	Molar fraction Al(III)/Al(III)+Mg(II)	Molar fraction urea/Al(III)+Mg(II)	Molar fraction Al(III)/Al(III)+Mg(II)	Molar ratio CO ₃ ²⁻ /Al(III)	Crystallinity degree ^[a]
0.1	0.33	3.3	0.36	—	l
0.5	0.20	4	0.32	—	fg
0.5	0.25	2	0.41	—	g
0.5	0.25	3.3	0.32	0.5	vg
0.5	0.25	4	0.34	0.49	m
0.5	0.33	2	0.38	—	g
0.5	0.33	3.3	0.34	0.5	vg
0.5	0.33	4	0.35	0.5	vg
0.5	0.33	6	0.36	0.5	m
0.5	0.40	4	0.40	0.48	vg
1	0.33	3.3	0.36	—	—

^[a] g = good; m = medium; l = low; f = fairly; v = very.

ues near to 0.44 value, indicated by Pausch et al.^[11] as the maximum for a pure HTlc.

However, in order to prove the absence of co-precipitated Al(OH)₃ in the samples, the molar ratio CO₃²⁻/Al³⁺ in the solid was determined. In all cases the molar ratio CO₃²⁻/Al³⁺ in the solid was found to be near to 0.5 (see Table 2), as expected for pure HTlc and we may exclude the presence of co-precipitated aluminium hydroxide.

Therefore, the urea-method is not indicated for the preparation of Mg-Al HTlc with low charge density but allows the preparation of compounds with high charge density not easily obtainable with the other proposed procedures^[4]. However, if the M(II) hydroxide is much more insoluble than the Mg(OH)₂, the HTlc obtained has a composition very near to that predicted from the composition of the solution. This is the case, for example, for the Zn-Al and Ni-Al systems. As may be seen from the data of Table 3 the Al molar ratio in the solid was found to be very near to that of the precipitating solutions.

Table 3. Effect of the metal ion concentration on the crystallinity degree and on the composition of Zn-Al-HTlc and Ni-Al-HTlc; conditions of precipitation: total metal ion concentration 0.5 mol/dm³, molar fraction urea/M(II) + Al(III) = 3.3, temperature and time 100 °C and 36 h

Molar fraction in solution Al(III)/Al(III) + M(II)	Molar fraction in the solid Al(III)/Al(III) + M(II)	Crystallinity degree ^[a]
M(II) = Zn		
0.20	0.23	g
0.25	0.28	g
0.33	0.35	vg
0.40	0.37	g
M(II) = Ni		
0.25	0.27	g
0.33	0.31	g

^[a] g = good; v = very.

At the end of this investigation, we suggest the following simple procedure to obtain HTlc with a good crystallinity degree in a relatively short time. Solid urea is dissolved in a solution 0.5 mol/dm³ in the chosen metal chlorides, [mo-

lar ratio M(III)/M(II) + M(III) equal to 0.33 M(III) = Al; M(II) = Mg or Ni or Zn], to reach urea/metal ions molar ratio of 3.3. The clear solution is maintained at 100 °C, or even at the refluxing temperature, for 36 h. If the digestion time is prolonged, the crystallinity degree of the samples is slightly improved. The solids, separated from the solution, are washed with distilled water up to a negative test for chloride ions. Finally, they are air-dried and stored in a desiccator with P₄O₁₀ at room temperature.

Physico-Chemical and Structural Characterisation

Empirical formula and water content were determined by thermoanalytical methods. Specific surface-area and particle-size distributions of selected samples were also measured. The crystallographic parameters of a well-crystallised Al-Mg HTlc were obtained from X-ray powder diffraction patterns.

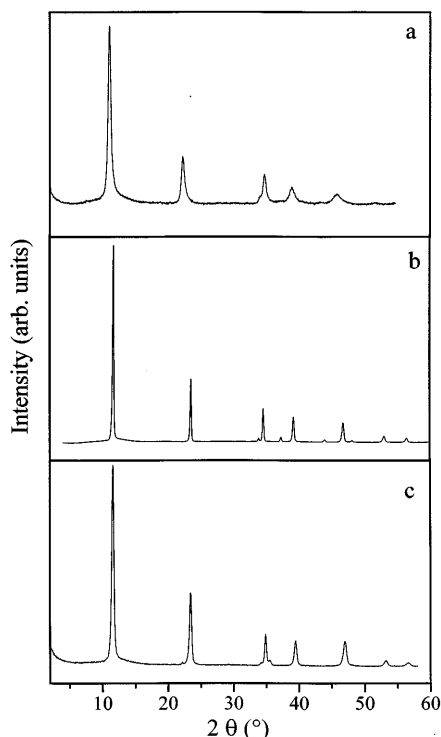
Table 4 collects the data of composition, interlayer distance and B.E.T. specific surface area. The XRPD patterns of these samples are reported in Figure 2.

Table 4. Composition, interlayer distance and B.E.T. specific surface area for HTlc obtained by urea hydrolysis; conditions of precipitation: total metal ion concentration 0.5 mol/dm³, molar ratio urea/M(II) + Al(III) = 3.3, temperature and time 100 °C and 36 h

M(II)-M(III)- HTlc	Composition	<i>d</i> [Å]	Surface area [m ² /g]
Mg-Al			
	[Mg _{0.67} Al _{0.33} (OH) ₂](CO ₃) _{0.165} · 0.48 H ₂ O	7.57	24.1
Zn-Al			
	[Zn _{0.65} Al _{0.35} (OH) ₂](CO ₃) _{0.175} · 0.48 H ₂ O	7.55	24.9
Ni-Al			
	[Ni _{0.69} Al _{0.31} (OH) ₂](CO ₃) _{0.155} · 0.76 H ₂ O	7.98	47.4

Figure 3 shows the coupled TG-DTA curves of the Al-Mg and Al-Ni HTlc. The shape of the curves reflects the good crystallinity degree of the samples and, in both cases, the curves may be divided into two well-differentiated main regions. In the first one, ranging from 80 to 250 °C there is a broad endothermic peak related to the dehydration of the

Figure 2. XRPD patterns of the HTlc obtained by urea hydrolysis: (a) $[\text{Ni}_{0.69}\text{Al}_{0.31}(\text{OH})_2(\text{CO}_3)_{0.155} \cdot 0.76 \text{ H}_2\text{O}]$; (b) $[\text{Zn}_{0.65}\text{Al}_{0.35}(\text{OH})_2(\text{CO}_3)_{0.175} \cdot 0.48 \text{ H}_2\text{O}]$; (c) $[\text{Mg}_{0.66}\text{Al}_{0.34}(\text{OH})_2(\text{CO}_3)_{0.17} \cdot 0.48 \text{ H}_2\text{O}]$; conditions of precipitation: total metal ion concentration 0.5 mol/dm^3 , molar ratio $\text{urea}/\text{M(II)} + \text{Al(III)} = 3.3$, temperature and time 100°C and 36 h



samples. The second region, corresponds to the weight loss due to the dehydroxylation and de-carbonation reactions, that, as discussed by Rey et al., overlap in this temperature range^[12]. The XRD patterns of the samples heated at 1000°C show the typical reflections of MgO (or NiO) and of the MgAlO_2 (or NiAlO_2).

Figure 4 shows the cumulative particle-size distribution of the Mg-Al HTlc. It shows that more than 90% of particles have a diameter between 10 and $0.5 \mu\text{m}$. The microcrystals are well formed and appear as hexagonal platelets, as shown in the SEM photograph (Figure 5).

Having at our disposition microcrystalline powders of good crystallinity degree, attempts were done to use the Rietveld method to refine the Al-Mg HTlc structure. Accurate positions of XRPD maxima were first determined by a peak-fitting procedure, using a pseudo Voigt function for the peak-profile description. The pattern was then indexed by the TREOR program^[13] using the first 18 peaks. The parameters of the hexagonal cell found were $a = 3.044 \text{ Å}$, $c = 22.703 \text{ Å}$ [$M(18) = 35$] in good agreement with those already known^[6]. All the reflection indexes followed the $-h + k + l = 3n$ rule, in agreement with the expected $R\bar{3}m$ space group. The Rietveld refinement was then carried out by the GSAS program^[14] using, as starting model, the structural parameters reported in ref.^[7]. The refinement included a 5-terms Fourier cosine series function for the background and a modified pseudo Voigt peak-profile function. March-Dollase correction was employed to model

Figure 3. TG (solid line) and DTA (dashed line) curves of (a) Al-Mg-HTlc and (b) Al-Ni-HTlc previously equilibrated over P_4O_{10} ; heating rate 5°C/min , air-flow 30 ml/min

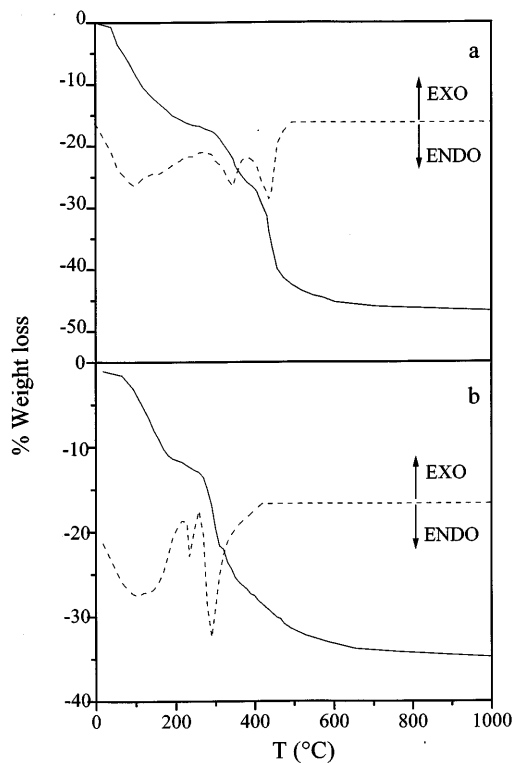
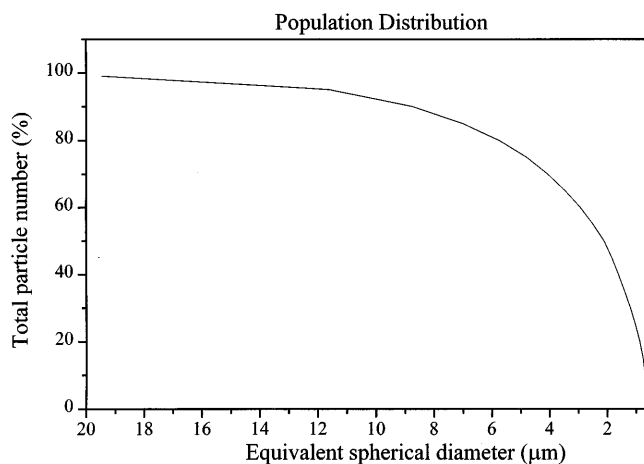
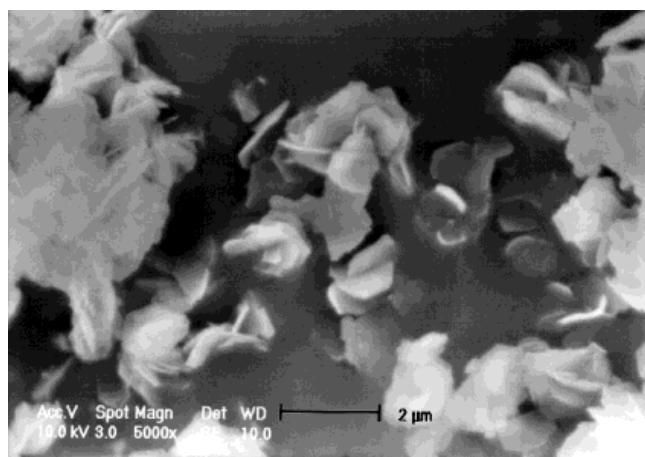


Figure 4. Population distribution as a function of equivalent spherical diameter for microcrystals of Al-Mg-HTlc

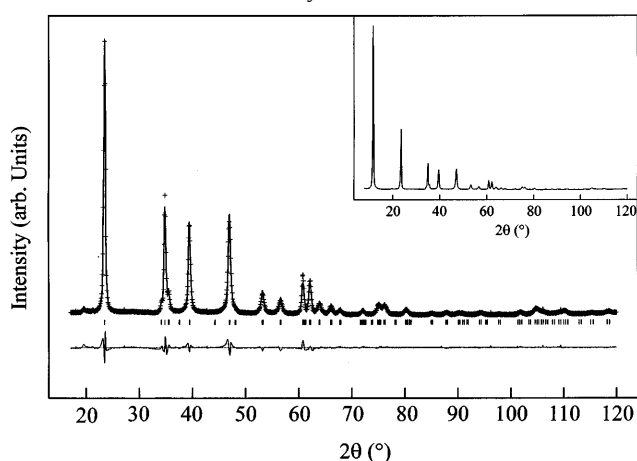


the preferred orientations. No corrections were made for absorption effects. The 003 reflection was not included in the refinement because of its strong asymmetry. When the refinement was stopped, the shifts in all the refined parameters were less than their estimated standard deviations, and the following residual values were reached: $wRp = 8.7\%$; $Rp = 6.6\%$; $R_F = 4.4\%$. A difference Fourier map calculated at this stage, did not reveal any peak larger than 0.5 electron density units. The Rietveld plot is shown in Figure 6. The atomic parameters and main geometrical data ob-

Figure 5. SEM micrograph of Al-Mg-HTlc microcrystals



tained for $\text{Mg}_{0.67}\text{Al}_{0.33}(\text{OH})_2(\text{CO}_3)_{0.165} \cdot 0.4 \text{ H}_2\text{O}$ are reported in Tables 5, 6, and 7. They are in good agreement with those already published^[7].

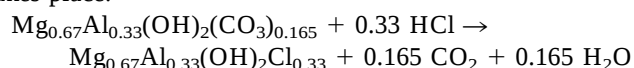
Figure 6. Experimental (+), calculated (–) and difference (lower) profiles for the $[\text{Mg}_{0.67}\text{Al}_{0.33}(\text{OH})_2(\text{CO}_3)_{0.165} \cdot 0.4 \text{ H}_2\text{O}]$ microcrystalsTable 5. Crystallographic data for $[\text{Mg}_{0.67}\text{Al}_{0.33}(\text{OH})_2(\text{CO}_3)_{0.165} \cdot 0.48 \text{ H}_2\text{O}]$

Formula	$\text{Mg}_{0.67}\text{Al}_{0.33}\text{O}_{2.975}\text{C}_{0.165}\text{H}_{2.96}$
Formula weight	234.7
Crystal system	trigonal
Space group	$R\bar{3}m$
<i>a</i> [Å]	3.04535(9)
<i>b</i> [Å]	3.04535(9)
<i>c</i> [Å]	22.7010(13)
α [°]	90
β [°]	90
γ [°]	120
<i>V</i> [Å ³]	182.327(13)
<i>Z</i>	3
<i>d</i> _{calcd.} [g/cm ³]	2.137
<i>R</i> _{wp}	0.1037
<i>R</i> _p	0.0798
<i>R</i> _F	0.0556
χ	3.51

Chemical Reactivity

A large research program, involving the ion-exchange properties, the interlayer reactivity, the storage in the interlayer region and subsequent release of species of pharmacological and biological interest has been undertaken to study the chemical reactivity of the HTlc, prepared by the urea method. Here we report new methods to convert the HTlc in the Cl^- and OH^- forms. These exchanged forms are commonly considered^[4] the best precursors to intercalate other charged and neutral species even of large dimensions.

The carbonate anions fit well in the hexagonal arrangement of the hydroxy ions of the brucite-like sheets, and this accounts for their high affinity for HTlc^[1]. The exchange of carbonate for others anions (Cl^- , NO_3^- , SO_4^{2-}) is then performed by treating the solid with diluted solutions of the corresponding mineral acid^[15]. The exchange reaction is driven by the release of gaseous CO_2 , but a concomitant slight dissolution of the solid can take place. To avoid these effects we used the gas-solid exchange reactions already employed to convert layered zirconium phosphate into some salt forms^[16]. We passed a stream of water vapour and gaseous HCl through Mg-Al- CO_3 HTlc maintained at 140–160°C in a glass tube. At these temperatures Mg-Al- CO_3 HTlc has a very small CO_2 vapour pressure^[17] and in the presence of hydrochloric acid the following reaction takes place:



After preliminary positive tests, the procedure was optimised as follows: 1 g of Mg-Al CO_3 HTlc was heated at 150°C in a glass tube for one hour. A stream of N_2 , passed through a 6 mol/dm³ HCl solution at a flux of about 40 ml/min, was allowed to flow over the sample for 8 h. From time to time the presence of CO_2 was monitored by bubbling the escaping gas in barite solution. When the $\text{Ba}(\text{OH})_2$ solution was clear, the heating was stopped and the sample recovered. Ion-chromatography analysis showed that the conversion was completed and the XRPD patterns (see Figure 7) showed that the material maintained a good crystallinity degree.

It is well known that Mg-Al HTlc may be obtained in the OH^- form taking advantage of the so-called “memory effect”^[12]. According to this method, hydrotalcite in carbonate form is first heated to 400–450°C, the mixture of metal oxides thus obtained is then dispersed in water and reconstruction of the layered structure occurs, the positive charges being balanced by the OH^- . Alternatively, the chloride ions of Mg-Al-Cl HTlc may be replaced by hydroxide ions by equilibrating the solid with a diluted NaOH solution. A slight dissolution of the solid may also occur. However, in both cases a loss in crystallinity degree of the samples is observed.

Searching for methods that would lead to hydrotalcites in hydroxy form, in the cases in which they do not show the “memory effect” or when it is difficult to perform the ion exchange process in water, we considered the exchange of Cl^- for alkoxide ion in alkanol media. The alkoxide

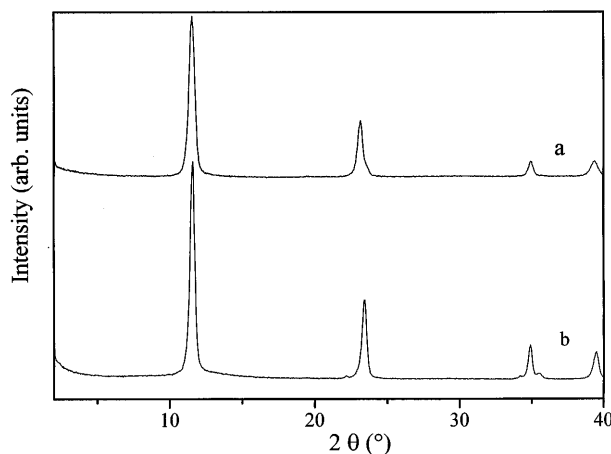
Table 6. Positional and thermal parameters for $[\text{Mg}_{0.67}\text{Al}_{0.33}(\text{OH})_2](\text{CO}_3)_{0.165} \cdot 0.48 \text{H}_2\text{O}$

Name	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	100 U_{iso} [$\text{\AA}^2$] ^[a]	Occupancy
Mg	0.0	0.0	0.0	1.37(6)	2/3
Al	0.0	0.0	0.0	1.37(6)	1/3
O(1)	0.0	0.0	0.37631(10)	2.66(9)	1
O(2)	0.1075(10)	−0.1075(10)	0.50034(48)	1.98(22)	1/6
C	1/3	2/3	0.5003(5)	5.3(11)	1/12
H(1)	0.0	0.0	0.4220(17)	8.2(13)	1
H(2)	1/3	2/3	0.5006(5)	8.2(13)	1/2

^[a] U_{iso} = mean square displacement, $B_{\text{iso}} = 8\pi^2 U_{\text{iso}}$.

Table 7. Selected interatomic distances and angles for $[\text{Mg}_{0.67}\text{Al}_{0.33}(\text{OH})_2](\text{CO}_3)_{0.165} \cdot 0.48 \text{H}_2\text{O}$

Distances [$\text{\AA}$]	
Mg,Al–O(1)	2.0107(11)
O(1)–O(1) across the layer	2.6264(34)
O(1)–O(2)	2.857(11)
C–O(2)	1.191(5)
Angles [$^\circ$]	
O(1)–Mg,Al–O(1)	98.45(7)
O(1)–Mg,Al–O(1)	81.55(7)
O(2)–C–O(2)	119.980(27)

Figure 7. XRPD patterns of Mg-Al-Cl-HTlc obtained by streaming gaseous HCl through Mg-Al-CO₃-HTlc (a); the pattern of the parent compound is reported for comparison (b)

form, treated with water, would immediately give rise to the hydroxide form. Furthermore, it was of interest to see whether bases stronger than the OH^- , would be stabilised in the interlayer region of the hydrotalcites.

One gram of $\text{Mg}_{0.67}\text{Al}_{0.33}(\text{OH})_2\text{Cl}_{0.33}$, prepared as above, and dehydrated at 150°C , was equilibrated in 100 cm^3 of ROH containing 0.1 mol/dm^3 of RONa ($\text{R} = n\text{C}_3\text{H}_7$, $n\text{C}_4\text{H}_9$, $n\text{C}_5\text{H}_{11}$, $n\text{C}_6\text{H}_{13}$) for two days at room temperature. The solid was separated from the solution by centrifuging under N_2 . The equilibrating solution did not contain an appreciable amount of Cl^- ions as though the ion exchange process had not taken place. The XRPD patterns of the solid samples, still wet with the alkanol solution, showed indeed a large shift of the first diffraction maxima towards low angles, indicating that an intercalation process had occurred. Figure 8 shows the XRPD patterns of the sample

treated with sodium butoxide in *n*-butanol. Two sharp reflections at $2\Theta = 27.25^\circ$ and 31.47° , typical of cubic NaCl, are present. The exchange Cl^-/RO^- has indeed occurred, driven by the segregation of NaCl crystals, insoluble in alkanols.

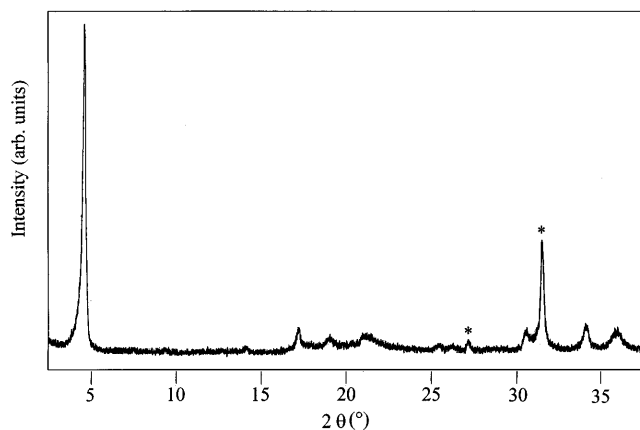
Figure 8. XRPD patterns of the Mg-Al-Cl-HTlc equilibrated with 0.1 mol/dm^3 sodium butoxide in *n*-butanol; the peaks of NaCl microcrystals are marked by an asterisk

Figure 9 shows the interlayer distance of the alkoxide-exchanged HTlc as a function of the number of carbon atoms in the alkyl chain. Note that the intercept is close to the value of the interlayer distance of the compound in OH form, while the increment of the interlayer distance for each additional carbon atom, $2.3 \text{ \AA}/\text{carbon atom}$, is consistent with the presence of a bi-layer of alkyl chain in the interlayer region. Since the cross-sectional area of a *trans-trans*-alkyl chains is estimated to be $18.6 \text{ \AA}^2$ ^[18] and the free area surrounding each positive charge on one side of the layer is $48 \text{ \AA}^2$, the interpenetration of the alkyl chain of the alkoxide ions interacting with the two facing sides of the lamellae was expected to produce a monolayer similar to that depicted in Figure 10 and found in the intercalation of *n*-alkyl carboxylate anions^[2]. The formation of the bi-layer may be explained by the fact that the Cl^-/RO^- exchange occurs in ROH media and that the alkanol molecules are co-intercalated to produce a bi-layer similar to the one shown in Figure 11. Treating the alkoxide-exchanged HTlc with water, we observed a partial washing of the NaCl crystals and a sudden increase of the pH of the washing solution. In the presence of water, the RO^- is readily transformed into the corresponding ROH and the OH^- assumes the role of bal-

ancing charge. No variation of the pH of the solution should occur. In the presence of Cl^- ions, however, some Cl^-/OH^- exchange takes place and the pH increases.

Figure 9. Interlayer distance of Mg-Al-HTlc exchanged with alkoxide ions in the presence of the corresponding *n*-alkanols as a function of the number of carbon atoms in the *n*-alkyl chain

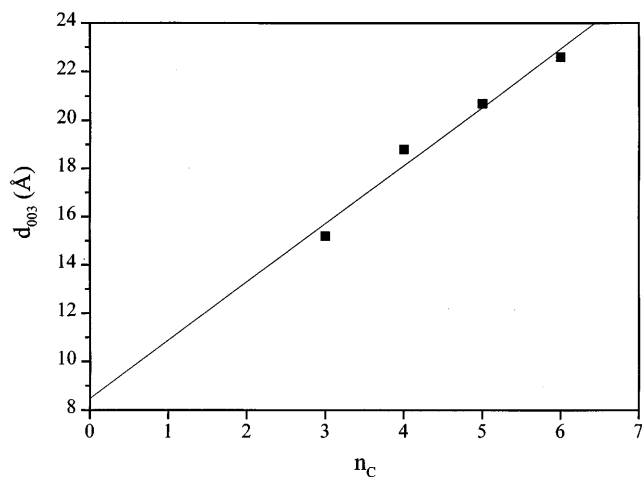


Figure 10. Schematic representation of a Mg-Al-HTlc intercalated with an interdigitate mono-layer of pentoxide anions

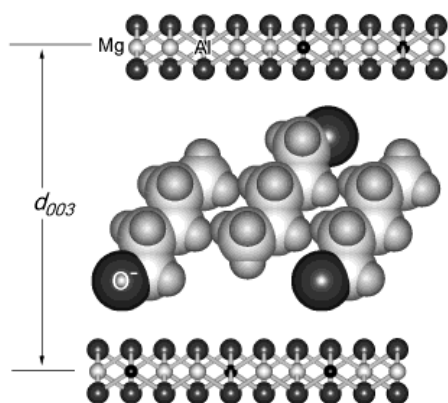
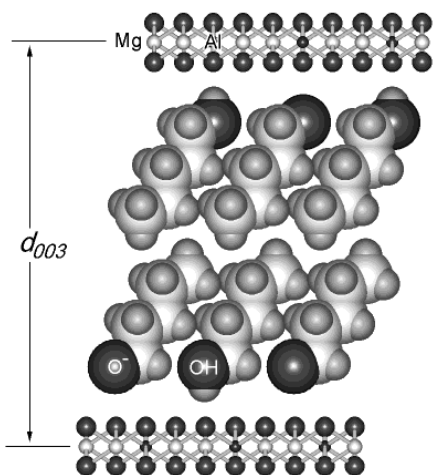


Figure 11. Schematic representation of a Mg-Al-HTlc intercalated with a bi-layer of pentoxide anions and pentanol molecules



Conclusion

At present we do not know whether the urea method, proposed in this paper, to prepare HTlc has general applicability. Preliminary results indicate that the method also works well for the Mg-Fe- CO_3 and for the Al-Li- CO_3 HTlc. Some difficulties arise in the presence of cations such as Cr(III) or Cu(II). In such cases the method will require some modification and improvement. This is not surprising, if we agree with the concept already expressed by Riechle^[1], that each layered double hydroxide requires its own procedure to be obtained in the best way. However, Mg-Al, Ni-Al and Zn-Al hydrotalcites have been obtained with the urea procedure and the materials have a high crystallinity degree and a narrow distribution of particle size. The high crystallinity degree has allowed the refinement of the structure with the Rietveld method.

A novel method to convert the carbonate into the chloride form, based on a gas-solid reaction has been proposed. Bases as strong as alkoxides were successfully intercalated. Further study is in progress to obtain the pure OH^- form, starting from alkoxide derivatives.

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Experimental Section

Materials: All the reagents used were of analytical grade (C. Erba RPE-ACS). Alkoxides were prepared by a reaction of metallic sodium and the corresponding alkanol, previously dehydrated over CaO.

Analytical Procedures: To obtain the chemical composition of the HTlc, weighed amounts of the samples (ca. 100 mg) were dissolved in a few drops of concentrated HCl and diluted with water to 50 ml. The metal ion content of the latter solution was determined with standard EDTA titrations [Mg(II), Al(III), Ni(II), Zn(II)] and atomic absorption spectroscopy [Mg(II), Ni(II), Zn(II)]. The carbonate anion content of HTlc was obtained both with C elemental analysis and thermogravimetry. Anions, unlike carbonate, were determined by ion chromatography (DIONEX 2000 I/SP), after elution of the anion with 1 mol/dm³ sodium carbonate solution. The water content was obtained by thermogravimetry.

Instrumentation: Coupled TG-DTG-DTA thermogravimetric curves were obtained with a Stanton-Redcroft STA 780 Analyzer at a heating rate of 5°C/min, under an air flow. — X-ray powder diffraction (XRPD) patterns were taken with a computer-controlled PW 1710 Philips diffractometer operating at 40 kV, 30 mA, using a PW 1820 goniometer, supplied with a bent graphite monochromator in the diffracted beam, and Cu- K_α radiation. XRPD patterns for indexing and structure refinement were taken with the step-scanning technique. The samples were prepared using the side-loading procedure in order to minimize preferred orientations. Diffractograms were collected from $2\theta = 6$ to 120° using steps of 0.01° and a counting time of 20 s per step. — N_2 adsorption-desorption isotherms were taken by Sorptomatic 1800 supplied with an out-gassing unit (C. Erba Strumentazione). — Particle-size distribution was obtained by means of an AccuSizerTM 770 Optical Particle Sizer, Santa Barbara, CA 93117, USA. — The scanning electron microscopy (SEM) photographs of the microcrystals were taken with a Philips XL30 apparatus.

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