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THERMAL DECOMPOSITION OF THE COMPOSITE HYDROTALCITES OF IOWAITE AND WOODALLITE

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The thermal stability and thermal decomposition pathways for synthesized composite iowaite/woodallite have been determined using thermogravimetry analysis in conjunction with evolved gas mass spectrometry. Dehydration of the hydrotalcites occurred over a range of 56–70°C. The first dehydroxylation step occurred at around 255°C and, with the substitution of more iron(III) for chromium(III) this temperature increased to an upper limit of 312°C. This trend was observed throughout all decomposition steps. The release of carbonate ions as carbon dioxide gas initialised at just above 300°C and was always accompanied by loss of hydroxyl units as water molecules. The initial loss of the anion in this case the chloride ion was consistently observed to occur at about 450°C with final traces evolved at 535 to 780°C depending of the Fe:Cr ratio and was detected as HCl (*m*/*z*=36). Thus for this to occur, hydroxyl units must have been retained in the structure at temperatures upwards of 750°C. Experimentally it was found difficult to keep CO_2 from reacting with the compounds and in this way the synthesized iowaite–woodallite series somewhat resembled the natural minerals.

Keywords: *dehydration, dehydroxylation, hydrotalcite, iowaite, thermogravimetric analysis, woodallite*

Introduction

There exists in nature a group of minerals based upon the brucite structure in which the divalent cation Mg^{2+} is replaced by a trivalent cation (Al^{3+}, Fe^{3+} or Cr^{3+}), resulting in a positive charge on the brucite-like surface. This positive charge is counterbalanced by anions held within the brucite layers. Hydrotalcites are layered double hydroxides (LDHs) and are fundamentally anionic clays. These clays are less well known than cationic clays like smectites. The structure of hydrotalcite can be derived from a brucite structure ($Mg(OH)_2$) in which e.g. Al^{3+} or Fe^{3+} (pyroaurite–sjögrenite) substitutes a part of the Mg^{2+}. Further mixtures of these mineral phases with multiple anions in the interlayer are observed. When LDHs are synthesized any appropriate anion can be placed in the interlayer. This substitution creates a positive layer charge on the hydroxide layers, which is compensated by interlayer anions or anionic complexes [1, 2]. The hydrotalcite may be considered as a gigantic cation, which is counterbalanced by anions in the interlayer. In hydrotalcites a broad range of compositions are possible of the type $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}]_{x/n}\cdot yH_2O$, where M^{2+} and M^{3+} are the di- and trivalent cations in the octahedral positions within the hydroxide layers with x normally between 0.17 and 0.33. A^{n-} is an exchangeable interlayer anion [3].

In the hydrotalcites reevesite and pyroaurite, the divalent cations are Ni^{2+} and Mg^{2+} respectively with the trivalent cation being Fe^{3+}. For iowaite, the divalent cation is Mg^{2+} and the trivalent cation Fe^{3+}. Woodallite is like iowaite but simply has Cr^{3+} instead of Fe^{3+}. In these cases the chloride anion is the major interlayer counter anion. Of course when synthesizing hydrotalcites any anion may be used. Normally the hydrotalcite structure based upon takovite (Ni,Al) and hydrotalcite (Mg,Al) has basal spacings of ~8.0 Å where the interlayer anion is carbonate. Slight differences in the *d*(003) spacing occurs when different anions are placed in the interlayer. In the case of iowaite and woodallite, the naturally occurring minerals contain carbonate as well as the chloride anions. These types of minerals are often formed as a result of the chemical degradation of crysotile. As such the minerals may be formed below the sea.

Thermal analysis using thermogravimetric techniques (TG) enables the mass loss steps, the temperature of the mass loss steps and the mechanism for the mass loss to be determined. Thermoanalytical methods provide a measure of the thermal stability of the hydrotalcite [4–6]. The iowaite-woodallite mineral series is of interest [7, 8]. Interest in the study of these hydrotalcites results from their potential use as catalysts, adsorbents and anion exchangers [9–13]. The reason for the potential application of hydrotalcites as catalysts rests with the ability to make mixed metal oxides at the atomic

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level, rather than at a particle level. Such mixed metal oxides are formed through the thermal decomposition of the hydrotalcite [14, 15]. One would expect that the potential application of hydrotalcites as catalysts will rest on reactions occurring on their surfaces. The significance of the formation of the mixed metal oxides is their importance as a transition material in the synthesis of catalysts. In this work we report the stability and thermal decomposition of the hydrotalcites iowaite and woodallite with chloride in the interlayer.

Experimental

Synthesis of hydrotalcite minerals

Minerals such as iowaite and woodallite may be synthesized in the laboratory. The reason for using synthetic minerals as opposed to the natural minerals is that difficulties associated with multiple anions in the interlayer can be minimised. The iowaite–woodallite series was synthesized by the coprecipitation method. Two solutions were prepared using boiled ultra pure water: solution 1 contained 2 M NaOH while solution 2 contained 0.75 M Mg^{2+} ($MgCl_2\cdot6H_2O$) and a combined 0.25 M Fe^{3+} ($FeCl_3\cdot6H_2O$) and Cr^{3+} ($CrCl_3\cdot6H_2O$). That is, to synthesize $Mg_6(Fe_{0.5}Cr_{0.5})_2(OH)_{16}Cl_2$, solution 2 contained 0.75 M Mg^{2+} combined with 0.125 M Fe^{3+} and 0.125 M Cr^{3+}. Prior to the addition of the two solutions the sealed vessel was purged with nitrogen for 20 min. Solution 2 was added to solution 1 under vigorous stirring using a peristaltic pump set at 40 cm^3 min^{-1}. The resulting gelatinous substance was again purged with nitrogen for a further 20 min and then washed three to four times via vacuum filtration with boiled ultra pure water at room temperature to remove residual salts. The composition of the minerals was checked using electron probe analysis, while the phase composition was verified using X-ray diffraction.

Methods

X-ray diffraction

X-ray diffraction patterns were collected using a Philips X’pert wide angle X-ray diffractometer, operating in step scan mode, with CoK_α radiation (1.78897 Å). Patterns were collected in the range 3 to 75° 2θ with a step size of 0.02° and a rate of 1.2 s per step. Samples were prepared in ethanol and placed on glass slides as thin films.

Thermal analysis

Thermal decompositions of the hydrotalcites, woodallite and iowaite and their composite mixtures were carried out in a TA® Instruments incorporated high-resolution thermogravimetric analyzer (series Q500) in a flowing nitrogen atmosphere (80 cm^3 min^{-1}). Approximately 50 mg of sample was heated in an open platinum crucible at a rate of 2.0°C min^{-1} up to 1000°C.

TG instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. Several gases (and isotopic analogues) and their ionic fragments were analysed including: Cl_2, CO, CO_2, HCl and H_2O. Mass/charge ratios were measured for example H_2O is 18/1.

Results and discussion

X-ray diffraction

The XRD patterns of the iowaite-woodallite series are shown in Fig. 1a as is the reference patterns of iowaite (020-0500) and woodallite (053-1185). The *d*(003) spacing generally increases with the inclusion of more chromium and hence less iron. However, interestingly the spacing for a pure iron sample is larger than the $Fe_{0.8}Cr_{0.2}$ and similarly the pure chromium specimen has a spacing smaller than that of the $Fe_{0.2}Cr_{0.8}$ mixture. This suggests that the trends exhibited by the mixtures are not simply an interpolation of the two end members but in fact, the inclusion of small amounts of iron and chromium introduce a new maximum and minimum outside the limits of the pure sample. For future work it would be interesting to synthesize mixtures with 5, 10, 15% substitutions and hence observe the effects on the *d*(003) spacing.

The XRD of the thermal decomposition products along with the reference is shown in Fig. 1b. This figure shows that all mixtures decompose into MgO (045-0946) and the spinel which in this case is a combination of $MgFe_2O_4$ (088-1942) and $MgCr_2O_4$ (010-0351). This conclusion correlates well with the decomposition mechanism for each mixture and is illustrated by a mixed spinel formula $Mg(Fe_xCr_{1-x})O_4$. Table 1 shows the calculations of the X-ray diffracting crystallite size as a function of composition. The size varies from 11.66 nm for iowaite to 3.73 nm for woodallite. The crystallite size is larger for those hydrotalcites with higher Fe content.

Table 1 Particle size as a function of composition of the iowaite–woodallite hydrotalcites

Compound	Crystallite size
Iowaite	11.66
$Fe_{0.8}Cr_{0.2}$	6.68
$Fe_{0.6}Cr_{0.4}$	5.26
$Fe_{0.4}Cr_{0.6}$	3.90
$Fe_{0.2}Cr_{0.8}$	3.73
Woodallite	3.73

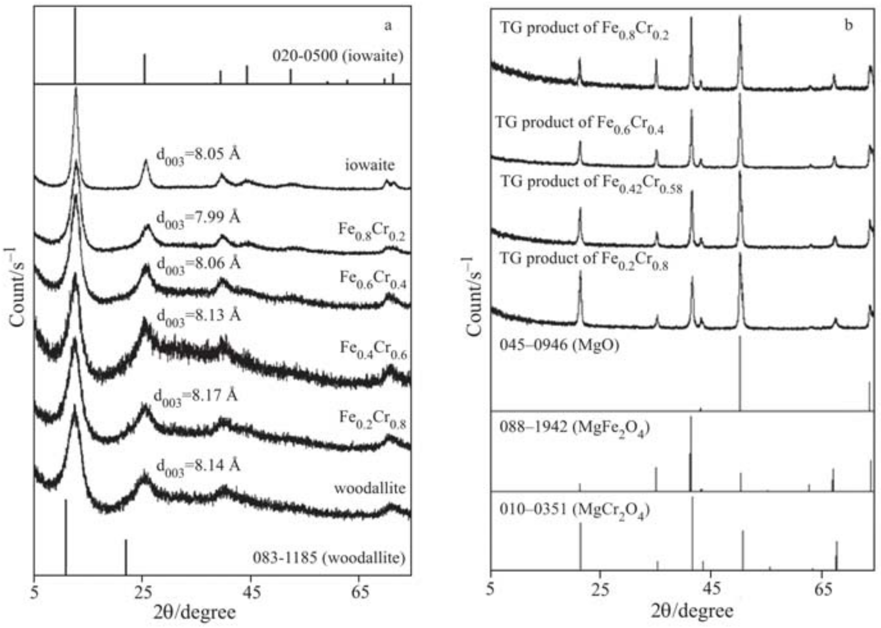

Fig. 1 X-ray diffraction patterns of a – iowaite–woodallite with Fe/Cr ratios of 1:0, 0.8:0.2, 0.6:0.4, 0.5:0.5, 0.4:0.6, 0.2:0.8 and 0.0:1.0; b – thermal decomposition products

EDAX analysis

The results of the EDX analyses are summarised in Table 2. The table shows the Fe/Cr ratios, the theoretical formula and the averaged results from EDX analyses. The calculated formula of the hydrotalcite is given in column 3. The formulae are worked out in terms of charge balance with the reference point taken as 16 OH^- units. The remaining positive charge from the cations was then counterbalanced with Cl^- and CO_3^{2-} units using the EDX and thermal information.

Thermal analysis

Thermal analysis can provide fundamental understanding of the behaviour of hydrotalcites. In particular the temperature at which decomposition takes place and the measurement of the thermal stability of the decomposition products. This is illustrated in Figs 2a–5a which show the TG and DTG plots of the mixed hydrotalcites of iowaite and woodallite. TG and DTG curves for iowaite–woodallite series with Fe:Cr=0.2:0.8, 0.4:0.6, 0.6:0.4; 0.8:0.2 are shown. Typical ion current curves for the evolved gases are shown in Figs 2b–5b. Figure 2 shows the results for an Fe:Cr ratio of 0.2:0.8; Fig. 3 Fe:Cr ratio of 0.4:0.6; Fig. 4 Fe:Cr ratio of 0.6:0.4; Fig. 5 Fe:Cr ratio of 0.8:0.2.

All TG curves of the iowaite–woodallite compounds show a mass loss around 56–70°C. Dehydroxylation occurred around 255°C for the iron(III) rich LDHs and increased to 312°C as more chromium(III) substituted the iron. This trend was observed throughout all decomposition steps, therefore indicating that iron(III) rich hydrotalcites were more stable than those with more chromium(III). The releases of carbonate ions as carbon dioxide gas (*m*/*z*=44) commenced at about 300°C and was always accompanied by loss of hydroxyl units as water molecules (*m*/*z*=17 and *m*/*z*=18). Both isotopes of Cl^- (*m*/*z*=35 and *m*/*z*=37) were analysed and subsequently HCl (*m*/*z*=36 and *m*/*z*=38) was scouted. The initial loss of the interlayer anion (Cl^-) was consistently observed to occur at about 450°C with final traces evolved between 535 to 780°C depending of the Fe:Cr ratio and was detected as predominately HCl (*m*/*z*=36). Thus for this to occur, hydroxyl units must have been retained in the structure at temperatures upwards of 750°C.

Table 2 EDX analyses of the iowaite–woodallite hydrotalcites

Compound	Theoretical formula	Charge balanced formula
Iowaite	$Mg_6Fe_2Cl_2(OH)_{16}$	$Mg_{6.27}Fe_{1.73}Cl_{1.07}(OH)_{16}(CO_3)_{0.33}$
$Fe_{0.8}Cr_{0.2}$	$Mg_6(Fe_{0.8}Cr_{0.2})_2Cl_2(OH)_{16}$	$Mg_{6.01}(Fe_{0.8}Cr_{0.2})_{1.99}Cl_{0.89}(OH)_{16}(CO_3)_{0.55}$
$Fe_{0.6}Cr_{0.4}$	$Mg_6(Fe_{0.6}Cr_{0.4})_2Cl_2(OH)_{16}$	$Mg_{6.18}(Fe_{0.6}Cr_{0.4})Cl_{1.08}(OH)_{16}(CO_3)_{0.37}$
$Fe_{0.4}Cr_{0.6}$	$Mg_6(Fe_{0.4}Cr_{0.6})_2Cl_2(OH)_{16}$	$Mg_{6.25}(Fe_{0.42}Cr_{0.58})_{1.75}Cl_{1.15}(OH)_{16}(CO_3)_{0.30}$
$Fe_{0.2}Cr_{0.8}$	$Mg_6(Fe_{0.2}Cr_{0.8})_2Cl_2(OH)_{16}$	$Mg_{6.12}(Fe_{0.2}Cr_{0.8})_{1.88}Cl_{1.22}(OH)_{16}(CO_3)_{0.33}$
Woodallite	$Mg_6Cr_2Cl_2(OH)_{16}$	$Mg_{6.28}Cr_{1.72}Cl(OH)_{16}(CO_3)_{0.36}$

Mechanism for the decomposition of iowaite–woodallite mixture with 0.2:0.8 ratio of Fe(III):Cr(III) with chloride anion in the interlayer

The following steps describe the thermal decomposition of the chloride–carbonate anions in the interlayer (Figs 2a and b). The summary of the thermal decomposition steps of synthesized iowaite–woodalites are reported in Table 3.

Step 1 at 62°C

$$Mg_{6.12}(Fe_{0.2}Cr_{0.8})_{1.88}Cl_{1.22}(OH)_{16}(CO_3)_{0.33}\cdot 6.15H_2O\rightarrow$$
$$Mg_{6.12}(Fe_{0.2}Cr_{0.8})_{1.88}Cl_{1.22}(OH)_{16}(CO_3)_{0.33}+6.15H_2O$$

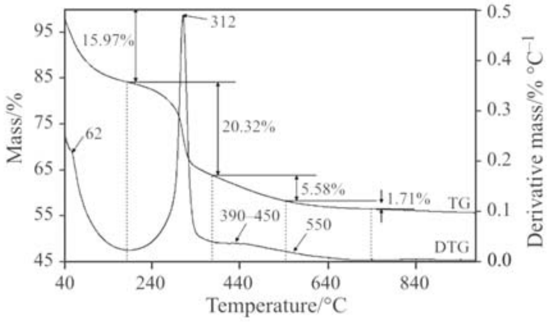

Fig. 2a TG and DTG curves for the hydrotalcite of composition Fe/Cr 0.2:0.8

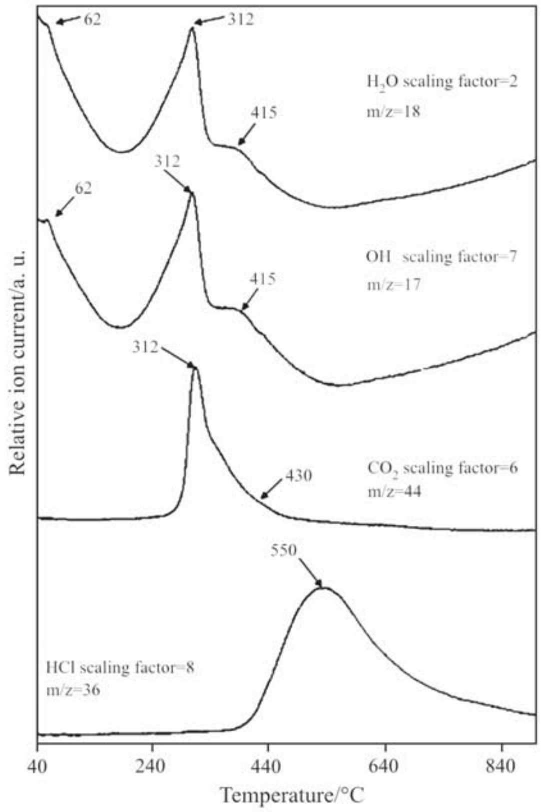

Fig. 2b Relative ion current curves for the hydrotalcite of composition Fe/Cr 0.2:0.8

This initial step shows a loss of water at 62°C and is the only dehydration step for the decomposition. There is a 15.97% mass loss at this step. This mass depletion is accounted for by the loss of 6.15 moles of water.

Step 2 at 312°C

$$Mg_{6.12}(Fe_{0.2}Cr_{0.8})_{1.88}Cl_{1.22}(OH)_{16}(CO_3)_{0.33}\rightarrow$$
$$Mg_{(6.12-x)}(Fe_{0.2}Cr_{0.8})_{1.88}Cl_{1.22}O_{(7.40-x)}(OH)_{1.8}(CO_3)_{0.03}+$$
$$+7.1H_2O+0.3CO_2+x\text{MgO}$$

This step shows a 20.32% mass loss and represents the first of the dehydroxylation steps. At this temperature 14.2 moles of hydroxyl ions are lost in the form of 7.1 moles of water. Also at this stage the hydrotalcite changes to a higher oxidation state (i.e. the ratio of Mg/Cr decreases). This is caused by the commencement of the formation of the oxide (most likely MgO). This transition is expected for all the synthetic hydrotalcites discussed in this study and usually takes place between 250–320°C. Unfortunately the exact proportion of MgO is not known but its formation at this temperature has been verified by X-ray diffraction.

Step 3 at 390–450°C

$$Mg_{6.12}(Fe_{0.2}Cr_{0.8})_{1.88}Cl_{1.22}O_{7.40}(OH)_{1.8}(CO_3)_{0.03}\rightarrow$$
$$Mg_{6.12}(Fe_{0.2}Cr_{0.8})_{1.88}Cl_{0.33}O_{8.61}(OH)_{0.33}+0.29H_2O+$$
$$+0.03CO_2+0.89HCl$$

This step represents another dehydroxylation step where at this temperature 0.29 moles of water are liberated. Traces of carbon dioxide are also lost in this step. This step accounts for the major loss of the chloride ions in the form of 0.89 moles of hydrogen chloride. This results from the carbonate impurity in the interlayer. There is a 5.58% mass loss at this temperature.

Step 4 at 550°C

$$Mg_{6.12}(Fe_{0.2}Cr_{0.8})_{1.88}Cl_{0.33}O_{8.61}(OH)_{0.33}(CO_3)_{0.03}\rightarrow$$
$$Mg_{6.12}(Fe_{0.2}Cr_{0.8})_{1.88}O_{8.94}+0.33HCl$$

This final step in the decomposition of synthetic iowaite–woodallite mixture and represents the loss of the rest of the chloride ions in the form of 0.33 moles of hydrogen chloride which, accounts for 1.71% mass loss. The products of the thermal decomposition are a spinel $0.94Mg(Fe_{0.2}Cr_{0.8})_2O_4$ and 5.18MgO. Thus the total mass loss equates to approximately 44% and occurred over 4 steps.

Table 3 Results of the thermal decomposition of iowaite–woodallite hydrotalcites

Iowaite–woodallite	Step 1			Step 2			Step 3		
	mass loss/%	temperature/°C	species lost	mass loss/%	temperature/°C	species lost	mass loss/%	temperature/°C	species lost
$Fe_{0.2}Cr_{0.8}$	15.97	62	H_2O	20.32	312	OH^-/CO_3	5.58	390–450	$OH^-/CO_3/Cl^-$
$Fe_{0.42}Cr_{0.58}$	17.81	67	H_2O	3.65	265	OH^-	15.24	311	OH^-/CO_3
$Fe_{0.6}Cr_{0.4}$	16.43	65	H_2O	4.57	254	OH^-	15.00	305	OH^-/CO_3
$Fe_{0.8}Cr_{0.2}$	15.17	59	H_2O	5.05	255	OH^-	3.70	308	OH^-/CO_3

Iowaite–woodallite	Step 4			Step 5			Step 6		
	mass loss/%	temperature/°C	species lost	mass loss/%	temperature/°C	species lost	mass loss/%	temperature/°C	species lost
$Fe_{0.2}Cr_{0.8}$	1.71	550	Cl^-/OH^-	*	*	*	*	*	*
$Fe_{0.42}Cr_{0.58}$	5.16	370–500	$OH^-/CO_3/Cl^-$	2.03	615	Cl^-/OH^-	0.88	780	Cl^-/OH^-
$Fe_{0.6}Cr_{0.4}$	4.70	371–490	$OH^-/CO_3/Cl^-$	1.70	575	$OH^-/CO_3/Cl^-$	1.22	760	Cl^-/OH^-
$Fe_{0.8}Cr_{0.2}$	13.68	329	OH^-/CO_3	2.23	450	Cl^-/OH^-	2.89	535	Cl^-/OH^-

Mechanism for the decomposition of iowaite–woodallite mixture with 0.42:0.58 ratio of Fe(III):Cr(III) with chloride anion in the interlayer

The following steps describe the thermal decomposition of the chloride–carbonate anions in the interlayer (Figs 3a and b).

Step 1 at 67°C

$$Mg_{6.25}(Fe_{0.42}Cr_{0.58})_{1.75}Cl_{1.15}(OH)_{16}(CO_3)_{0.30}\cdot 6.94H_2O\rightarrow$$
$$Mg_{6.25}(Fe_{0.42}Cr_{0.58})_{1.75}Cl_{1.15}(OH)_{16}(CO_3)_{0.30}+6.94H_2O$$

Dehydration occurs at 67°C with a 17.81% mass loss.

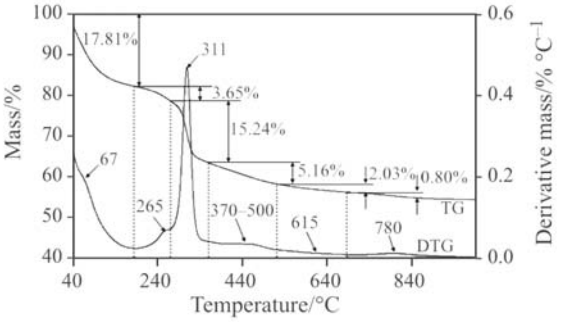

Fig. 3a TG and DTG curves for the hydrotalcite of composition Fe/Cr 0.4:0.6

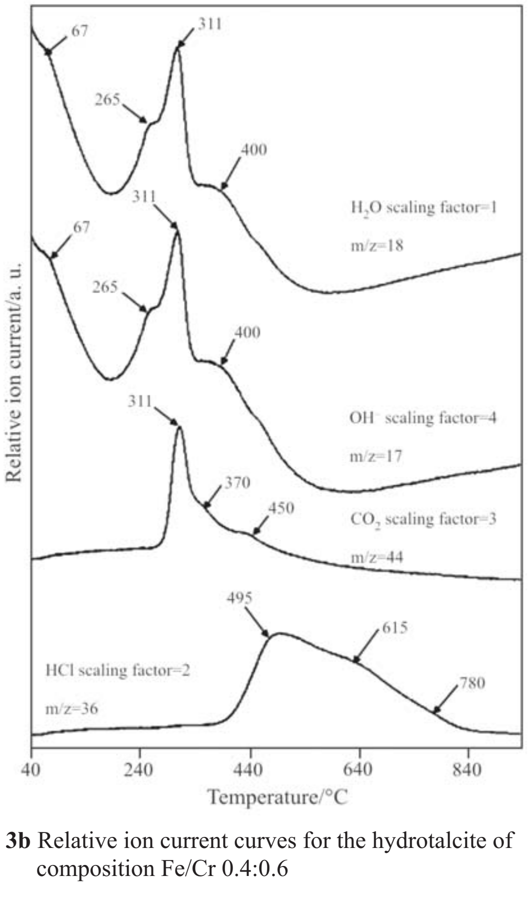

Fig. 3b Relative ion current curves for the hydrotalcite of composition Fe/Cr 0.4:0.6

Step 2 at 265°C

$$Mg_{6.25}(Fe_{0.42}Cr_{0.58})_{1.75}Cl_{1.15}(OH)_{16}(CO_3)_{0.30}\rightarrow$$
$$Mg_{(6.25-x)}(Fe_{0.42}Cr_{0.58})_{1.75}Cl_{1.15}O_{(1.42-x)}(OH)_{13.16}(CO_3)_{0.30}+$$
$$+1.42H_2O+x\mathrm{MgO}$$

At this temperature there is a 3.65% mass loss associated with dehydroxylation.

Step 3 at 311°C

$$Mg_{6.25}(Fe_{0.42}Cr_{0.58})_{1.75}Cl_{1.15}O_{1.42}(OH)_{13.16}(CO_3)_{0.30}\rightarrow$$
$$Mg_{6.25}(Fe_{0.42}Cr_{0.58})_{1.75}Cl_{1.15}O_{7.07}(OH)_{2.26}(CO_3)_{0.10}+$$
$$+5.45H_2O+0.2CO_2$$

At this temperature there is a 15.24% mass loss. This decomposition step is associated with dehydroxylation and loss of carbonate.

Step 4 at 370–500°C

$$Mg_{6.25}(Fe_{0.42}Cr_{0.58})_{1.75}Cl_{1.15}O_{7.07}(OH)_{2.26}(CO_3)_{0.10}\rightarrow$$
$$Mg_{6.25}(Fe_{0.42}Cr_{0.58})_{1.75}Cl_{0.55}O_{8.33}(OH)_{0.55}+0.56H_2O+$$
$$+0.1CO_2+0.6HCl$$

This decomposition step is associated with loss of the interlayer anion which evolves as HCl with a 5.16% mass loss.

Step 5 at 615°C

$$Mg_{6.25}(Fe_{0.42}Cr_{0.58})_{1.75}Cl_{0.55}O_{8.33}(OH)_{0.55}\rightarrow$$
$$Mg_{6.25}(Fe_{0.42}Cr_{0.58})_{1.75}Cl_{0.15}O_{8.73}(OH)_{0.15}+0.4HCl$$

There is a 2.03% mass loss at this step associated with the evolution of HCl.

Step 6 at 780°C

$$Mg_{6.25}(Fe_{0.42}Cr_{0.58})_{1.75}Cl_{0.15}O_{8.73}(OH)_{0.15}\rightarrow$$
$$Mg_{6.25}(Fe_{0.42}Cr_{0.58})_{1.75}O_{8.88}+0.15HCl$$

At this temperature there is a 0.88% mass loss associated with the evolution of HCl. The final products are the spinel $0.88Mg(Fe_{0.42}Cr_{0.58})_2O_4$ and 5.37MgO. The total mass loss was 45% and took place over 6 steps.

Mechanism for the decomposition of iowaite–woodallite mixture with 0.6:0.4 ratio of Fe(III):Cr(III) with chloride anion in the interlayer

The following steps describe the thermal decomposition of the chloride–carbonate anions in the interlayer.

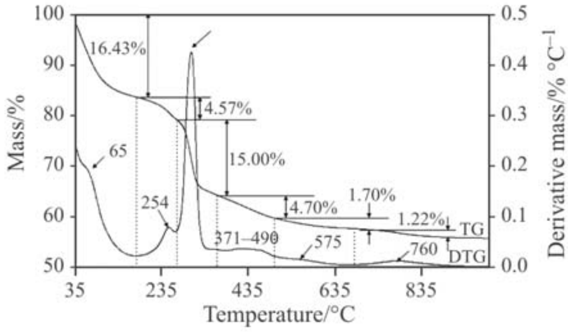

Fig. 4a TG and DTG curves for the hydrotalcite of composition Fe/Cr 0.6:0.4

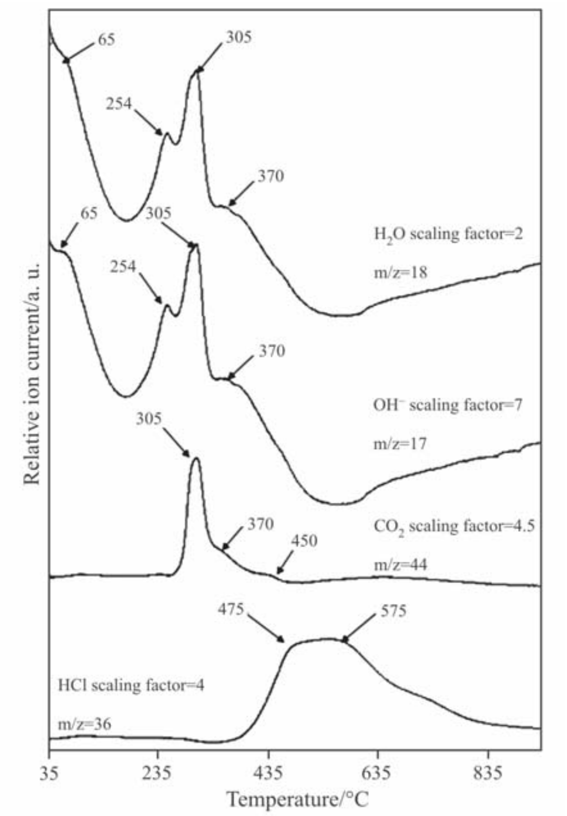

Fig. 4b Relative ion current curves for the hydrotalcite of composition Fe/Cr 0.6:0.4

Step 1 at 65°C

$$\mathrm{Mg_{6.18}(Fe_{0.6}Cr_{0.4})_{1.82}Cl_{1.08}(OH)_{16}(CO_3)_{0.37}\cdot 6.35H_2O}\rightarrow$$
$$\mathrm{Mg_{6.18}(Fe_{0.6}Cr_{0.4})_{1.82}Cl_{1.08}(OH)_{16}(CO_3)_{0.37}+6.35H_2O}$$

For this hydrotalcite there is a 16.43% mass loss at 65°C associated with dehydration.

Step 2 at 254°C

$$\mathrm{Mg_{6.18}(Fe_{0.6}Cr_{0.4})_{1.82}Cl_{1.08}(OH)_{16}(CO_3)_{0.37}}\rightarrow$$
$$\mathrm{Mg_{(6.18-\mathit{x})}(Fe_{0.6}Cr_{0.4})_{1.82}Cl_{1.08}O_{(1.77-\mathit{x})}(OH)_{12.46}(CO_3)_{0.37}+}$$
$$\mathrm{+1.77H_2O+\mathit{x}MgO}$$

There is a 4.57% mass loss at 254°C associated with dehydroxylation.

Step 3 at 305°C

$$\mathrm{Mg_{6.18}(Fe_{0.6}Cr_{0.4})_{1.82}Cl_{1.08}O_{1.77}(OH)_{12.46}(CO_3)_{0.37}}\rightarrow$$
$$\mathrm{Mg_{6.18}(Fe_{0.6}Cr_{0.4})_{1.82}Cl_{1.08}O_{7.14}(OH)_{2.32}(CO_3)_{0.07}+}$$
$$\mathrm{+5.07H_2O+0.3CO_2}$$

At 305°C there is a 15.0% mass loss attributed to the loss of carbon dioxide and water from the hydroxyl units.

Step 4 at 371–490°C

$$\mathrm{Mg_{6.18}(Fe_{0.6}Cr_{0.4})_{1.82}Cl_{1.08}O_{7.14}(OH)_{2.32}(CO_3)_{0.07}}\rightarrow$$
$$\mathrm{Mg_{6.18}(Fe_{0.6}Cr_{0.4})_{1.82}Cl_{0.54}O_{8.35}(OH)_{0.54}(CO_3)_{0.02}+}$$
$$\mathrm{+0.62H_2O+0.05CO_2+0.54HCl}$$

Between 371 and 490°C there is a 4.7% mass loss attributed to the loss of carbon dioxide, HCl and water from the hydroxyl units.

Step 5 at 575°C

$$\mathrm{Mg_{6.18}(Fe_{0.6}Cr_{0.4})_{1.82}Cl_{0.54}O_{8.35}(OH)_{0.54}(CO_3)_{0.02}}\rightarrow$$
$$\mathrm{Mg_{6.18}(Fe_{0.6}Cr_{0.4})_{1.82}Cl_{0.24}O_{8.67}(OH)_{0.24}+}$$
$$\mathrm{+0.02CO_2+0.3HCl}$$

At 575°C there is a 1.7% mass loss attributed to the loss of carbon dioxide and HCl.

Step 6 at 760°C

$$\mathrm{Mg_{6.18}(Fe_{0.6}Cr_{0.4})_{1.82}Cl_{0.24}O_{8.67}(OH)_{0.24}}\rightarrow$$
$$\mathrm{Mg_{6.18}(Fe_{0.6}Cr_{0.4})_{1.82}O_{8.91}+0.24HCl}$$

There is a 1.22% mass loss associated with this step. The final products are the spinel $\mathrm{0.91Mg(Fe_{0.6}Cr_{0.4})_2O_4}$ and 5.27MgO. The total mass loss was just under 44% and occurred over a series of 6 steps.

Mechanism for the decomposition of iowaite–woodallite mixture with 0.8:0.2 ratio of Fe(III):Cr(III) with chloride anion in the interlayer

The following steps describe the thermal decomposition of the chloride–carbonate anions in the interlayer (Figs 5a and b).

Step 1 at 59°C

$$\mathrm{Mg_{6.01}(Fe_{0.8}Cr_{0.2})_{1.99}Cl_{0.89}(OH)_{16}(CO_3)_{0.55}\cdot 5.84H_2O}\rightarrow$$
$$\mathrm{Mg_{6.01}(Fe_{0.8}Cr_{0.2})_{1.99}Cl_{0.89}(OH)_{16}(CO_3)_{0.55}+5.84H_2O}$$

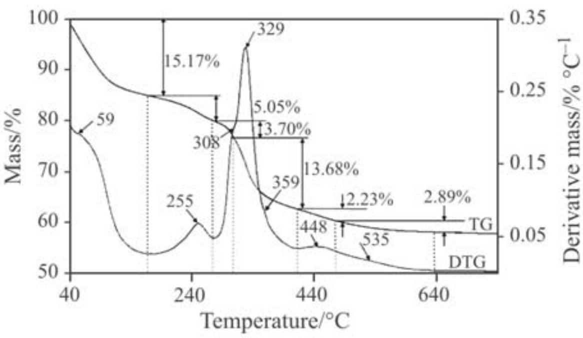

Fig. 5a TG and DTG curves for the hydrotalcite of composition Fe/Cr 0.8:0.2

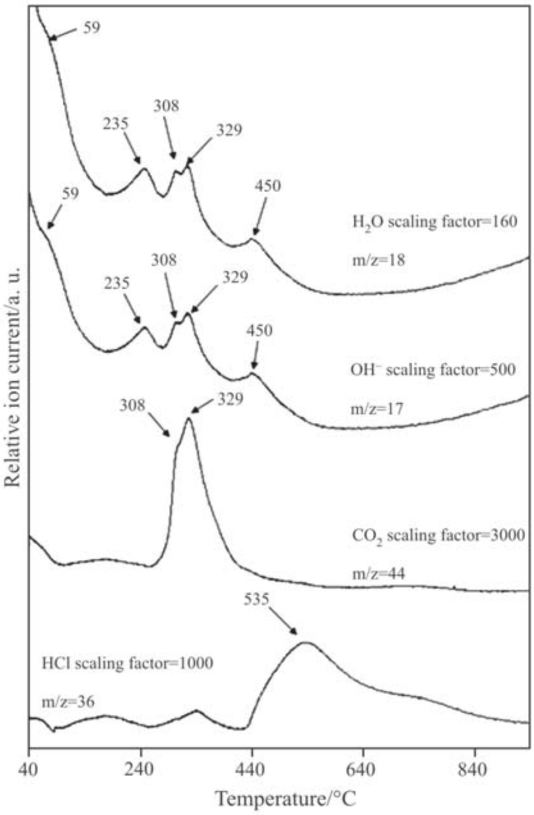

Fig. 5b Relative ion current curves for the hydrotalcite of composition Fe/Cr 0.8:0.2

This initial step shows a loss of water at 59°C and is the only dehydration step for the decomposition. There is a 15.17% mass loss at this step. This mass depletion is accounted for by the loss of 5.84 moles of water.

Step 2 at 255°C

$$Mg_{6.01}(Fe_{0.8}Cr_{0.2})_{1.99}Cl_{0.89}(OH)_{16}(CO_3)_{0.55}\rightarrow$$

$$Mg_{(6.01-x)}(Fe_{0.8}Cr_{0.2})_{1.99}Cl_{0.89}O_{(1.96-x)}(OH)_{12.08}(CO_3)_{0.55}+$$

$$+1.96H_2O+x\text{MgO}$$

This step shows a 5.05% mass loss and represents the first of the dehydroxylation steps. At this temperature 3.92 moles of hydroxyl ions are lost in the form of 1.96 moles of water.

Step 3 at 308°C

$$Mg_{6.01}(Fe_{0.8}Cr_{0.2})_{1.99}Cl_{0.89}O_{1.96}(OH)_{12.08}(CO_3)_{0.55}\rightarrow$$

$$Mg_{6.01}(Fe_{0.8}Cr_{0.2})_{1.99}Cl_{0.89}O_{3.18}(OH)_{9.94}(CO_3)_{0.40}+$$

$$+1.07H_2O+0.15CO_2$$

This step represents another dehydroxylation step where at this temperature 1.07 moles of water are liberated. Traces of carbon dioxide are also lost in this step. This results from the carbonate impurity in the interlayer. There is a 3.70% mass loss at this temperature.

Step 4 at 329°C

$$Mg_{6.01}(Fe_{0.8}Cr_{0.2})_{1.99}Cl_{0.89}O_{3.18}(OH)_{9.94}(CO_3)_{0.40}\rightarrow$$

$$Mg_{6.01}(Fe_{0.8}Cr_{0.2})_{1.99}Cl_{0.89}O_{7.90}(OH)_{1.30}+$$

$$+4.32H_2O+0.4CO_2$$

At this temperature both carbon dioxide and hydroxide are liberated. In this step the last traces of carbon dioxide are lost. There is a total of 13.68% mass loss at this temperature.

Step 5 at 450°C

$$Mg_{6.01}(Fe_{0.8}Cr_{0.2})_{1.99}Cl_{0.89}O_{7.90}(OH)_{1.30}\rightarrow$$

$$Mg_{6.01}(Fe_{0.8}Cr_{0.2})_{1.99}Cl_{0.56}O_{8.44}(OH)_{0.56}+$$

$$+0.33HCl+0.21H_2O$$

At this temperature both water and hydrogen chloride are given off. It is here where the number of hydroxyl moles equals that of chloride ions. This step accounts for 2.23% mass loss.

Step 6 at 535°C

$$Mg_{6.01}(Fe_{0.8}Cr_{0.2})_{1.99}Cl_{0.56}O_{8.44}(OH)_{0.56}\rightarrow$$

$$Mg_{6.01}(Fe_{0.8}Cr_{0.2})_{1.99}O_9+0.56HCl$$

This final step in the decomposition of synthetic iowaite–woodallite mixture and represents the loss of the rest of the chloride ions in the form of 0.56 moles of hydrogen chloride which, accounts for 2.89% mass loss. The products of the thermal decomposition are a spinel $Mg(Fe_{0.8}Cr_{0.2})_2O_4$ and 5.01MgO. It was found that the total mass loss for this mechanism was about 43% and occurred over 6 steps.

Conclusions

Thermogravimetry in conjunction with evolved gas mass spectrometry has been used to study the thermal decomposition of a series of a new intermediate compound of synthetic iowaite and woodallite. In this work a sample of the composite mineral with minimal carbonate was synthesized but was found to still contain small amounts of carbonate and therefore a less than expected number of chloride ions per unit cell. It was found that the total mass loss for all intermediates was about 43–45% and the decomposition product was periclase (MgO) and a mixed spinel of $Mg(Fe_xCr_{1-x})_2O_4$. From these results it seems that the thermal stability of the synthetic mineral increased as the content of iron increased. This was evident in the rise in temperature of each step as the series progressed from high chromium to low chromium content. Furthermore the decomposition mechanism for the composite with the least iron was finalised in four steps while those with higher ratios of iron to chromium had a more complex mechanism with six steps.

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