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THERMAL DECOMPOSITION OF THE SYNTHETIC HYDROTALCITE IOWAITE

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The thermal stability and thermal decomposition pathways for synthetic iowaite have been determined using thermogravimetry in conjunction with evolved gas mass spectrometry. Chemical analysis showed the formula of the synthesised iowaite to be $Mg_{6.27}Fe_{1.73}(Cl)_{1.07}(OH)_{16}(CO_3)_{0.33}\cdot 6.1H_2O$ and X-ray diffraction confirms the layered structure. Dehydration of the iowaite occurred at 35 and 79°C. Dehydroxylation occurred at 254 and 291°C. Both steps were associated with the loss of CO_2. Hydrogen chloride gas was evolved in two steps at 368 and 434°C. The products of the thermal decomposition were MgO and a spinel $MgFe_2O_4$. Experimentally it was found to be difficult to eliminate CO_2 from inclusion in the interlayer during the synthesis of the iowaite compound and in this way the synthesised iowaite resembled the natural mineral.

Keywords: *dehydration, dehydroxylation, high-resolution thermogravimetric analysis, hydrotalcite, iowaite*

Introduction

There exists in nature a group of minerals based upon the brucite structure in which the divalent cation (Mg) 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. Further mixtures of these mineral phases with multiple anions in the interlayer are observed. When LDH's 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 and the trivalent cation Fe^{3+}. Woodalite is like iowaite but simply has chromium 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 woodalite, 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 chrysotile. 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-woodalite mineral series is of interest [7, 8]. Research into the use of these hydrotalcites results from their potential application 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 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.

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A previous thermoanalytical study of a natural iowaite has been undertaken [16]. This study showed that the natural iowaite contained significant quantities of $(CO_3)^{2-}$. This means that the hydrotalcite was a mixed anion system. Such a system lends itself to studies by vibrational spectroscopy [17–19]. In this research a synthetic iowaite with minimal CO_2 was produced. In this work we report the stability and thermal decomposition of the hydrotalcite iowaite with chloride in the interlayer.

Experimental

Minerals

Minerals such as iowaite and woodalite 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.

Iowaite was synthesised by the co-precipitation method. Two solutions were prepared using boiled ultra pure water, solution 1 contained 2 M NaOH, and solution 2 contained 0.75 M Mg^{2+} ($MgCl_2 \cdot 6H_2O$), together with 0.25 M Fe^{3+} (as ($FeCl_3 \cdot 9H_2O$)). Solution 2 was added to solution 1 using a peristaltic pump at a rate of 40 cm^3 min^{-1}, under vigorous stirring, in a sealed nitrogen vessel, maintaining a pH of 10. The precipitated minerals are washed at ambient temperatures thoroughly with boiled ultra pure water to remove any residual salts. The compositions of the iowaite were checked by electron probe analyses. The phase composition was checked by X-ray diffraction (Fig. 1).

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 CuK_α radiation (1.54052 Å). Patterns were collected in the range 3 to 90° 2θ with a step size of 0.02° and a rate of 30 s per step. Samples were prepared as a finely pressed powder into aluminium sample holders.

SEM

Iowaite samples were coated with a thin layer of evaporated carbon and images were obtained using an FEI Quanta 200 scanning electron microscope (SEM). For X-ray microanalysis (EDX), three samples were embedded in Araldite resin and polished with diamond paste on Lamplan 450 polishing cloth using water as a lubricant. The samples were coated with a thin layer of evaporated carbon for conduction and examined in a JEOL 840A analytical SEM at 25 kV accelerating voltage. Preliminary analyses of the iowaite samples were carried out on the FEI Quanta SEM using an EDAX microanalyser, and microanalysis of the clusters of fine crystals was carried out using a full standards quantitative procedure on the JEOL 840 SEM using a Moran Scientific microanalysis system.

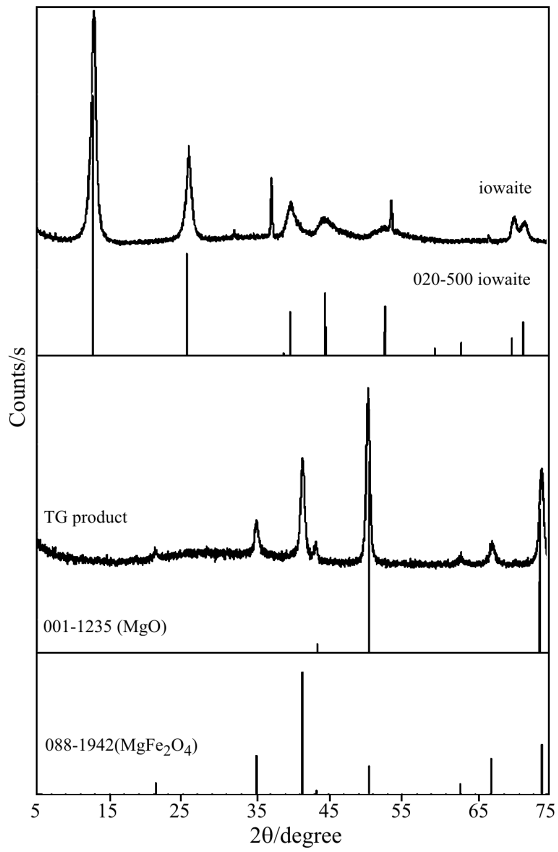

Fig. 1 XRD patterns of the synthesised iowaite and the thermal decomposition products

Thermal analysis

Thermal decompositions of iowaite was 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. The TG instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. The following gases were analyzed: Cl, Cl_2, CO, CO_2 and H_2O. Mass/charge ratios are measured for example O_2 is 32/1 and 32/2.

Band component analysis of the DTG curves was undertaken using the Jandel 'Peakfit' software package, which 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

Gauss–Lorentz 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.

Results and discussion

X-ray diffraction

The X-ray diffraction patterns of the synthesised iowaite and the standard reference pattern (020-0500 iowaite) are shown in Fig. 1. Clearly the compound synthesised is iowaite. No major impurities can be observed in the XRD pattern. Some visible differences in intensity of the reflections may be observed between the synthesised iowaite and the standard reference pattern 020-0500. This intensity difference may be accounted for by the presence of carbonate and the different ratios of Mg relative to Fe and Cl.

Also shown is the XRD pattern of the decomposition products after TG-MS analysis. Figure 1 shows the analysis of the thermal decomposition products as MgO and a magnesioferrite ($MgFe_2O_4$).

SEM and EDAX analyses

The SEM images of the iowaite are shown in Fig. 2. Such an image is typical of hydrotalcites. The image gives the impression of a deposition/corrosion process. The image also shows that the surface has grown by deposition from solution.

The EDAX analysis of the iowaite is displayed in Fig. 3. The analysis clearly shows the very low amount of carbon in this area of the analysis. This carbon is in part due to the carbon coating of the sample. The EDAX analyses gave a ratio of Mg/Fe of 7.25/2. The total number of cations must add up to 8. This means the ratio of Mg/Fe is 6.27/1.73. The ratio of cations to Cl is 8/1.07. This means the formula of the iowaite is $Mg_{6.27}Fe_{1.73}(Cl)_{1.07}(OH)_{16}(CO_3)_{0.33}\cdot 6.1H_2O$.

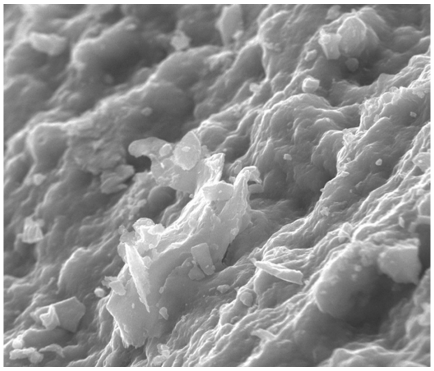

Fig. 2 SEM image of iowaite (×6000)

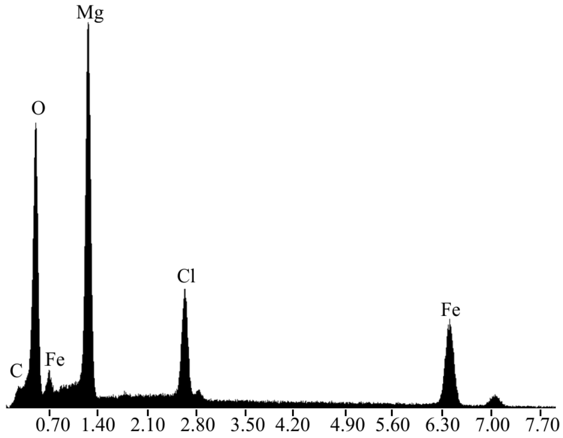

Fig. 3 EDAX analysis of iowaite

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 Fig. 4 which shows the TG and DTG plots of the synthetic hydrotalcite iowaite. The ion current curves for the evolved gases are shown in Fig. 5.

The iowaite DTG curve shows a mass loss around 35°C. This mass loss is ascribed to the dehydration step due to peaks in the ion current curves for *m*/*z* ratios of 18 (H_2O) and 17 (OH). The DTG curves for iowaite show two mass loss steps at 254 and 291°C. The first mass loss is 7.19% and the second 14.17%. The ion current curves for *m*/*z*=18, shows mass losses at 251 and 291°C. A similar ion current curve is shown for *m*/*z*=17. The first mass loss step at 252°C is assigned to the mass loss of the hydroxyl units. Based upon the ion current curves for OH (*m*/*z*=17), the second mass loss step at 293°C is assigned to the loss of hydroxyl units. Some CO_2 was evolved after this decomposition step. In the thermal decomposition of many hydrotalcites the mass loss step of the OH units and the carbonate anion occur simultaneously. In the case of the thermal decomposition of iowaite these two steps also occur simultaneously.

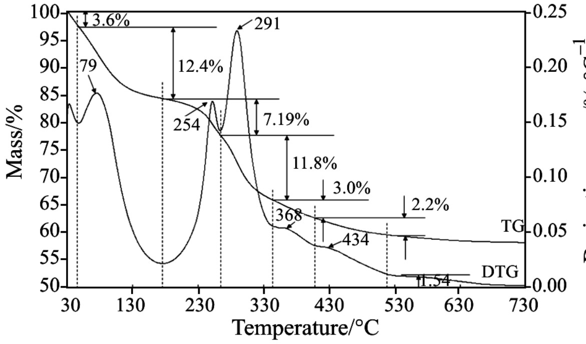

Fig. 4 Thermal analysis of iowaite

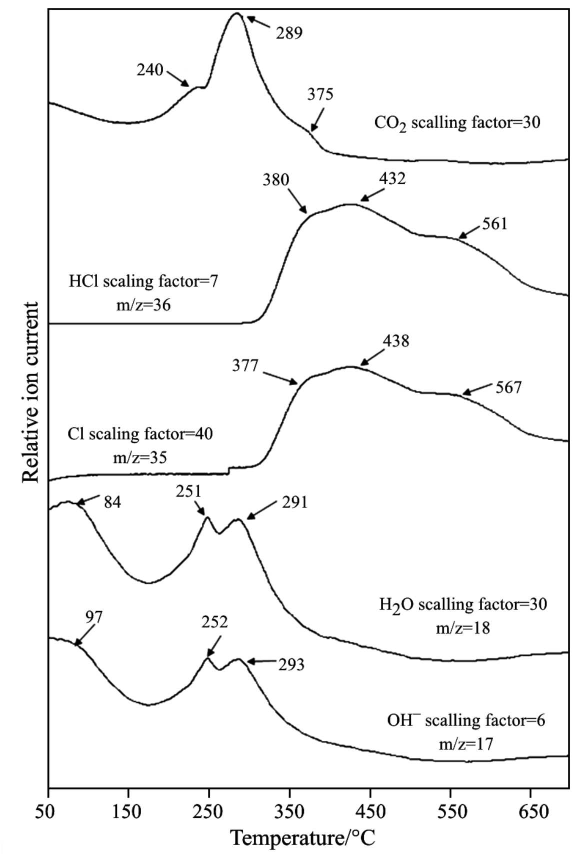

Fig. 5 MS analysis of evolved gases of iowaite

Mechanism for the decomposition of iowaite with chloride anion in the interlayer

The following steps describe the thermal decomposition of the hydroxyl, chloride and carbonate anions in the interlayer. The equations are based upon the chemical analyses and the mass loss as determined by the ion current curves. In steps 1 and 2, only water is lost. Thus the chemical formula as determined by chemical analysis is modified only by the number of moles of water that is lost. In steps 3 and 4 both water and CO_2 is lost. Thus the chemical formulae of the compounds are modified accordingly. In steps 5, 6 and 7, ion current curves indicated that HCl is lost, the chemical formula in these steps are modified according to the loss of HCl.

Step 1 at 35°C

$$\mathrm{Mg_{6.27}Fe_{1.73}Cl_{1.07}(OH)_{16}(CO_3)_{0.33}\cdot 6.1H_2O\rightarrow}$$
$$\mathrm{Mg_{6.27}Fe_{1.73}Cl_{1.07}(OH)_{16}(CO_3)_{0.33}\cdot 4.7H_2O+1.4H_2O}$$

This initial step shows a loss of some water at 35°C. There is a 3.67% mass loss at this step. This mass loss is accounted for by the loss of 1.4 moles of water.

Step 2 at 79°C

$$\mathrm{Mg_{6.27}Fe_{1.73}Cl_{1.07}(OH)_{16}(CO_3)_{0.33}\cdot 4.7H_2O\rightarrow}$$
$$\mathrm{Mg_{6.27}Fe_{1.73}Cl_{1.07}(OH)_{16}(CO_3)_{0.33}+4.7H_2O}$$

This step shows a 12.32% mass loss. 4.7 moles of water are lost at this temperature. This is the major dehydration step. All the water molecules are lost by this temperature.

Step 3 at 254°C

$$\mathrm{Mg_{6.27}Fe_{1.73}Cl_{1.07}(OH)_{16}(CO_3)_{0.33}\rightarrow}$$
$$\mathrm{Mg_{6.27}Fe_{1.73}O_{2.6}Cl_{1.07}(OH)_{11}(CO_3)_{0.23}+2.5H_2O+0.1CO_2}$$

This step represents the first of the dehydroxylation steps. Traces of carbon dioxide are also lost in this step. There is a 7.19% mass loss at this temperature.

Step 4 at 291°C

$$\mathrm{Mg_{6.27}Fe_{1.73}O_{2.6}Cl_{1.07}(OH)_{11}(CO_3)_{0.23}\rightarrow}$$
$$\mathrm{Mg_{6.27}Fe_{1.73}O_{7.75}Cl_{1.07}(OH)_{1.07}(CO_3)_{0.05}}$$
$$\mathrm{+4.9H_2O+0.18CO_2}$$

There is a 11.8% mass loss at this temperature. This step represents the second dehydroxylation step.

Step 5 at 368°C

$$\mathrm{Mg_{6.27}Fe_{1.73}O_{7.75}Cl_{1.07}(OH)_{1.07}(CO_3)_{0.05}\rightarrow}$$
$$\mathrm{Mg_{6.27}Fe_{1.73}O_{8.16}Cl_{0.66}(OH)_{0.66}+0.41HCl+0.05CO_2}$$

There is a 2.2% mass loss at this step.

Step 6 at 434°C

$$\mathrm{Mg_{6.27}Fe_{1.73}O_{8.16}Cl_{0.71}(OH)_{0.71}\rightarrow}$$
$$\mathrm{Mg_{6.27}Fe_{1.73}O_{8.58}Cl_{0.13}(OH)_{0.29}+0.53HCl}$$

Step 7 at 574°C

$$\mathrm{Mg_{6.27}Fe_{1.73}O_{8.58}Cl_{0.29}\rightarrow}$$
$$\mathrm{Mg_{6.27}Fe_{1.73}O_{8.58}+0.13HCl}$$

There is a mass loss of 1.54% at this temperature. The products of the thermal decomposition are a spinel $0.87MgFe_2O_4$ and $5.4MgO$.

Conclusions

Iowaite has been synthesised with a minimal amount of carbonate in the interlayer. The iowaite compound was analysed by XRD and shown to be pure. EDAX analysis gave a formula of the iowaite compound to be $\mathrm{Mg_{6.27}Fe_{1.73}(Cl)_{1.07}(OH)_{16}(CO_3)_{0.33}\cdot 6.1H_2O}$.

Thermogravimetry in conjunction with evolved gas mass spectrometry has been used to study the thermal decomposition of a compound equivalent to iowaite. The natural sample contained both carbonate and chloride in about equal molar ratios. A previous study showed the thermal decomposition of the natural sample to be complex. In this work a sample of iowaite with minimal carbonate was synthesised. The thermal decomposition was found to be just as complex as the natural mineral with 7 decomposition steps.

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