

Synthesis and thermal stability of hydrotalcites based upon gallium

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Abstract Hydrotalcites based upon gallium as a replacement for aluminium in hydrotalcite over a Mg/Al ratio of 2:1 to 4:1 were synthesised. The $d(003)$ spacing varied from 7.83 Å for the 2:1 hydrotalcite to 8.15 Å for the 3:1 gallium containing hydrotalcite. A comparison is made with the Mg/Al hydrotalcite in which the $d(003)$ spacing for the Mg/Al hydrotalcite varied from 7.62 Å for the 2:1 Mg hydrotalcite to 7.98 Å for the 4:1 hydrotalcite. The thermal stability of the gallium containing hydrotalcite was determined using thermogravimetric analysis. Four mass loss steps at 77, 263–280, 485 and 828 °C with mass losses of 10.23, 21.55, 5.20 and 7.58% are attributed to dehydration, dehydroxylation and decarbonation. The thermal stability of the gallium containing hydrotalcite is slightly less than the aluminium hydrotalcite.

Keywords Hydrotalcite · Hydrocalumite · Gallium · Synthesis · Thermal stability

Introduction

Hydrotalcites (HTs) have been known for an extended period of time [1–3]. Hydrotalcites or layered double hydroxides (LDHs) are fundamentally known as anionic clays [4]. Hydrotalcites consist of stacked layers of metal cations (M^{2+} and M^{3+}) similar to brucite ($Mg(OH)_2$). 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 for Mg^{2+} [2, 5–7]. This substitution creates a positive layer charge on the hydroxide layers, which is compensated by interlayer anions or anionic complexes. In general, any divalent cation could substitute for magnesium in the brucite-like layer. Equally as well, any trivalent cation may substitute for aluminium in the brucite layer. In hydrotalcites a broad range of compositions are possible of the type $[M_{1-x}^{2+}M_x^{3+}(OH)_2]_{x/n} \cdot yH_2O$, 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 [8]. The positively charged hydroxyl layers are neutralised through the intercalation and adsorption of anionic species, therefore stabilising the structure. Anions that are intercalated between the hydroxyl layers need to meet certain criteria, including having a high charge density and small anionic radius.

Few studies of hydrotalcites with the replacement of the aluminium by gallium have been reported. Yet such materials are of importance to industry. There is some evidence that in bauxite, gallium is found as a minor impurity as gallium oxyhydroxide [9–11]. The reaction of red mud and seawater results in the formation of hydrotalcites based not only upon aluminium but also gallium. This study focusses upon the synthesis and characterisation of hydrotalcites with gallium substituting for aluminium in the brucite layer.

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Experimental

Synthesis of hydrotalcite samples

Hydrotalcites can be synthesised in the laboratory using analytical grade chemicals. The reason for using synthetic

Table 1 Concentrations and volumes of salts used for the synthesis of gallium-based hydrotalcites

	2:1	2.5:1	3:1	3.5:1	4:1
Concentration of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}/\text{M}$	0.67	0.71	0.75	0.77	0.80
Masses of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}/\text{g}$	6.81	7.26	7.62	7.92	8.13
Concentration of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}/\text{M}$	0.33	0.29	0.25	0.22	0.20
Masses of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}/\text{g}$	4.22	3.71	3.20	2.81	2.56

compounds as opposed to the natural minerals are that difficulties associated with multiple anions in the interlayer can be minimised, and allow for trends and characteristics to be more readily determined. The hydrotalcites were synthesised by the co-precipitation method. Two solutions were prepared: solution 1 contained 2 M NaOH and 0.2 M Na_2CO_3 , and solution 2 contained Mg^{2+} ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) at different concentrations, together with $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$. Solution 2 was added at a steady rate to solution 1 drop-wise, under vigorous stirring. A separating funnel was used to deliver solution 2 to solution 1. The precipitated minerals were washed at ambient temperatures thoroughly with ultra pure water to remove any residual salts and dried in an oven (85 °C) overnight (Table 1).

Characterisation techniques

Thermal decomposition of approximately 50 mg of hydrotalcite was carried out in a TA[®] Instruments incorporated high-resolution thermogravimetric analyser (series Q500) in a flowing nitrogen atmosphere (80 cm³/min), at a rate of 2.0 °C/min up to 1000 °C. X-ray diffraction

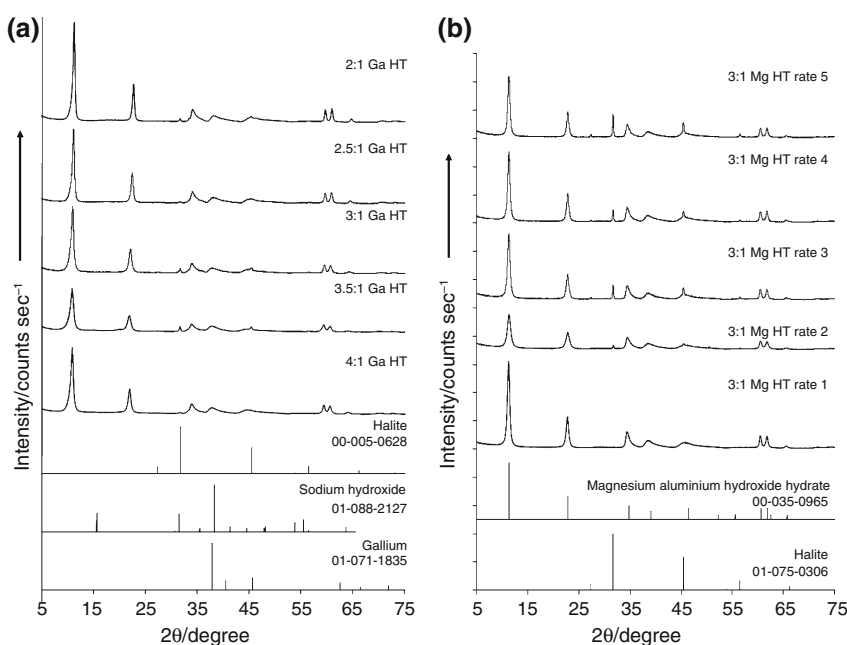
patterns were collected using a Philips X'pert wide angle X-Ray diffractometer, operating in step scan mode, with Cu K α radiation (1.54052 Å). For more information on the experimental and analysis techniques used, refer to previous work by the authors [11–16].

Results and discussion

X-ray diffraction

Hydrotalcites, both synthetic and natural, are normally characterised in the first instance using X-ray diffraction. A typical pattern will show the $d(003)$ peak and subsequent diffraction peaks. The powder XRD patterns of the synthesised gallium containing hydrotalcites are shown in Fig. 1a together with possible impurity phases. For comparison the XRD patterns of the hydrotalcite based upon aluminium is displayed in Fig. 1b. The $d(003)$ spacing for a series of gallium containing hydrotalcites with varying Mg/Ga ratios varies from 7.8 Å for the 2:1 hydrotalcite to 8.2 Å for the 3:1 gallium containing hydrotalcite. The synthesised gallium containing LDH show excellent purity. Some minor impurity phases probably halite and/or sodium hydroxide were found. The $d(003)$ spacing for the Mg/Al hydrotalcite varies from 7.6 Å for the 2:1 Mg hydrotalcite to 8.0 Å for the 4:1 hydrotalcite. For this hydrotalcite the effect of increasing the Mg/Al ratio is to increase the interlayer spacing of the hydrotalcite. The interlayer spacing for the hydrotalcite based upon gallium is larger than that for the Mg:Al hydrotalcite.

Fig. 1 Powder X-ray diffraction of the synthesised **a** gallium and **b** aluminium hydrotalcites in the 2:1 to 4:1 ratio



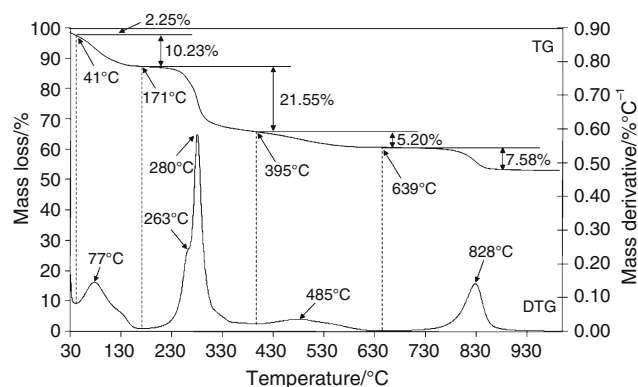


Fig. 2 Thermogravimetric and derivative thermogravimetry (DTG) analysis of the gallium containing hydrotalcite

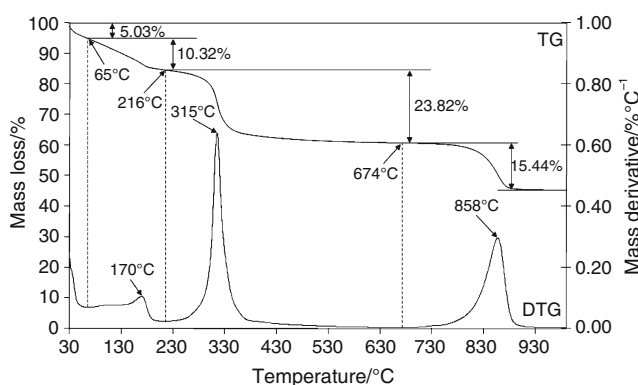


Fig. 3 Thermogravimetric and derivative thermogravimetry (DTG) analysis of the aluminium containing hydrotalcite

A comparison may be made with the *d*-spacings of natural hydrotalcites. There exists in nature a significant number of hydrotalcites which are formed as deposits from ground water containing Ni^{2+} and Fe^{3+} [17]. These are based upon the dissolution of Ni–Fe sulphides during weathering. Normally the hydrotalcite structure based upon takovite (Ni, Al) and hydrotalcite (Mg, Al) has basal spacings of $\sim 8.0 \text{ \AA}$, where the interlayer anion is carbonate. If the carbonate is replaced by sulphate then the mineral carboydite is obtained. Similarly, reevesite is the (Ni, Fe) hydrotalcite with carbonate as the interlayer anion, which when replaced by sulphate the minerals honessite and hydrohonessite are obtained. Among the naturally occurring hydrotalcites are carboydite and hydrohonessite [18, 19]. These two hydrotalcites are based upon the incorporation of sulphate into the interlayer with expansions of $10.3\text{--}10.8 \text{ \AA}$.

Thermal analysis—TG and DTG

The thermal analysis patterns of the hydrotalcite based upon gallium and aluminium are shown in Figs. 2 and 3.

Five mass loss steps are observed for the gallium containing hydrotalcite at 77, 263 and 280, 485 and 828 °C with mass losses of 10.23, 21.55, 5.20 and 7.58%. The theoretical mass loss of water for the Ga-HT is 10.46%. The experimentally determined value for this mass loss compares well with this value. The two overlapping mass loss steps at 263 and 280 °C are attributed to the dehydroxylation of the hydrotalcite. The experimentally determined mass loss of 21.55% compares reasonably well with the theoretical mass loss of 19.75%. The higher mass loss at 280 °C is believed to be due to the loss of both OH and CO_3^{2-} units. It must be remembered that the carbonate anion is the stabilising anion which holds the hydrotalcite layers together through the counterbalance of the positive surface charges on the brucite-like layers. The broad mass loss at 485 °C is ascribed to the loss of carbonate as carbon dioxide (CO_2). It is proposed that a small amount of carbonate species (both magnesium and gallium) formed, thus causing this small mass loss. The higher temperature mass loss at 828 °C is attributed to the decomposition of residual salt (halite). The XRD of the products of the thermal decomposition is shown in Fig. 4. Periclase and a mixed magnesium–gallium oxide are found.

A comparison may be made with the thermal decomposition of the Mg/Al HT. Three mass loss steps are observed at 170, 315 and 658 °C with mass losses of 10.32, 28.82 and 15.44%. These mass losses are attributed to dehydration, dehydroxylation and decarbonation. The theoretical mass losses for the 3:1 Mg:Al HT are 10.99, 22.6% and 10.0%. These experimentally determined values compare well with these theoretical values. The products of the thermal decomposition of the 3:1 Mg–Al HT as shown in Fig. 4b are periclase and magnesium–aluminium oxide.

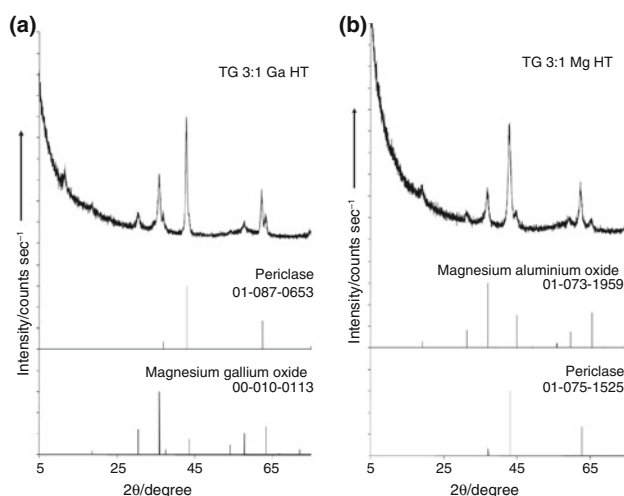


Fig. 4 XRD of the products of the thermal decomposition of **a** gallium containing hydrotalcite and **b** magnesium containing hydrotalcite

Conclusions

Hydrotalcites based upon gallium instead of aluminium were successfully synthesised and characterised by X-ray diffraction and thermogravimetric analysis. A comparison of the interlayer spacing between the gallium and aluminium hydrotalcites is made. The gallium hydrotalcite showed larger interlayer spacing and was found to be less stable than the aluminium hydrotalcite.

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