

# Sulfate intercalated layered double hydroxides prepared by the reformation effect

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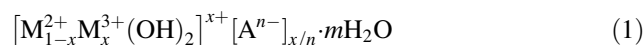
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**Abstract** The removal of the sulfate anion from water using synthetic hydrotalcite (Mg/Al LDH) was investigated using powder X-ray diffraction (XRD) and thermogravimetric analysis (TG). Synthetic hydrotalcite  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$  was prepared by the co-precipitation method from aluminum and magnesium chloride salts. The synthetic hydrotalcite was thermally activated to a maximum temperature of 380 °C. Samples of thermally activated hydrotalcite were then treated with aliquots of 1000 ppm sulfate solution. The resulting products were dried and characterized by XRD and TG. Powder XRD revealed that hydrotalcite had been successfully prepared and that the product obtained after treatment with sulfate solution also conformed well to the reference pattern of hydrotalcite. The  $d_{(003)}$  spacing of all samples was found to be within the acceptable region for a LDH structure. TG revealed all products underwent a similar decomposition to that of hydrotalcite. It was possible to propose a reasonable mechanism for the thermal decomposition of a sulfate containing Mg/Al LDH. The similarities in the results may indicate that the reformed hydrotalcite may contain carbonate anion as well as sulfate. Further investigation is required to confirm this.

**Keywords** Sulfate · Layered double hydroxide · Hydrotalcite · Powder X-ray diffraction · Thermogravimetric analysis · Water purification

## Introduction

Layered double hydroxides (LDHs) are also known as hydrotalcite like materials or anionic clays. Many LDHs such as hydrotalcite, takovite, carboydite, reevesite, honessite, pyroaurite, and iowaite occur in nature while others have been prepared synthetically in the laboratory [1–6]. LDHs are based on the brucite ( $\text{Mg}(\text{OH})_2$ ) structure in which some divalent layer cations are replaced with trivalent cations ( $\text{Al}^{3+}$  in the case of hydrotalcite). The result of this substitution is a layered structure carrying a net positive charge. This positive charge is balanced by anions intercalated between the layers [7, 8]. LDHs follow the general formula:



where  $\text{M}^{2+}$  and  $\text{M}^{3+}$  are the divalent and trivalent layer cations respectively,  $0.2 < x < 0.33$  and  $\text{A}^{n-}$  is the exchangeable anion [8–11].

LDHs exhibit several unusual properties, the most interesting is known as the reformation effect. When a LDH is calcined usually at 300–500 °C interlayer water and anions as well as the hydroxyl groups are eliminated. The result is a mixed metal oxide [3, 12, 13]. This process is also known as thermal activation. When the calcined LDH is placed in solution containing anions, the LDH structure can re-form. Whether the original structure is formed depends on a number of factors, including the nature of the lattice cations and the calcination temperature [8, 14]. In this process water is adsorbed to form the hydroxyl layers, and anions present in the solution will be adsorbed into the interlayer to balance the positive charge of the layers [12]. The reformation effect already has been used to remove a range of anions from water [14–19]. In this article, we report on the removal of the sulfate anion

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from water under normal atmospheric conditions (not under an inert atmosphere) using synthetic hydroxalite prepared by the co-precipitation method.

## Experimental procedure

### Preparation of $\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)_4\cdot 4\text{H}_2\text{O}$

All reagents used in the experiments described in this article were AR grade. Sodium hydroxide and sodium sulfate were obtained from Ajax Finechem Pty Ltd. Magnesium chloride hexahydrate and aluminum chloride hexahydrate were obtained from Clem-Supply. Sodium carbonate was obtained from MERCK Pty Limited. All chemicals were used as received with no additional purification or pretreatment.

A large batch of  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)_4\cdot 4\text{H}_2\text{O}$  (synthetic hydroxalite) was prepared by the co-precipitation method for the use in this and other experiments. A mixed metal solution was prepared by dissolving aluminum chloride hexahydrate (603.6 g) and magnesium chloride hexahydrate (1524.7 g) in deionised water (10,000  $\text{cm}^3$ ). The caustic solution was prepared by slowly dissolving sodium hydroxide (800.2 g) and sodium carbonate (1690.9 g) in deionised water (10,000  $\text{cm}^3$ ). The mixed metal solution was added drop wise from a separating funnel to the caustic solution while stirring. The pH of the solution was monitored using a pH probe and found to average 12.2. Additional sodium hydroxide was added first in granular form then in a solution to keep the pH above 10.

As soon as the two solutions were combined the hydroxalite formed as a white precipitate. The hydroxalite was collected by vacuum filtration and washed with 0.1 M sodium carbonate solution (10,000  $\text{cm}^3$ ). The hydroxalite was collected and dried in an oven at approximately 80 °C. When the hydroxalite was dry it was ground with a mortar and pestle and then homogenized by combining all the samples into a large glass dish and thoroughly mixed. The total mass of hydroxalite obtained was 927.6 g.

### Thermal activation and reformation

Approximately 150 g of the Mg/Al LDH was thermally activated in a furnace to a maximum temperature of 380 °C. The rate of heating averaged at 20 °C/min up to the set temperature, and was left at that temperature for 1 h. A 1000 ppm solution was prepared by dissolving sodium sulfate (2.2158 g) in deionised water (500  $\text{cm}^3$ ). Two amounts of sample were used in this investigation, 3 and 10 g. The experiment was repeated to confirm the results.

Each sample was then treated with a 20  $\text{cm}^3$  aliquot of the 1000 ppm sulfate solution. Each sample was then stirred for 30 min. The mixture was separated by vacuum filtration. The solids were recovered for further analysis and dried in an oven at approximately 80 °C for ~2 days. The filtrate was collected using a syringe filter (0.45  $\mu\text{m}$ ) to remove any remaining particulate material before further analysis.

### Characterization of synthetic hydroxalite

X-ray diffraction patterns were collected using a Philips X'pert wide angle X-Ray diffractometer, with Cu K $\alpha$  radiation (1.54052 Å).

Thermal analysis was carried out using a TA<sup>®</sup> Instruments incorporated high resolution thermogravimetric analyser (series Q500) under a flowing nitrogen atmosphere (40  $\text{cm}^3/\text{min}$ ). The sample (77.365 and 63.228 mg for the 1 and 10 g samples respectively) was placed in an open platinum pan and heated from room temperature at a rate of 2.50 °C/min to a maximum temperature of 1000 °C. TG and DTG curves were obtained however a mass spectrometer was not available for evolved gas analysis.

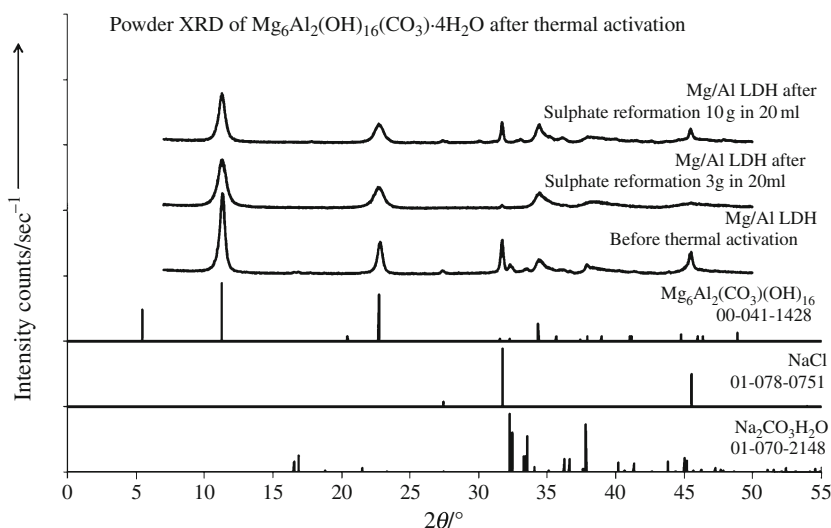
## Results and discussion

### Powder XRD

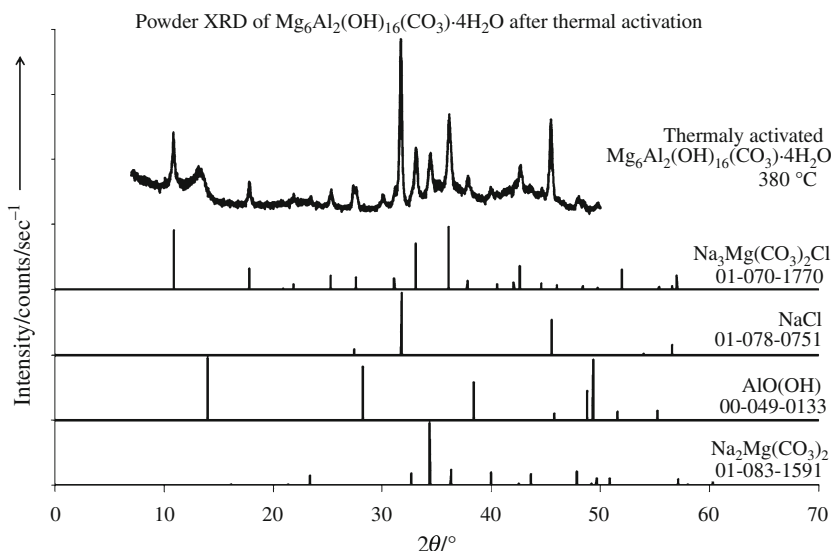
The Powder XRD results shown in Fig. 1 indicate that a LDH structure was successfully formed. The XRD pattern closely fits that of synthetic hydroxalite which is the Mg/Al LDH. Sodium chloride was still present in the sample despite the washing process. There was also some indication that small amounts of sodium carbonate hydrate may be present in the precipitate. The  $d_{(003)}$  spacing was found to be 7.81 Å, which was consistent with a LDH structure [8, 14].

Thermal activation caused a clear change in the XRD pattern as expected. The results are presented in Fig. 2. Comparison of pattern shown in Fig. 1 with that of the thermally activated LDH shown in Fig. 2 shows the LDH structure was lost with thermal activation and regenerated after treatment with sulfate solution. This observation confirms the reformation process of LDH structures. Some phases that may be present in the thermally activated hydroxalite include NaCl,  $\text{Na}_3\text{Mg}(\text{CO}_3)_2\text{Cl}$ ,  $\text{AlO}(\text{OH})$ , and  $\text{Na}_2\text{Mg}(\text{CO}_3)_2$ . The  $d_{(003)}$  spacing was found to increase to 8.13 Å. After reformation in the sodium sulfate solution, the LDH structure was successfully reconstructed. Minimal change in the  $d_{(003)}$  spacing was observed for the treated thermally activated hydroxalites (7.83 and 7.76 Å for the 3 and 10 g samples, respectively)

**Fig. 1** XRD pattern of Mg/Al LDH before thermal activation, after treatment of 3 and 10 g of Mg/Al LDH in 20 cm<sup>3</sup> of sodium sulfate solution and references



**Fig. 2** XRD pattern of Mg/Al LDH after thermal activation with references of possible phases



compared to the original hydrotalcite (7.81 Å). There did not appear to be any additional phases that formed after the reformation process compared to the original hydrotalcite sample. The peaks corresponding to sodium chloride were lower in intensity in the 3 g sample compared to the 10 g sample.

#### Thermal analysis

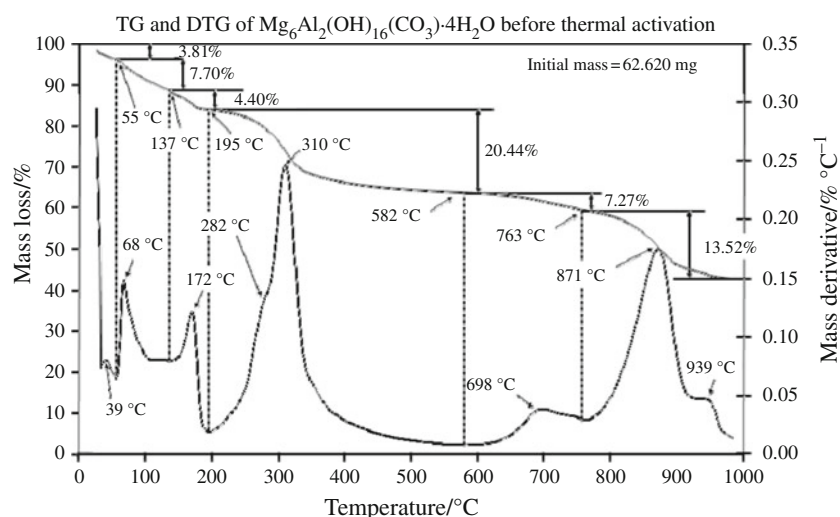
Thermogravimetric analysis was performed on samples of the hydrotalcite before thermal activation (BTA) and after the adsorption of sulfate. There are only a few possible units that could be lost from the sample as it undergoes decomposition; these include water, carbon dioxide, hydroxyl units and oxygen. As evolved mass spectrometry was not carried out it is impossible to conclusively identify any gases evolved, however as the mechanism of the thermal decomposition of hydrotalcite is described in the literature

it is possible to propose a decomposition mechanism based on previous experiments [1, 9, 10, 20–27].

Six mass losses were observed during the decomposition of hydrotalcite BTA shown in Fig. 3. The first two peaks occurred at 39 and 69 °C and accounted for mass losses of 3.81 and 7.70% respectively. Due to the relatively low temperatures of these mass losses it is fairly safe to assume they correspond to weakly adsorbed water. The next mass loss at 170 °C accounted for 4.40% of the mass loss. This peak occurs at a high enough temperature for the loss of interlayer water but not high enough for the removal of the carbonate anions or hydroxyl groups.

The fourth mass loss was the largest occurring at 310 °C accounting for 20.44% of the mass loss. When the DTG curve was examined two overlapping features could be clearly distinguished one occurring at ~282 °C and a second larger feature at 310 °C. Mass losses at this temperature range can usually be attributed to loss of interlayer

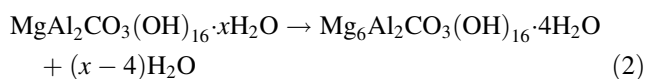
**Fig. 3** TG and DTG curves of Mg/Al LDH Before thermal activation or absorption experiments



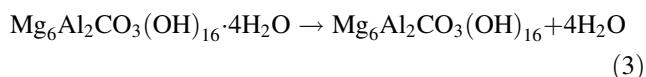
anions. In this case, carbonate (decarbonation) and the loss of hydroxyl groups (dehydroxylation) are proposed to have been removed at this decomposition step. These processes usually overlap and are usually the largest contributor to the mass loss in LDH structures.

A small mass loss occurred at 698 °C with 7.27% mass loss. The final mass loss at 871 °C with a percentage mass loss of 13.52 also appeared to have two overlapping features. The first larger feature occurred at 871 °C while a much smaller feature was observed at 939 °C. The temperature at which these mass losses occur is too high for dehydroxylation or decarbonation. They can most likely be attributed to decomposition of the metal oxide into a spinel phase resulting in the loss of oxygen. The following mechanism can be proposed for the thermal decomposition of the synthetic hydrotalcite [1, 10, 22–24].

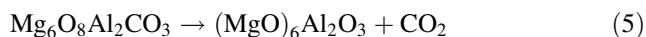
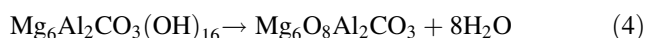
The first step in the thermal decomposition involves removal of weakly adsorbed water (up to 100 °C).



The next step is elimination of interlayer water (100–200 °C).



Dehydroxylation and decarbonation then appear to occur simultaneously (200–400 °C). The hydroxyl and carbonate groups are lost as water and carbon dioxide, leaving a magnesium/aluminum oxide mixture.



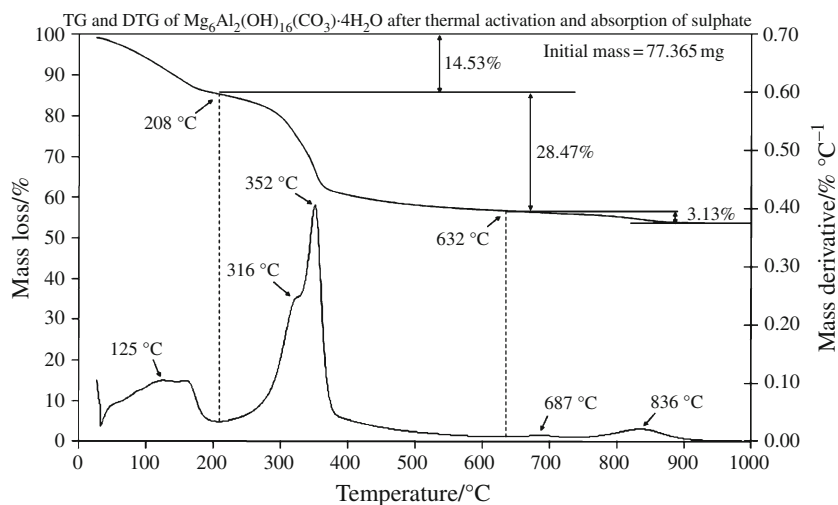
Decomposition of the mixed metal oxide at temperatures above 400 °C into a spinel phase resulting in a loss of oxygen.



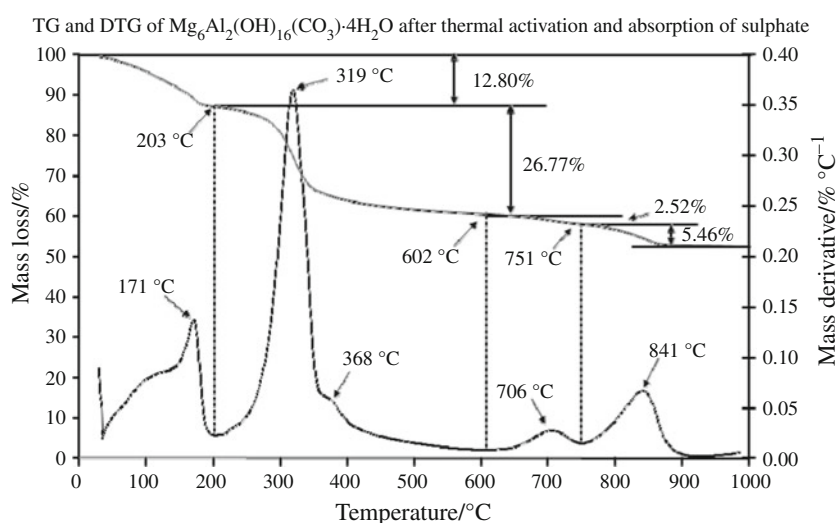
The TG curve of the 3 g of reformed hydrotalcite by treatment in a 1000 ppm sulfate solution is shown in Fig. 4. Three mass losses were observed. The first mass loss occurred at ~125 °C accounting for 14.53% mass loss. A broad feature is observed in the DTG curve indicating the mass loss is likely due to loss of adsorbed water and interlayer water. The next mass loss occurred at approximately 352 °C and accounted for 28.47% mass loss. The increase in decomposition temperature, compared to BTA, may indicate that sulfate anions have been successfully intercalated. The carbonate only hydrotalcite had a decomposition temperature of only 310 °C. It is also possible that the increase in decomposition temperature may result from the reformed hydrotalcite having a different structure to that of the original. Once again the DTG curve showed two peaks overlapping at 316 and 352 °C. This mass loss was attributed to loss of interlayer anions (carbonate and sulfate) and dehydroxylation (hydroxide). The final mass loss of 3.13% occurred between 632 and 1000 °C. Two small broad peaks were observed in the DTG curve in this region.

Only four mass loss steps were observed in the TG curve of the 10 g sample of reformed hydrotalcite, the results are presented in Fig. 5. The first mass loss at 171 °C can be attributed to the loss of water. The DTG curve shows a broad feature that can likely be attributed to the loss of adsorbed water while the sharp peak at 171 °C is most likely due to the loss of interlayer water. The second and largest mass loss occurred at 319 °C accounting for 26.77%. A small peak at 368 °C was observed in the DTG curve overlapping with the larger peak at 319 °C. Comparison of this DTG curve with the DTG curve of the hydrotalcite BTA suggests that the small peak at 368 °C represents the loss of intercalated sulfate anions, while the larger peak at 319 °C is associated with the loss of

**Fig. 4** TG and DTG curves of Mg/Al LDH After thermal activation and reformation by treatment of 3 g of Mg/Al LDH with 1000 ppm sodium sulfate solution (20 cm<sup>3</sup>)

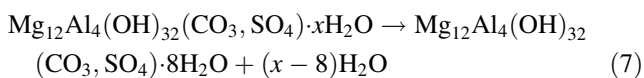


**Fig. 5** TG and DTG curves of Mg/Al LDH After thermal activation and reformation by treatment of 10 g of Mg/Al LDH with 1000 ppm sodium sulfate solution (20 cm<sup>3</sup>)

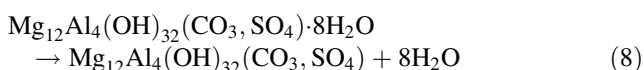


intercalated carbonate anions. This mass loss is attributed to loss of interlayer anions (carbonate and sulfate) and loss of hydroxyl groups. The next mass loss at 706 °C was the smallest with a percent mass loss of only 2.52%. The final mass loss occurred at 841 °C with a percent mass loss of 5.46%. A similar mechanism can be proposed for the decomposition of the sulfate intercalated LDH.

Again the first step in the thermal decomposition is the removal of weakly adsorbed water from the surface.

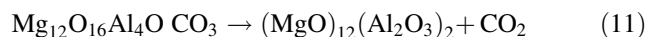
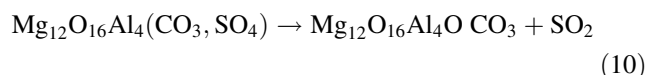
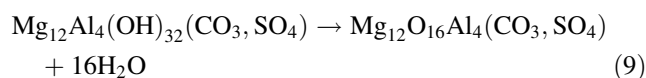


The next step involves the removal of interlayer water.



The next step involves elimination of the hydroxyl groups as water. Interlayer anions (carbonate and sulfate) will be eliminated in this step most likely as sulfur dioxide and

carbon dioxide resulting in the formation of the same mixed metal oxide observed for BTA.



Finally, decomposition of the metal oxide can result in the formation of a spinel phase.



## Conclusions

Powder XRD indicated the  $d_{(003)}$  spacing was within the accepted range for a LDH structure. Thermal activation was found to cause a small increase in the  $d_{(003)}$  spacing (0.32 Å).



Reformation with sulfate anions caused the  $d_{(003)}$  spacing to resemble the  $d_{(003)}$  of the original hydrotalcite. It is possible that the majority of sulfate anions are adsorbed on the surface of the regenerated hydrotalcite, while carbonate and a small amount of sulfate has been intercalated into the structure however further investigation is required to confirm this. When the powder XRD patterns were compared to the reference pattern of hydrotalcite a number of characteristic peaks were observed. Several peaks in the powder XRD pattern could be attributed to the presence of sodium chloride. This was not unexpected as it was the main byproduct of the synthesis method used. These results indicate that synthetic Mg/Al hydrotalcite was successfully prepared.

Comparison of the dehydroxylation and decarbonation temperature indicated that the reformed LDH has intercalated sulfate anions. This is shown by an increase in decomposition temperature of the peak between 300 and 400 °C. The carbonate only hydrotalcite had a decomposition temperature of 310 °C, while the reformed hydrotalcites from sulfate solutions had a decomposition temperature of 352 and 368 °C. All hydrotalcite samples appear to undergo decomposition through a similar mechanism. The similarity of the powder XRD and TG results may indicate that a mixed LDH containing both sulfate and carbonate anions was prepared. The intercalation of carbonate in the reformed hydrotalcites is possible as no attempts were made to prevent the intercalation of carbonate which LDHs have a high affinity for. Further investigation is required to determine the exact composition of the hydrotalcite interlayer.

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