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THERMAL DECOMPOSITION OF STICHTITE

Jocelyne Bouzaid and Ray L. Frost[*]

Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology
GPO Box 2434, Brisbane Queensland 4001, Australia

The mineral stichtite was synthesised and its thermal decomposition measured using thermogravimetry coupled to an evolved gas mass spectrometer. Mass loss steps were observed at 52, 294, 550 and 670°C attributed to dehydration, dehydroxylation and loss of carbonate. The loss of carbonate occurred at higher temperatures than dehydroxylation.

Keywords: *hydrotalcite, iowaite, pyroaurite, stichtite, thermogravimetry*

Introduction

A group of minerals exists which are known as hydrotalcites or anionic clays [1–4]. These clay minerals are often of a very small particle size. It has been said that the minerals are rare, but such a comment is questionable since deposits exist in Australia, mixed with other minerals through complex paragenic relations. These anionic clays are more widespread than is commonly believed. Among the common hydrotalcites are hydrotalcite, takovite, carrboydite, reevesite, honessite, pyroaurite, iowaite and stichtite. Stichtite is often found in association with serpentinite deposits with associated chromate. Such a pargenetic relationship is found at Stichtite Hill, Dundas, Tasmania, Australia. The mineral is a very distinct pink to purple colour.

Interest in the study of these hydrotalcites results from their potential use as catalysts, adsorbents and anion exchangers [5–9]. 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 [10, 11]. Hydrotalcites may also be used as components in new nano-materials such as nano-composites [12]. Incorporation of low levels of hydrotalcite into polymers enables polymeric materials with new and novel properties to be manufactured. There are many other uses of hydrotalcites. Hydrotalcites are important in the removal of environmental hazards in acid mine drainage [13, 14]. Hydrotalcites may also be used as anion exchangers. Hydrotalcite formation also offer a mechanism for the disposal of radioactive wastes [15]. Hydrotalcite formation may also serve as a means of heavy metal removal from contaminated waters [16]. Thermal analysis has been applied to the study of hydrotalcites [17–24]. An important study of these hydrotalcites is the thermal decomposition as this information provides concepts on the molecular structure of stichtite.

Experimental

Synthetic minerals

Stichtite was synthesised by the co-precipitation method. Two solutions were prepared using boiled ultrapure water, solution 1 contained 2 M NaOH and Na_2CO_3, and solution 2 contained 0.75 M Mg^{2+} ($Mg(NO_3)_2\cdot 6H_2O$), together with 0.25 M Cr^{3+} (as ($CrCl_3\cdot 9H_2O$)). 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 composition of the stichtite was checked by electron probe analyses. The phase composition was checked by X-ray diffraction.

Thermal analysis

Thermal decomposition of the stichtite 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 500°C. With the quasi-isothermal, quasi-isobaric heating program of the instrument the furnace temperature was regulated precisely to provide a uniform rate of decomposition in the main decomposition stage. The TG instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. Only selected gases such as water and carbon dioxide were analyzed.

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[*] Author for correspondence: r.frost@qut.edu.au

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Results and discussion

Stichtite is the mineral $Mg_6Cr_2CO_3(OH)_{16}\cdot 4H_2O$ and as such there are four possible units which could be lost during decomposition, namely water, hydroxyl units, carbon dioxide and oxygen. The TG curves for stichtite are shown in Fig. 1. Four mass loss steps are identified at (a) 52°C with the loss of 24.9% at (b) 294°C with a mass loss of 22.5% at (c) ~550°C with a mass loss of 2.5% and at (d) 670°C with a mass loss of 1.2%. The theoretical mass loss of water according to the formula $Mg_6Cr_2CO_3(OH)_{16}\cdot 4H_2O$ is 11.0%. There is a large variation between the experimentally determined mass loss and the theoretical prediction. One interpretation of this result is that there are more water molecules in the formula unit than expected. Using a mass loss of 24.9% would give the moles of water as 9 moles. Such a result has been observed for other hydrotalcites namely honessite and hydrohonessite which have 4 and 7 moles, respectively. The experimental mass loss for hydroxyl units is 20.9%. The experimental value is 22.5% which is a reasonable result. The difference may be accounted for by the loss of carbon dioxide.

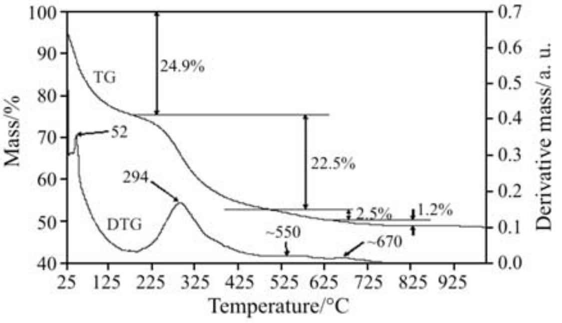

Fig. 1 TG and DTG curves of stichtite

The relative ion current curves for H_2O, OH and O are shown in Fig. 2 and the ion current curves for O_2 and CO_2 are shown in Fig. 3. The MS curves in Fig. 2 clearly show that the hydroxyl units are lost as water at 280°C. The MS=44 curve shows that carbon dioxide is lost at three temperatures namely 338, 545 and 675°C. The mass loss curve (Fig. 1) at 294°C is asymmetric on the high temperature side. This asymmetry represents the mass loss of hydroxyl units followed by the mass loss of carbonate. Figures 2 and 3 show that the carbon dioxide is lost after the water is evolved. This observation is somewhat unusual as normally the water and carbon dioxide are lost simultaneously for hydrotalcites. The evolution of carbon dioxide at 545 and 675°C suggests that some carbonate as reacted with the metal oxide surfaces.

The following steps show the possible mechanism for the decomposition of stichtite.

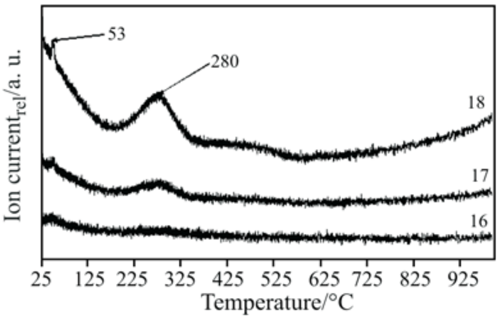

Fig. 2 Relative ion current of H_2O, OH and O as a function of temperature

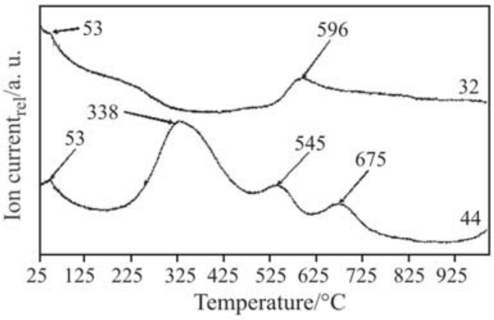

Fig. 3 Relative ion current of CO_2 and O_2 as a function of temperature

- Mass loss step 1 at 52°C:

$$Mg_6Cr_2CO_3(OH)_{16}\cdot 4H_2O\rightarrow Mg_6Cr_2CO_3(OH)_{16}+4H_2O \tag{1}$$

- Mass loss step 2 at 294°C:

$$Mg_6Cr_2CO_3(OH)_{16}\rightarrow (MgO)_6Cr_2CO_5+8\ H_2O \tag{2}$$

- Mass loss step 3 at 338°C:

$$(MgO)_6Cr_2CO_5\rightarrow 6MgO+Cr_2O_3+CO_2 \tag{3}$$

Further reactions

$$MgO+CO_2\rightarrow MgCO_3 \tag{4}$$

and

$$Cr_2O_3+CO_2\rightarrow Cr_2CO_3 \tag{5}$$

- Mass loss step 4 at 545 and 675°C:

$$MgCO_3\rightarrow MgO+CO_2 \tag{6}$$

and

$$Cr_2CO_3\rightarrow Cr_2O_3+CO_2 \tag{7}$$

Equation (2) shows that dehydroxylation is occurring as a different step to the loss of carbonate. This loss of carbonate occurs at a higher temperature. During the evolution of carbon dioxide some of the CO_2 reacts with the metal oxides as is shown in Eqs (4) and (5). It is not known if the oxide is formed first and then reacts with the evolving CO_2 or whether the carbonate anion reacts with the MO surfaces after the loss of CO_2. The loss of carbonate then occurs at higher temperatures according to Eqs (6) and (7).

Conclusions

The thermal decomposition of stichtite occurs in steps with dehydration followed by dehydroxylation and decarbonation. The temperatures of these steps are significantly different and in particular dehydroxylation although overlapping with the loss of carbonate occurs at a lower temperature. Stichtite does have the potential for use as a catalyst [25]. The thermal decomposition studies show the temperatures to which stichtite must be heated to obtain the mixed metal oxides.

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