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THERMAL DECOMPOSITION OF HYDROTALCITE WITH MOLYBDATE AND VANADATE ANIONS IN THE INTERLAYER

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Hydrotalcites containing carbonate, vanadate and molybdate were prepared by coprecipitation. The resulting materials were characterized by XRD, and TG/DTA to determine the stability of the hydrotalcites synthesized. The thermal decomposition of carbonate hydrotalcites consist of two decomposition steps between 300 and 400°C, attributed to the simultaneous dehydroxylation and decarbonation of the hydrotalcite lattice. Water loss ascribed to dehydroxylation occurs in two decomposition steps, where the first step is due to the partial dehydroxylation of the lattice, while the second step is due to the loss of water interacting with the interlayer anions. Dehydroxylation results in the collapse of the hydrotalcite structure to that of its corresponding metal oxides, including MgO, Al_2O_3, $MgAl_2O_4$, $NaMg_4(VO_4)_3$ and $Na_2Mg_4(MoO_4)_5$. The presence of oxy-anions proved to be beneficial in the stability of the hydrotalcite structure, shown by the delay in dehydroxylation of oxy-anion containing hydrotalcites compared to the carbonate hydrotalcite. This is due to the substantial amount of hydroxyl groups involved in a network of hydrogen bonds involving the intercalated anions. Therefore, the stability of the hydrotalcite structure appears to be dependent on the type of anion present in the interlayer. The order of thermal stability for the synthesized hydrotalcites in this study is Syn-HT-V>Syn-HT-Mo> Syn-HT-CO_3-V>Syn-HT-CO_3-Mo>Syn-HT-CO_3. Carbonate containing hydrotalcites prove to be less stable than oxy-anion only hydrotalcites.

Keywords: *carbonate, hydrotalcite, iowaite, molybdate, pyroaurite, stitchtite, thermogravimetry, vanadate*

Introduction

A group of minerals exist which are known as hydrotalcites or anionic clays [1–4]. Among the natural hydrotalcites are hydrotalcite, takovite, carboydite, reevesite, honessite, pyroaurite, iowaite and stichtite [5–13]. Hydrotalcites, also known as layered double hydroxides (LDH's) or ionic clays are based upon the brucite [$Mg(OH)_2$] structure in which some of the divalent cations are replaced by trivalent cations (e.g. Al or Fe) resulting in a layer charge. This layer charge is counterbalanced by anions such as carbonate or sulphate 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 [14].

Thermal analysis using thermogravimetric techniques enables the mass loss steps, the temperature of the mass loss steps and the mechanism for the mass loss to be determined [7, 10, 15–19]. Thermoanalytical methods provide a measure of the thermal stability of the hydrotalcite. 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 [20, 21]. There are many other important uses of hydrotalcites such as in the removal of environmental hazards in acid mine drainage [22, 23], and a mechanism for the disposal of radioactive wastes [24]. Their ability to exchange anions presents a system for heavy metal removal from contaminated waters [25]. Structural information on different minerals has successfully been obtained recently by sophisticated thermal analysis techniques [7, 15–19]. In this work we report the thermal analysis of hydrotalcite with molybdate and vanadate in the interlayer.

Experimental

Synthesis of hydrotalcite samples

Hydrotalcites are able to be synthesised in the laboratory using analytical grade chemicals. The reason for using synthetic compounds as opposed to the natural minerals is 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 pre-

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pared, solution 1 contained 2 M NaOH and a combination of Na_2CO_3 and Na_2MoO_4 to give a concentration of 0.2 M, and solution 2 contained 0.75 M Mg^{2+} ($MgCl_2{\cdot}6H_2O$), together with 0.25 M Al^{3+} ($AlCl_3$). In the case of the intercalation of vanadate, the following procedure was used: Two solutions were prepared, solution 1 contained 2 M NaOH and a combination of Na_2CO_3 and $NaVO_3$ to give a concentration of 0.2 M, and solution 2 contained 0.75 M Mg^{2+} ($MgCl_2{\cdot}6H_2O$), together with 0.25 M Al^{3+} ($AlCl_3$). Solution 2 was added at a steady rate to solution 1 drop wise, under vigorous stirring. A peristaltic pump was not used in the synthesis of these hydrotalcites. Instead a separating funnel was used to deliver solution 2 to 1. The precipitated minerals were washed at ambient temperatures thoroughly with ultra pure water to remove any residual salts.

Concentrations of Na_2CO_3 and Na_2MoO_4 are given below for the three hydrotalcites synthesised:

- Syn-HT-CO_3: 0.2 M Na_2CO_3
- Syn-HT-CO_3, Mo: 0.1 M Na_2CO_3 and 0.1 M Na_2MoO_4
- Syn-HT-Mo: 0.2 M Na_2MoO_4

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. The Profile Fitting option of the software uses a model that employs twelve intrinsic parameters to describe the profile, the instrumental aberration and wavelength dependent contributions to the profile.

Thermal analysis

Thermal decomposition of the hydrotalcite 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. Only selected gases such as water and carbon dioxide were analyzed. The synthesized hydrotalcites were kept in an oven for 24 h before TG analysis. Thus the mass losses calculated as a percentage was on a dry basis.

Results and discussion

X-ray diffraction

The X-ray diffraction patterns of the synthesised hydrotalcite and the standard reference pattern (01-089-0460 Hydrotalcite, Syn) are shown in Fig. 1. Since all of the broad peaks of the synthetic samples correspond to those of hydrotalcite, the prepared hydrotalcites were confirmed to have the structure of hydrotalcite. Synthetised hydrotalcites normally have d_{003} spacing of 7.9 Å [26]. The synthesised hydrotalcites in this study gave d_{003} spacings 7.84, 7.97, 7.87, 7.88 and 8.01 Å. The d_{003} plane peak is responsible for the increase in interlayer spacing, and it appears that the intercalation of molybdate and vanadate anions has caused an increase in the basal spacing compared to the hydrotalcite with carbonate only (Fig. 1a).

The basal spacing of the hydrotalcites increased as the quantity of molybdate increased due to molybdate being larger in size than carbonate, forcing the layers of the hydrotalcite further apart. The hydrotalcite peaks are broad due to the lack of hydrothermal treatment, and indicates that the synthesised minerals are of poor crystallinity. The XRD pattern reveals that along with hydrotalcite being formed so does the impurity sodium chloride.

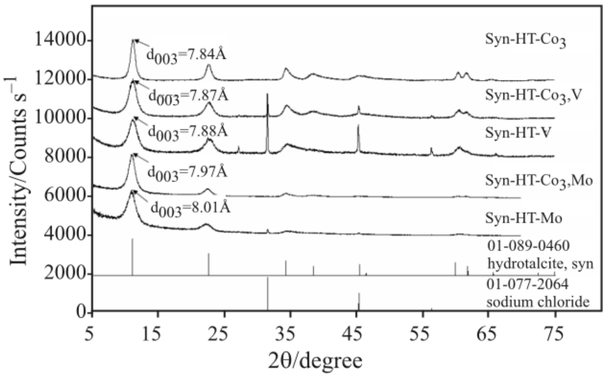

Fig. 1a XRD patterns of the synthesised molybdate and vanadate intercalated hydrotalcites

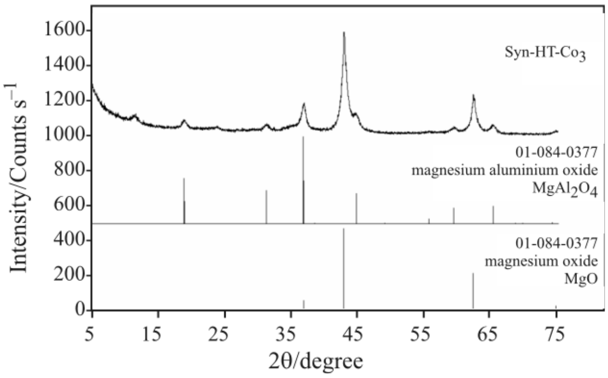

Fig. 1b XRD patterns of the heated residue of the synthesised carbonate only intercalated hydrotalcite

Thermogravimetry

Carbonate anion intercalated hydrotalcite

The thermogravimetric and differential thermogravimetric analysis of carbonate intercalated Mg–Al hydrotalcite are shown in Fig. 2a. The ion current curves for selected evolved gases are shown in Fig. 2b. A small mass loss step between 35 and 59°C of 3.44% is observed and attributed to the loss of adsorbed water. The *m*/*Z*=17 and 18 ion current curves proved water is the evolved gas at this temperature. The following thermal decomposition is proposed:

$$Mg_6Al_2(OH)_{16}CO_3{\cdot}5H_2O\rightarrow Mg_6Al_2(OH)_{16}CO_3+5H_2O$$

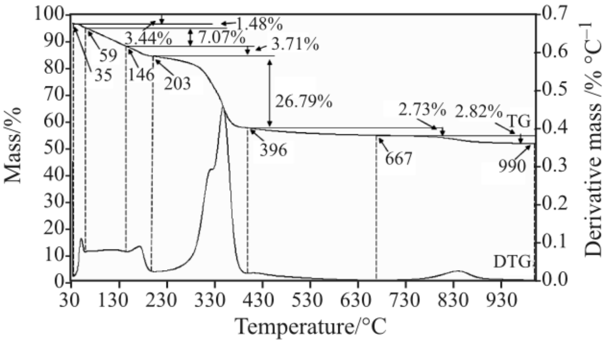

Fig. 2a TG ad DTG curves of carbonate intercalated Mg–Al hydrotalcite

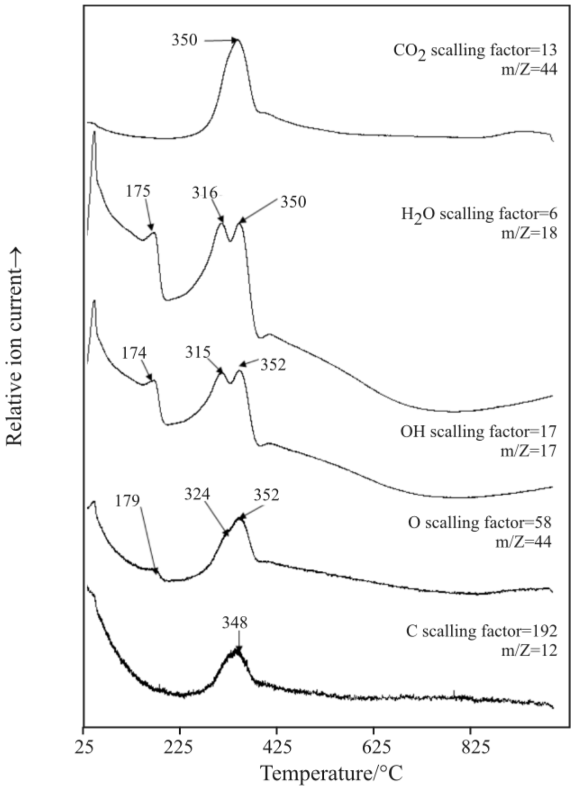

Fig. 2b The ion current curves for selected evolved gases in the thermal decomposition of carbonate intercalated Mg–Al hydrotalcite

Over the temperature range 59 to 203°C, a mass loss of 7.07+3.71% is observed. The ion current curves for *m*/*Z*=18 displays a broad peak over this temperature range, and is thus attributed to the further mass loss of water. Calculations as reported in the appendix show that the number of moles of water is 5.0 moles, as shown in the formula above.

Two mass loss steps are observed at 315 and 350°C with a total mass loss of 26.79%. The ion current curves for *m*/*Z*=17 and 18 show two maxima at 316 and 350°C attributed to evolved water vapour at these temperatures confirming the loss of OH units at these temperatures. The ion current curves for *m*/*Z*= 44 and 12 show maxima at ~350°C confirming the evolution of CO_2 at this temperature attributed to the thermal decomposition of the carbonate anion. The following reaction is proposed:

$$Mg_6Al_2(OH)_{16}CO_3\rightarrow MgAl_2O_{4+}5MgO+CO_2+8H_2O$$

The decomposition products proposed were confirmed by XRD analysis (Fig. 1b). The theoretical mass loss according to this reaction of water vapour and CO_2 is 27.16 and 8.30%. A higher temperature mass loss at around 830°C of 2.82% is observed and is assigned to the loss of oxygen from the decomposition of the oxides.

Carbonate and molybdate anion intercalated hydrotalcite

The thermogravimetric analysis of the synthetic hydrotalcite formed with equimolar amounts of carbonate and molybdate anions is reported in Fig. 3a. The equivalent ion current curves for selected gases are shown in Fig. 3b. If the synthetic hydrotalcite is prepared with equal amounts of carbonate and molybdate anions then the proposed formula of the hydrotalcite is $Mg_6Al_2(OH)_{16}(CO_3)_{0.5}(MoO_4)_{0.5}$. The molecular mass of this compound is 580 molecular mass units. The theoretical mass losses according to this formula of CO_2 and OH units are 5.17 and 24.82%, respectively. The mass loss between 700 and 880°C is attributed to the evolution of HCl originating from the reaction of NaCl.

The thermogravimetric curves for this hydrotalcite show strong resemblance for the hydrotalcite synthesised with carbonate anions. The mass loss over the temperature range 35 to 61°C is 2.46% attributed to the loss of adsorbed water. The ion current curves for *m*/*Z*=17 and 18 prove water is the evolved gas at this temperature range. Further mass losses of 1.66 and 4.71% are observed up to 110°C. Again the ion current curves indicate that water vapour is evolved at these temperatures. These mass losses are attributed to the loss of water from the interlayer of the hydrotalcite. An additional mass loss of 7.03% is

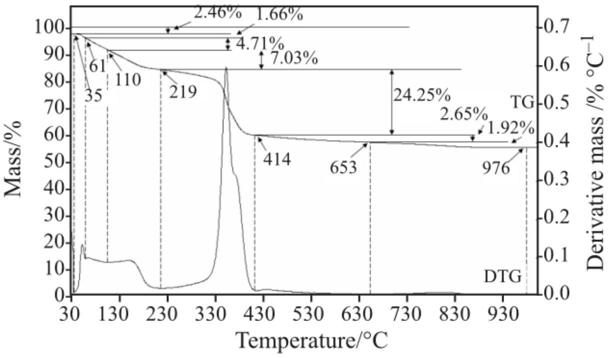

Fig. 3a TG ad DTG curves of carbonate and molybdate intercalated Mg–Al hydrotalcite

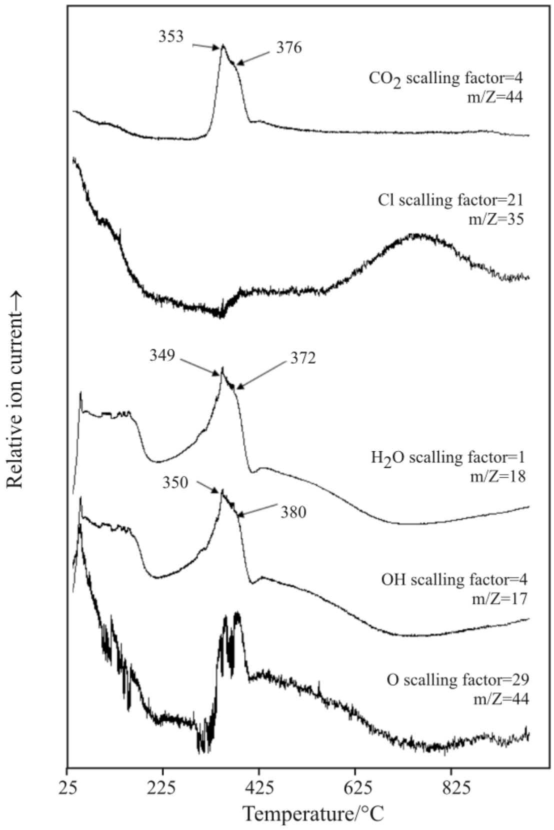

Fig. 3b The ion current curves for selected evolved gases in the thermal decomposition of carbonate and molybdate intercalated Mg–Al hydrotalcite

found for the 110 to 219°C temperature range. The following reaction is proposed for the removal of adsorbed water:

$$Mg_6Al_2(OH)_{16}(CO_3)_{0.5}(MoO_4)_{0.5}{\cdot}6H_2O\rightarrow$$
$$MgAl_2O_4{+}5MgO{+}CO_{2+}6H_2O$$

Calculations given in the appendix shows that the number of moles of water is 6.0 moles, as shown in the formula above.

The DTG pattern over the 300 to 430°C is the mirror image of the DTG pattern for the hydrotalcite formed with carbonate anion only. Two decomposition steps at 350 and 376°C with a total mass loss of 24.25%. The ion current curves for *m*/*Z*=44 shows that CO_2 is the evolved gas at 353 and 372°C. The *m*/*Z*=17 and 18 ion current curves prove that water vapour is evolved at around 350 and 372°C. Thus for the thermal decomposition of the carbonate-molybdate hydrotalcite the decomposition of the OH and carbonate units occur simultaneously.

Molybdate anion intercalated hydrotalcite

TG and DTG curves for the thermal decomposition of hydrotalcite intercalated with molybdate are shown in Fig. 4a. The ion current curves for this thermal decomposition are reported in Fig. 4b. The hydrotalcite with molybdate in the interlayer is given by the formula $Mg_6Al_2(OH)_{16}(MoO_4)$. Thus the molecular mass is 630 AMU. The theoretical mass loss due to the dehydroxylation is 20.31%.

A mass loss of 2.80% at low temperatures at around 35°C attributed to dehydration of the molybdate intercalated hydrotalcite. The ion current curves of *m*/*Z*=17 and 18 prove that water is the evolved gas at this temperature. A further mass loss of 10.91% is observed up to 197°C. The following reaction shows the proposed mechanism for the removal of water:

$$Mg_6Al_2(OH)_{16}(MoO_4){\cdot}5H_2O\rightarrow$$
$$MgAl_2O_4{+}5MgO\ {+}CO_2{+}5H_2O$$

The calculations for the number of moles of water removed, up to 197°C, is shown in the appendix.

A single mass loss of 21.42% is found at 350°C. The ion current curves of *m*/*Z*=17 and 18 prove that water is the evolved gas at this temperature. This water vapour results from the dehydroxylation of the hydrotalcite. This may be compared with the two former DTG curves for the carbonate and mixed carbonate-molybdate intercalated hydrotalcites where two distinct thermal decomposition steps were observed. The experimental mass loss of 21.42% may be compared with the theoretical mass loss of 20.31%. The ion current curve for *m*/*Z*=44 (with a scaling factor of 27) shows that low amounts of CO_2 are evolved at 350°C. Thus the difference between the experimental and theoretical mass losses (1.11%) may be accounted for by the presence of carbonate in the interlayer of the hydrotalcite.

Carbonate and vanadate anion intercalated hydrotalcite

TG and DTG curves for the thermal decomposition of hydrotalcite intercalated with vanadate and carbonate anions are shown in Fig. 5a. The ion current curves for this thermal decomposition are reported in Fig. 5b. The hydrotalcite with both carbonate and vanadate in

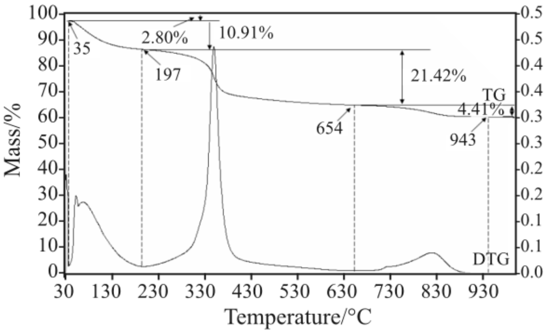

Fig. 4a TG ad DTG curves of molybdate intercalated Mg–Al hydrotalcite

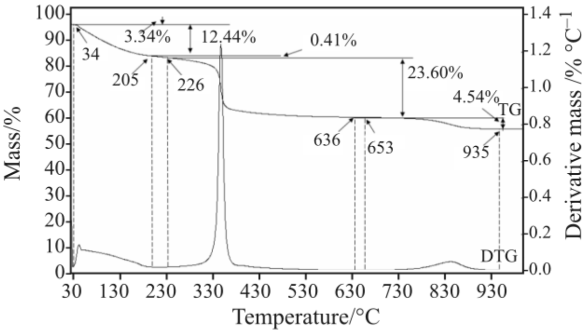

Fig. 5a TG ad DTG curves of carbonate and vanadate intercalated Mg–Al hydrotalcite

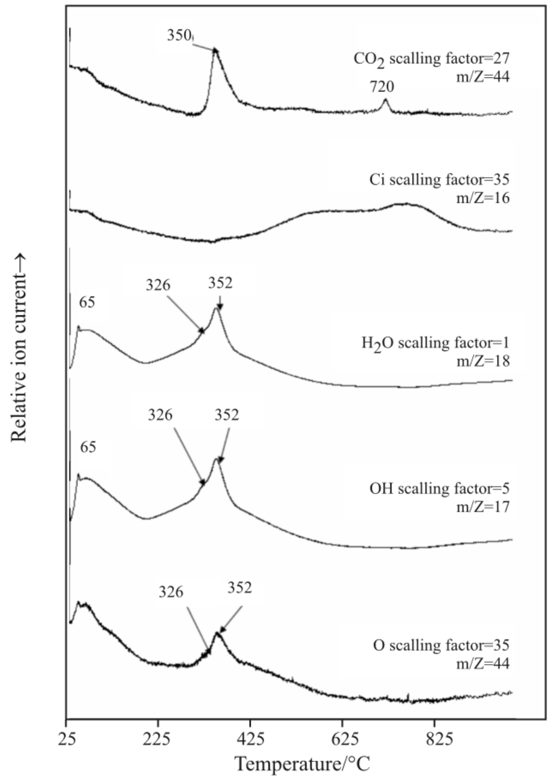

Fig. 4b The ion current curves for selected evolved gases in the thermal decomposition of molybdate intercalated Mg–Al hydrotalcite

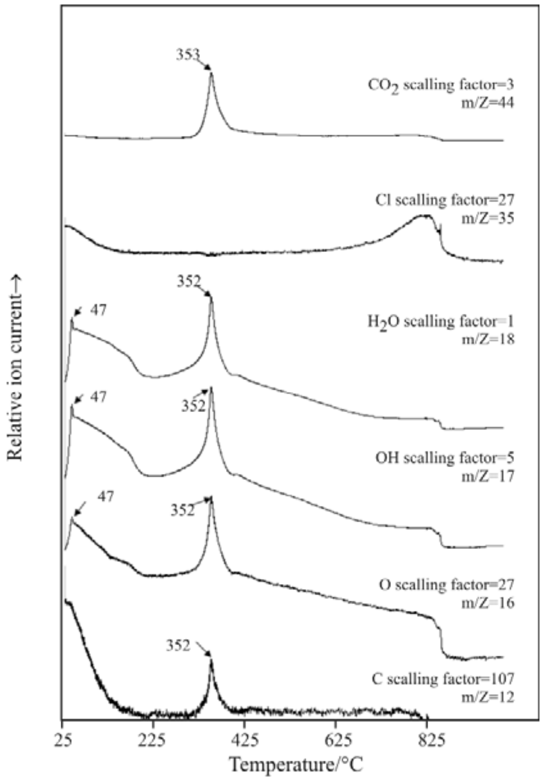

Fig. 5b The ion current curves for selected evolved gases in the thermal decomposition of carbonate and vanadate intercalated Mg–Al hydrotalcite

the interlayer is given by the formula $Mg_6Al_2(OH)_{16}(CO_3)_{0.5}(VO_4)_{0.5}$. Thus the molecular mass is 558 AMU. The theoretical mass loss due to the dehydroxylation is 25.83% and de-carbonation is 3.85%.

As with the other synthesised hydrotalcite a low temperature mass loss of 3.34% is observed and is attributed to the removal of some adsorbed water. A significant mass loss of 12.44+0.41% up to around 226°C is found and is ascribed to a further dehydration step resulting from the loss of water from the hydrotalcite interlayer. The ion current curves show water vapour is the evolved gas over this temperature range. The following reaction describes the dehydration step:

$$Mg_6Al_2(OH)_{16}(CO_3)_{0.5}(VO_4)_{0.5}{\cdot}6H_2O\rightarrow$$
$$MgAl_2O_4{+}5MgO{+}CO_2{+}6H_2O$$

Calculations as reported in the appendix show that the number of moles of water is 5.0 moles, as shown in the formula above.

A single mass loss step is found at 351°C with a mass loss of 23.60%. The ion current curves for *m*/*Z*=17, 18 and 44 show that H_2O vapour and CO_2 are the evolved gases at this temperature. Thus for this hydrotalcite the dehydroxylation and de-carbonation processes take place simultaneously.

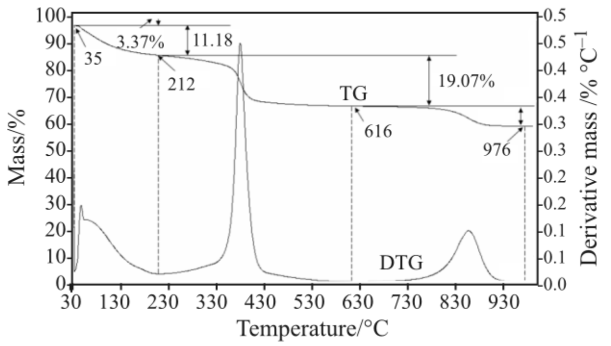

Fig. 6a TG and DTG curves of vanadate intercalated Mg–Al hydrotalcite

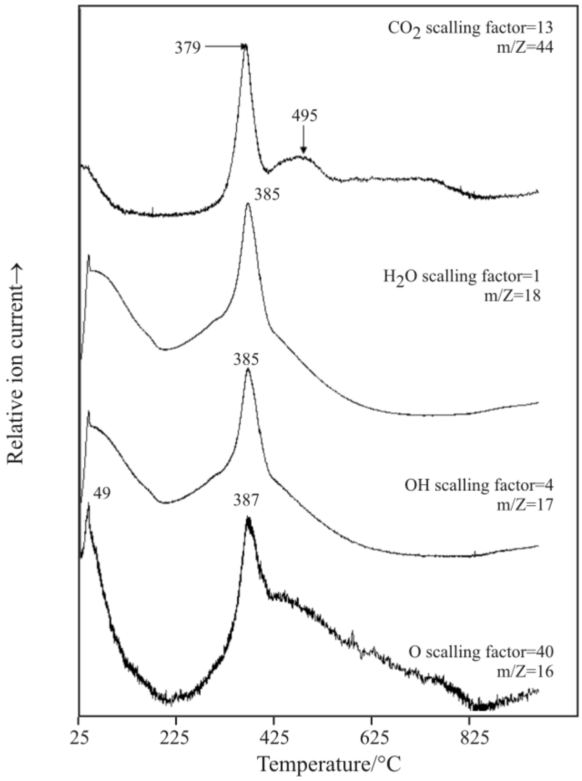

Fig. 6b The ion current curves for selected evolved gases in the thermal decomposition of vanadate intercalated Mg–Al hydrotalcite

Vanadate anion intercalated hydrotalcite

TG and DTG curves for the thermal decomposition of hydrotalcite intercalated with vanadate are shown in Fig. 6a. The ion current curves for this thermal decomposition are reported in Fig. 6b. The hydrotalcite with vanadate in the interlayer is given by the formula $Mg_6Al_2(OH)_{16}(VO_4)$. Thus the molecular mass is 585 AMU. The theoretical mass loss due to the dehydroxylation is 24.61% and de-carbonation should be 0%.

Two dehydration steps are observed at 35 and up to 212°C with mass losses of 3.37 and 11.18% attributed to desorption of water from the hydrotalcite and from dehydration of the hydrotalcite interlayer. The following reaction is proposed:

$$Mg_6Al_2(OH)_{16}(VO_4)\cdot 5H_2O\rightarrow$$
$$MgAl_2O_4+5MgO+CO_2+5H_2O$$

The calculations for the number of moles of water removed, up to 212°C, is shown in the appendix.

A single sharp dehydroxylation step at 380°C is observed with a mass loss of 19.07%. This value does not compare well with the theoretical mass loss of 24.61%. A possible chemical reaction is as follows:

$$Mg_6Al_2(OH)_{16}(VO_4)\rightarrow$$
$$8H_2O+MgVO_4+5\ MgO+Al_2O_3$$

(The XRD pattern proves the presence of MgO, $MgAl_2O_4$ and $NaMg_4(VO_4)_3$.) A small high temperature decomposition is observed at around 840°C. This reaction is attributed to the loss of oxygen from the oxides.

Conclusions

The asymmetric shape of the DTG curve indicates the existence of two types of interlamellar water molecules, those that are free (lower 300°C) and those solvating the anion species (high 300°C). The decomposition of the synthesised hydrotalcites occurred in 3 steps, (1) evaporation of adsorbed water (up to 100°C), (2) elimination of the interlayer structural water (up to 200°C), and (3) dehydroxylation and de-carbonation of the hydrotalcite framework (up to 400°C). The ion current curve revealed that dehydroxylation and de-carbonation occurred simultaneously. Dehydroxylation indicates the thermal stability of the hydrotalcite structure, where delays in dehydroxylation indicate a more stable hydrotalcite. Therefore, the order of stability for the synthesised hydrotalcites is Syn-HT-V>Syn-HT-Mo> Syn-HT-CO_3-V>Syn-HT-CO_3-Mo>Syn-HT-CO_3, where carbonate containing hydrotalcites proved to be less stable due to carbonates reactivity. Vanadate and molybdate anions are more stable and less reactive anions than carbonate, causing the delay in dehydroxylation, resulting in a more stable hydrotalcite. Therefore hydrotalcite stability is anion dependent, and can be controlled by the incorporation of more stable and less reactive anions. The collapse of the hydrotalcite structure produced corresponding metal oxides, including MgO, $MgAl_2O_4$, $NaMg_4(VO_4)_3$ and $Na_2Mg_4(MoO_4)_5$.

Appendix

Calculation of water content for carbonate anion intercalated hydrotalcite

Proposed composition: $Mg_6Al_2(OH)_{16}CO_3 \cdot xH_2O$

Total mass of hydrotalcite analysed: 64.422 mg
% mass loss of water up to 203°C: 15.70%
Mass of water removed up to 203°C: 9.6633 mg
Molar mass of water: 18.02 g mol^{-1}
Moles of water removed: 0.53655 mmol
Mass of dehydrated mineral:
64.422 mg–15.70%=54.759 mg
Molar mass of dehydrated mineral: 531.99 g mol^{-1}
Moles of dehydrated mineral: 0.10290 mmol
Calculation of *x*:

1 mol dehydrated mineral: x mol H_2O

0.10290 mmol dehydrated mineral:
0.53655 mmol H_2O

x=5.2143~5 mol

Formula: $Mg_6Al_2(OH)_{16}CO_3 \cdot 5H_2O$

Calculation of water content for carbonate and molybdate anion intercalated hydrotalcite

Proposed composition:
$Mg_6Al_2(OH)_{16}(CO_3)_{0.5}(MoO_4)_{0.5} \cdot xH_2O$

Total mass of hydrotalcite analysed: 46.288 mg
% mass loss of water up to 219°C: 15.86%
Mass of water removed up to 219°C: 7.3413 mg
Molar mass of water: 18.02 g mol^{-1}
Moles of water removed: 0.40740 mmol
Mass of dehydrated mineral:
46.288 mg–15.86%=38.947 mg
Molar mass of dehydrated mineral:
580.98 g mol^{-1}
Moles of dehydrated mineral: 0.06704 mmol
Calculation of *x*:

1 mol dehydrated mineral: x mol H_2O

0.06704 mmol dehydrated mineral:
0.40740 mmol H_2O

x=6.0770~6 mol

Formula: $Mg_6Al_2(OH)_{16}(CO_3)_{0.5}(MoO_4)_{0.5} \cdot 6H_2O$

Calculation of water content for molybdate anion intercalated hydrotalcite

Proposed composition:
$Mg_6Al_2(OH)_{16}(MoO_4) \cdot xH_2O$

Total mass of hydrotalcite analysed: 76.431 mg
% mass loss of water up to 197°C: 13.71%
Mass of water removed up to 197°C: 10.479 mg
Molar mass of water: 18.02 g mol^{-1}
Moles of water removed: 0.58152 mmol
Mass of dehydrated mineral:
76.431 mg–13.71%=68.952 mg
Molar mass of dehydrated mineral:
630.94 g mol^{-1}
Moles of dehydrated mineral: 0.10928 mmol
Calculation of *x*:

1 mol dehydrated mineral: x mol H_2O

0.10928 mmol dehydrated mineral:
0.58152 mmol H_2O

x=5.3214~5 mol

Formula: $Mg_6Al_2(OH)_{16}(MoO_4) \cdot 5H_2O$

Calculation of water content for carbonate and vanadate anion intercalated hydrotalcite

Proposed composition:
$Mg_6Al_2(OH)_{16}(CO_3)_{0.5}(VO_4)_{0.5} \cdot xH_2O$

Total mass of hydrotalcite analysed: 67.845 mg
% mass loss of water up to 226°C: 16.19%
Mass of water removed up to 226°C: 10.984 mg
Molar mass of water: 18.02 g mol^{-1}
Moles of water removed: 0.60954 mmol
Mass of dehydrated mineral:
67.845 mg–16.19%=56.861 mg
Molar mass of dehydrated mineral:
558.48 g mol^{-1}
Moles of dehydrated mineral: 0.10181 mmol
Calculation of *x*:

1 mol dehydrated mineral: x mol H_2O

0.10181 mmol dehydrated mineral:
0.60954 mmol H_2O

x=5.9871~6 mol

Formula: $Mg_6Al_2(OH)_{16}(CO_3)_{0.5}(VO_4)_{0.5} \cdot 6H_2O$

Calculation of water content for vanadate anion intercalated hydrotalcite

Proposed composition:
$Mg_6Al_2(OH)_{16}(VO_4) \cdot xH_2O$

Total mass of hydrotalcite analysed: 89.664 mg
% mass loss of water up to 212°C: 14.55%
Mass of water removed up to 212°C: 13.046 mg
Molar mass of water: 18.02 g mol^{-1}
Moles of water removed: 0.72397 mmol
Mass of dehydrated mineral:
89.664 mg–14.55%=76.618 mg
Molar mass of dehydrated mineral:
585.94 g mol^{-1}
Moles of dehydrated mineral: 0.13076 mmol
Calculation of *x*:

$$1\text{ mol dehydrated mineral: } x \text{ mol } H_2O$$

$$0.13076\text{ mmol dehydrated mineral: } 0.72397\text{ mmol } H_2O$$

$$x=5.5367\sim5\text{ mol}$$

Formula: $Mg_6Al_2(OH)_{16}(VO_4)\cdot5H_2O$

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