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THERMAL DECOMPOSITION OF HYDROTALCITE WITH HEXACYANOFERRATE(II) AND HEXACYANOFERRATE(III) ANIONS IN THE INTERLAYER
A controlled rate thermal analysis study

Sara J. Palmer[1], *J. Kristóf*[2], *Veronika Vágvölgyi*[2], *Erzsébet Horváth*[3] *and R. L. Frost*[1,*]

[1]Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology,
2 George Street, GPO Box 2434, Brisbane, Queensland 4001, Australia
[2]Department of Analytical Chemistry, University of Pannonia, 8201 Veszprém, PO Box 158, Hungary
[3]Department of Environmental Engineering and Chemical Technology, University of Pannonia, 8201 Veszprém, PO Box 158, Hungary

The mechanism for the decomposition of hydrotalcite remains unsolved. Controlled rate thermal analysis enables this decomposition pathway to be explored. The thermal decomposition of hydrotalcites with hexacyanoferrate(II) and hexacyanoferrate(III) in the interlayer has been studied using controlled rate thermal analysis technology. X-ray diffraction shows the hydrotalcites have a *d*(003) spacing of 10.9 and 11.1 Å which compares with a *d*-spacing of 7.9 and 7.98 Å for the hydrotalcite with carbonate or sulphate in the interlayer.

Calculations show dehydration with a total loss of 7 moles of water proving the formula of hexacyanoferrate(II) intercalated hydrotalcite is $Mg_6Al_2(OH)_{16}[Fe(CN)_6]_{0.5}\cdot 7H_2O$ and 9.0 moles for the hexacyanoferrate(III) intercalated hydrotalcite with the formula of $Mg_6Al_2(OH)_{16}[Fe(CN)_6]_{0.66}\cdot 9H_2O$. CRTA technology indicates the partial collapse of the dehydrated mineral. Dehydroxylation combined with CN unit loss occurs in two isothermal stages at 377 and 390°C for the hexacyanoferrate(III) and in a single isothermal process at 374°C for the hexacyanoferrate(III) hydrotalcite.

Keywords: *controlled rate thermal analysis (CRTA), hexacyanoferrate(II), hexacyanoferrate(III), hydrotalcite*

Introduction

Hydrotalcites, or layered double hydroxides (LDH's) are fundamentally anionic clays, and are less well-known than cationic clays like smectites [1, 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 some of the Mg^{2+} cations [3–14]. This substitution creates a positive layer charge on the hydroxide layers, which is compensated by interlayer anions or anionic complexes [15, 16]. Further mixtures of these mineral phases with multiple anions in the interlayer are observed. When LDHs are synthesised any appropriate anion can be placed in the interlayer. These anions may be any anion with a suitable negative charge including the hexacyanoferrate(II) and hexacyanoferrate(III) ions [17–19]. The incorporation of these ions has implications in electrochemistry [19–23]. 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 $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}]_{x/n}\bullet yH_2O$, 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 [24]. In the hydrotalcites reevesite and pyroaurite, the divalent cations are Ni^{2+} and Mg^{2+} respectively with the trivalent cation being Fe^{3+}. In these cases, the carbonate anion is the major interlayer counter anion. Of course when synthesising hydrotalcites any anion may be used [7, 14, 25–27]. Reevesite and pyroaurite are based upon the incorporation of carbonate into the interlayer with *d*(003) spacings of around 8 Å [28, 29]. 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.

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 [6, 11, 30–34]. Thermoanalytical methods can provide a measure of the thermal stability of the hydrotalcite. Controlled rate thermal analysis (CRTA) has proven extremely worthwhile in the study of the stability and thermal decomposition

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

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

pathways of minerals and modified minerals such as mechanochemically activated kaolinite and intercalated kaolinites [34–41]. The application of CRTA technology to the study of the thermal stability of hydrotalcites has to the best of our knowledge never been reported.

In this work we report the thermal analysis using CRTA technology of hydrotalcite with hexacyanoferrate(II) and hexacyanoferrate(III) anions 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 reported below were synthesised by the co-precipitation method.

A mixed solution of aluminium and magnesium nitrates ($[Al^{3+}]$=0.25 M and $[Mg^{2+}]$=0.75 M; 1 M=1 mol dm^{-3}) and a mixed solution of sodium hydroxide ($[OH^-]$=2 M) and the desired anion, at the appropriate concentration, were placed in two separate vessels and purged with nitrogen for 20 min (all compounds were dissolved in freshly decarbonated water). The cationic solution was added to the anions via a peristaltic pump at 40 mL min^{-1} and the pH maintained above 9. The mixture was then aged at 75°C for 18 h under a N_2 atmosphere. The resulting precipitate was then filtered thoroughly, with room temperature decarbonated water to remove nitrates and left to dry in a vacuum desiccator for several days. In this way hydrotalcites with different anions in the interlayer were synthesised. The phase composition was checked by X-ray diffraction and the chemical composition by EDXA analyses.

Thermal analysis

Conventional thermal analysis experiment

Thermal decomposition of the hydrotalcite was carried out in a Derivatograph PC type thermoanalytical equipment (Hungarian Optical Works, Hungary) capable of recording the thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) curves simultaneously. The sample was heated in a ceramic crucible in static air atmosphere at a rate of 5°C min^{-1}.

Thermal decompositions of the hydrotalcites were also carried out in a TA® Instruments incorporated high-resolution thermogravimetric analyser (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. The TG instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. Only selected gases were analysed.

Controlled rate thermal analysis experiment

Thermal decomposition of the intercalated hydrotalcite was carried out in the Derivatograph under static air at a pre-set, constant decomposition rate of 0.1 mg min^{-1}. (Below this threshold value the samples were heated under dynamic conditions at a uniform rate of 1.0°C min^{-1}.) The samples were heated in an open ceramic crucible at a rate of 1.0°C min^{-1} up to 300°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.

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$_\alpha$ 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.

Results and discussion

X-ray diffraction

The X-ray diffraction patterns for the hexacyanoferrate(II) and hexacyanoferrate(III) interlayered hydrotalcites are shown in Fig. 1. For comparison the XRD patterns of the sulphate and carbonate intercalated hydrotalcite are shown. The XRD patterns clearly show the formation of the hydrotalcites with the different anions in the interlayer. The XRD patterns also show no impurities in the synthesised hydrotalcites. Hydrotalcite normally has a d(003) spacing of 7.9 Å. The sulphate intercalated hydrotalcite has a spacing of 7.99 Å. The hexacyanoferrate(II) complex has a spacing of 10.9 Å and the hexacyanoferrate(III) hydrotalcite 11.1 Å. The increased interlayer spacing is due to the size of the anion between the brucite-like layers.

Thermal analysis

Dynamic thermal analysis of hexacyanoferrate(II) intercalated hydrotalcite

The dynamic thermal analysis of 157.95 mg of the hexacyanoferrate(II) intercalated hydrotalcite is shown

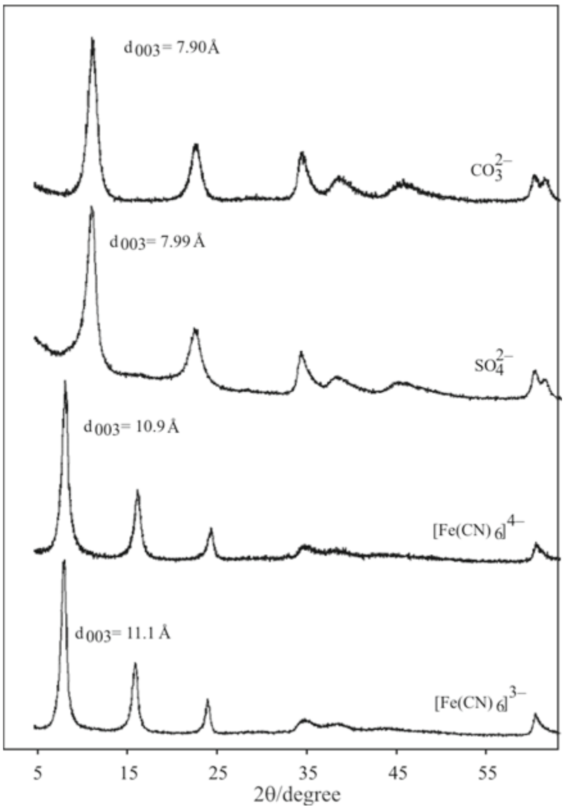

Fig. 1 X-ray diffraction patterns of hydrotalcite with carbonate, sulphate, hexacyanoferrate(II) and hexacyanoferrate(III) anions in the interlayer

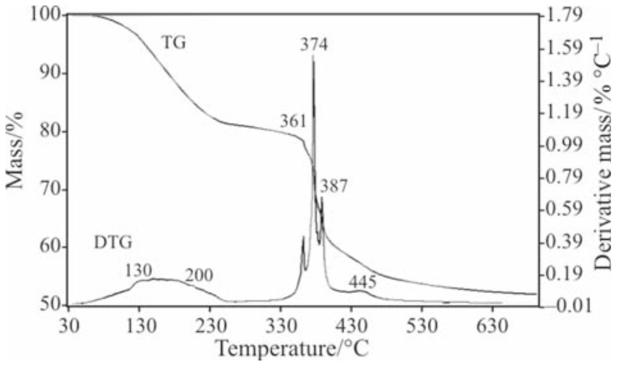

Fig. 2 The dynamic thermogravimetric analysis of hexacyanoferrate(II) interlayered hydrotalcite

in Fig. 2. Comparing the curves the following conclusions can be drawn. In the temperature range from ambient to about 600°C three main decomposition stages can be observed in the DTG curve: (a) from ambient to 280°C, (b) from 280 to 410°C and (c) between 410 and 600°C. The first mass loss step is associated with dehydration, the second with DTG peaks at 361, 374 and 387°C with dehydroxylation and the partial loss of the cyanide ligand, while the third mass loss step with loss of the CN units and also the loss of the additional OH units. It can be supposed that in the first step evolution of differently bound water occurs. Over 500°C a slow mass loss step is observed which is due to the degradation of the decomposed mineral.

The following steps describe the thermal decomposition of the hexacyanoferrate(II)-interlayered hydrotalcite.

Step 1 up to 280°C

$$Mg_6Al_2(OH)_{16}(Fe(CN)_6)_{0.5}\cdot 7H_2O\rightarrow$$
$$\rightarrow Mg_6Al_2(OH)_{16}(Fe(CN)_6)_{0.5}+7H_2O$$

This step includes the loss of hydration water. Based on the mass loss data, the mineral contains seven moles of water, although the presence of some adsorbed water cannot be excluded.

Step 2 between 280 and 410°C

$$Mg_6Al_2(OH)_{16}(Fe(CN)_6)_{0.5}\rightarrow$$
$$\rightarrow Mg_6Al_2O_2(OH)_{13}(Fe(CN)_4)_{0.5}+HCN+H_2O$$

$$Mg_6Al_2O_2(OH)_{13}(Fe(CN)_4)_{0.5}\rightarrow$$
$$\rightarrow Mg_6Al_2O_3(OH)_{11}(Fe(CN)_4)_{0.5}+H_2O$$

This step represents the simultaneous evolution of dehydroxylation water and the cyanide ligand in the form of HCN.

Step 3 between 410 and 600°C

$$4Mg_6Al_2O_3(OH)_{11}(Fe(CN)_4)_{0.5}+0.5O_2\rightarrow$$
$$\rightarrow 22MgO+2Al_2O_3+2MgAl_2O_4+Fe_2O_3+8HCN+18H_2O$$

In this step the decomposition is complete leading to the formation of the oxides of Mg and Al as well as the formation of a magnesium aluminate (spinel).

Dynamic thermal analysis of hexacyanoferrate(III) intercalated hydrotalcite

The dynamic thermal analysis of the hexacyanoferrate(III) intercalated hydrotalcite is shown in Fig. 3. Comparing the curves the following conclusions can be drawn. In the temperature range from ambient to about 280°C adsorbed and hydrated water are lost (the wide temperature range indicates differently bound water). Dissimilarly to the hexacyanoferrate(II)-type hydrotalcite the decomposition of the dehydrated mineral takes place in a more homogeneous process between 280 and 410°C (with a characteristic DTG peak at 372°C with shoulders only at 360 and 390°C). Between 410 and 600°C a slow process can be observed, as well. Again, in the 410 to 600°C range dehydroxylation and the loss of the CN units take place. The proposed decomposition pathway is as follows:

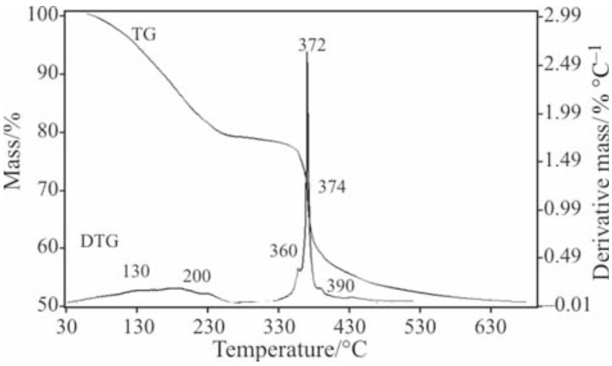

Fig. 3 The dynamic thermogravimetric analysis of hexacyanoferrate(III) interlayered hydrotalcite

Step 1 from ambient to 280°C

$$Mg_6Al_2(OH)_{16}(Fe(CN)_6)_{0.66}\cdot 9H_2O\rightarrow$$
$$\rightarrow Mg_6Al_2(OH)_{16}(Fe(CN)_6)_{0.66}+9H_2O$$

This step includes the loss of hydration water. Based on the mass loss data, the mineral contains nine moles of water.

Step 2 between 280 and 600°C

$$Mg_6Al_2(OH)_{16}(Fe(CN)_6)_{0.66}\rightarrow$$
$$\rightarrow Mg_6Al_2O_2(OH)_{12}(Fe(CN)_6)_{0.66}+2H_2O$$

$$3Mg_6Al_2O_2(OH)_{12}(Fe(CN)_6)_{0.66}\rightarrow$$
$$\rightarrow 18MgO+3Al_2O_3+Fe_2O_3+12HCN+12H_2O$$

This step represents a dehydroxylation step accompanied with cyanide loss.

In order to better resolve the decomposition processes, controlled rate thermal analysis (CRTA) experiments were carried out as well in the same equipment using the CRTA control facility. In this case the decomposition of the mineral was carried out at a preset, constant, slow rate to provide enough time for the slow heat and mass transfer processes to occur. The essence of the technique lies in that each sample particle shall be heated under identical conditions. With the slow and constant decomposition rate of 0.10 mg min^{-1} the decomposition is carried out under quasi-isothermal, quasi-equilibrium conditions. This is achieved by the control of the furnace temperature regulated by the DTG signal through the computer.

Controlled rate thermal analysis of hexacyanoferrate(II) intercalated hydrotalcite

Table 1 summarises the mass loss in mg and the % mass loss over a specific temperature range.

The CRTA curves of 156.22 mg sample are shown in Fig. 4. In the ambient to 267°C range dehydration occurs in a single step. The non-isothermal nature of dehydration process is rather unusual and needs to be explained. If a decomposition process of constant gas evolution rate is non-isothermal, it means that hidden processes slower than the heat transport have a role. We believe that the layers are partially collapsing upon dehydration (decrease in the *d*(003) spacing), therefore higher energy (i.e. higher temperature) is needed to maintain the preset, constant rate of decomposition (i.e. to drive out water vapor through a reduced space). The small peak between 267 and 310°C is probably due to the loss of more strongly

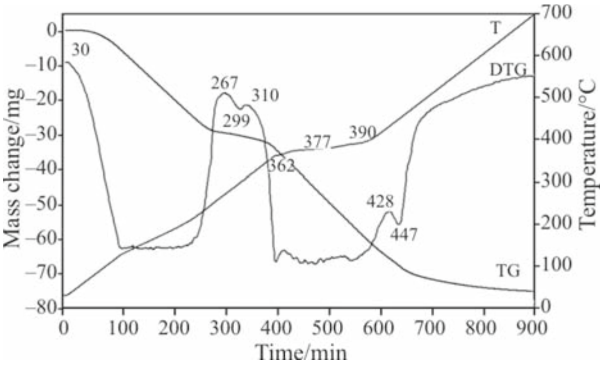

Fig. 4 The controlled rate thermal analysis of hexacyanoferrate(II) interlayered hydrotalcite

Table 1 Decomposition stages under CRTA conditions

Decomposition process	Hydrotalcite with hexacyanoferrate(II) (sample mass: 156.22 mg)			Hydrotalcite with hexacyanoferrate(III) (sample mass: 143.76 mg)		
	Temp. range/°C	Mass loss		Temp. range/°C	Mass loss	
		mg	%		mg	%
Dehydration	31–267	29.5	18.9	22–226 226–270	26.4 4.3	18.4 3.0
Dehydration	267–310	1.3	0.8	270–315	0.9	0.6
Dehydroxylation/CN loss	310–367	6.1	3.9	315–366	5.7	4.0
Dehydroxylation/CN loss	367–383	15.2	9.7	366–390	21.8	15.2
Dehydroxylation/CN loss	383–428	13.0	8.3	390–427	4.9	3.4
Oxygen loss	428–693	10.1	6.5	427–694	7.4	5.1

bonded water, although the possibility of early dehydroxylation cannot be excluded.

In the temperature range between 310 and 428°C dehydroxylation and the decomposition of the cyanide ligand take place simultaneously. Interestingly, two isothermal processes at 377 and 390°C can be distinguished (in harmony with the split DTG pattern) of the dynamic experiment. The separate decomposition process between 428 and 500°C correspond to the decomposition step between 410 and 600°C in the dynamic experiment. With the CRTA method a better resolution of the closely overlapping reactions can be made.

Controlled rate thermal analysis of hexacyanoferrate(III) interlayered hydrotalcite

The CRTA curves of 143.76 mg sample are shown in Fig. 5. In the ambient to 226°C range the non-isothermal process of dehydration takes place. This process can be interpreted as in the case of the hexacyanoferrate(II) complex. In this case, however, two separate dehydration steps can be distinguished between 226 and 270 as well as between 270 and 315°C. This separate processes indicate the presence of differently bound water in the interlayer space. Dissimilarly to the hexacyanoferrate(II) complex, only one isothermal process can be seen in the main decomposition stage at 374°C. This is in harmony with the dynamic experiment where the DTG peak shows a more homogeneous decomposition pattern. Again, the separate peak between 427 and 500°C indicates the complexity of the decomposition process.

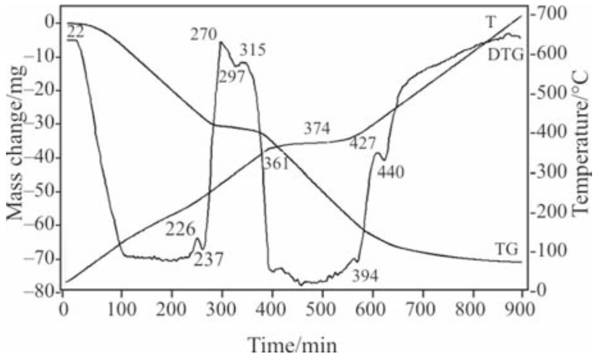

Fig. 5 The controlled rate thermal analysis of hexacyanoferrate(III) interlayered hydrotalcite

Conclusions

The thermal decomposition of hydrotalcites based upon a Mg/Al ratio of 6/2 with hexacyanoferrate(II) and (III) in the interlayer has been studied using dynamic and controlled rate thermal analysis techniques complemented with X-ray diffraction. Both the dynamic and the CRTA experiments show that mass loss occurs in two main stages corresponding to dehydration and to the decomposition of the water-free mineral.

CRTA offers a better resolution and a more detailed interpretation of the decomposition processes via approaching equilibrium conditions of decomposition through the elimination of the slow transfer of heat to the sample as a controlling parameter on the process of decomposition. Constant-rate decomposition processes of non-isothermal nature reveal partial collapse of the layers, since in these cases a higher energy (higher temperature) is needed to drive out gaseous decomposition products through a decreasing space at a constant, pre-set rate.

Appendix

Calculation of water content for hydrotalcite with hexacyanoferrate(II)

Composition: $Mg_6Al_2(OH)_{16}[Fe(CN)_6]_{0.5}\cdot xH_2O$
Removing water up to 280°C: 29.50 mg that is 1.637 mmol
Remaining dehydrated mineral up to 2807°C: 137.32 mg that is 0.238 mmol
Molar mass of dehydrated mineral: 577.97 g mol^{-1}
Calculation of x:

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

$$0.238 \text{ mol dehydrated mineral} - 1.637 \text{ mol } H_2O$$

$$x=6.88\sim 7 \text{ mol}$$

Formula: $Mg_6Al_2(OH)_{16}[Fe(CN)_6]_{0.5}\cdot 7H_2O$

Calculation of water content for hydrotalcite with hexacyanoferrate(III)

Composition: $Mg_6Al_2(OH)_{16}[Fe(CN)_6]_{0.66}\cdot xH_2O$
Removing water up to 280°C: 30.70 mg that is 1.704 mmol
Remaining dehydrated mineral up to 280°C: 116.06 mg that is 0.190 mmol
Molar mass of dehydrated mineral: 611.88 g mol^{-1}
Calculation of x:

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

$$0.190 \text{ mol dehydrated mineral} - 1.704 \text{ mol } H_2O$$

$$x=8.97\sim 9 \text{ mol}$$

Formula: $Mg_6Al_2(OH)_{16}[Fe(CN)_6]_{0.66}\cdot 9H_2O$

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