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Thermal behaviour and kinetic analysis of the thermogravimetric data of double ammonium sulphate hexahydrate salts of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)

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Abstract

The thermal behaviour of double ammonium sulphate hexahydrates of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) was studied in air using TG and DTA techniques. X-ray powder diffractometry was used to identify the solid decomposition products. The thermal stability of these double salts in the solid state is discussed and the mechanism of their decomposition is also suggested.

A kinetic analysis of the TG data was performed by using Jeres' modification of the Freeman-Carroll method to determine the apparent activation energy and order of reaction.

Keywords: Double salt; DTA; DTG; Kinetics; TG; XRPD

1. Introduction

The double sulphates of monovalent alkali metal or ammonium ions and mono-, di- or trivalent transition or inner-transition metals have a definite stoichiometry, with general formulae $A^{I}B^{I}(SO_4) \cdot xH_2O$, $(A^{I})_2B^{II}(SO_4)_2 \cdot xH_2O$ and $A^{I}B^{III}(SO_4)_2 \cdot xH_2O$, respectively. The double sulphates of trivalent metals such as aluminium and chromium are called alums. It is well known that double sulphates with the same monovalent cation are usually isomorphous.

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The thermal behaviour and thermal decomposition of alums [1–4], some double sulphates of monovalent inner-transition metals [5–7] and trivalent metals [8] have been studied. In this paper, we report the results of the thermal decomposition of double ammonium hexahydrates of the first series divalent transition metals, Mn(II), Fe(II), Co(II), Ni(II) and Cu(II).

2. Experimental

2.1. Preparation of double salts

Stoichiometric amounts of analytical grade ammonium sulphate and sulphates of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) were dissolved in hot water to obtain saturated solutions. Then the saturated solutions of metal sulphates and ammonium sulphate were mixed and allowed to cool. After several days, the double salt crystals formed were removed from the solution by suction. The crystals were washed with small amounts of cold water and ethanol respectively, and dried at room temperature.

2.2. Instrumental

TG, DTG and DTA curves were obtained simultaneously on a Rigaku TG 8110 thermal analyser combined with a TAS 100 thermogravimetric analyser. Samples were heated in platinum crucibles in a static air atmosphere within the temperature range 20–1000°C. The heating rate was 10 K min^{-1} and the sample sizes ranged in weight from 5 to 10 mg. Highly sintered α-Al_2O_3 was used as a reference compound. The solid decomposition products formed at different stages of thermal decomposition were identified using a Siemens X-ray powder diffractometer with Ni-filtered Cu Kα radiation.

3. Results and discussion

3.1. Thermal behaviour

All the double salts were subjected to TG and DTA analysis from ambient temperature to 1000°C in static air. The TG, DTG and DTA curves of the double salts are shown in Figs. 1–5; the temperature ranges, phase transition temperatures, experimental and calculated weight losses and identified solid decomposition products are given in Table 1.

The double salts contain six moles of crystallization water and the first decomposition stage, from approx. 50 to approx. 200°C, corresponds to dehydration. The dehydration of the double salts is a single-stage process, as shown in the TG curves, except the ammonium copper(II) sulphate hexahydrate which loses its crystallization in two steps with two endothermic maxima at 79°C ($-4H_2O$) and 135°C ($-2H_2O$) in the DTA curves (Fig. 5).

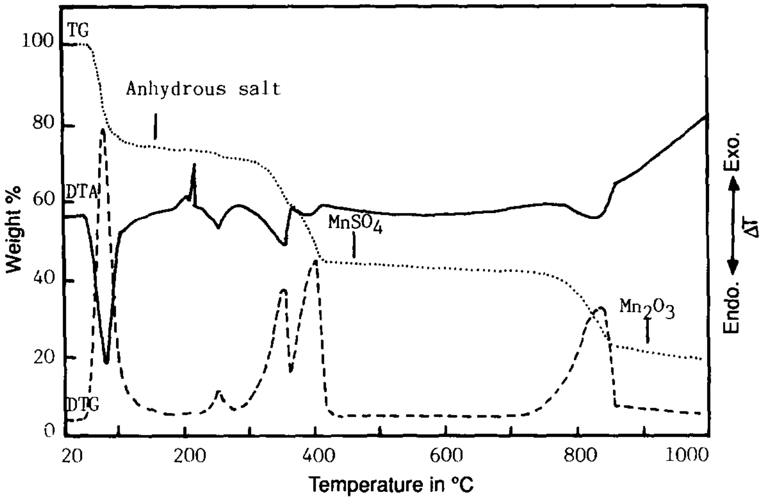

Fig. 1. TG, DTG and DTA curves of $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$.

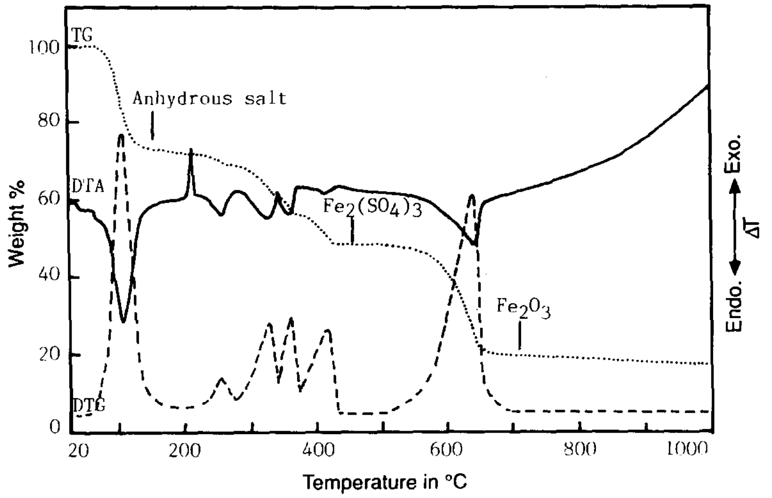

Fig. 2. TG, DTG and DTA curves of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$.

X-ray power diffractometry studies of the dehydrated double salts show that the anhydrous salts formed have very poor crystalline properties. The amorphous structure of the anhydrous double salts is attributed to the distortion of the crystal structure after dehydration. On gradual heating the anhydrous amorphous double salts show a phase transition (from the amorphous to the crystalline state) above 195°C due to a rearranging of the ions in the solid structure (Table 1). In general, the first-stage thermal decomposition reaction of the double salts can be written as

$$(NH_4)_2M(SO_4) \cdot 6H_2O(s) \rightarrow (NH_4)_2M(SO_4)(s) + 6H_2O(g)$$

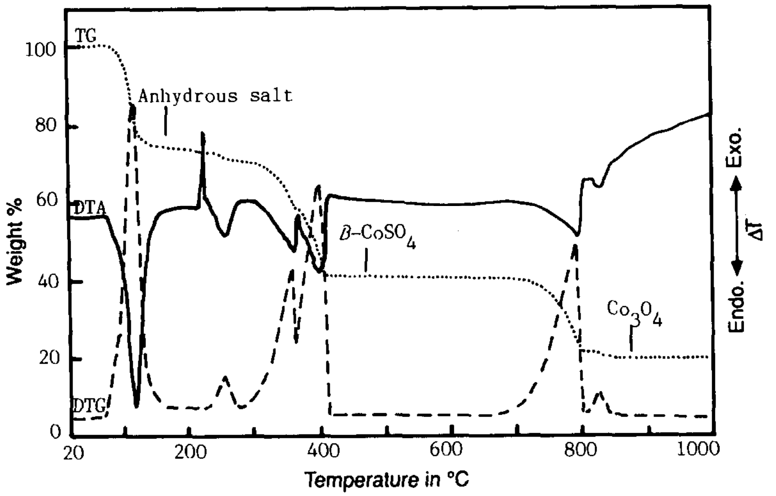

Fig. 3. TG, DTG and DTA curves of $(NH_4)_2Co(SO_4)_2 \cdot 6H_2O$.

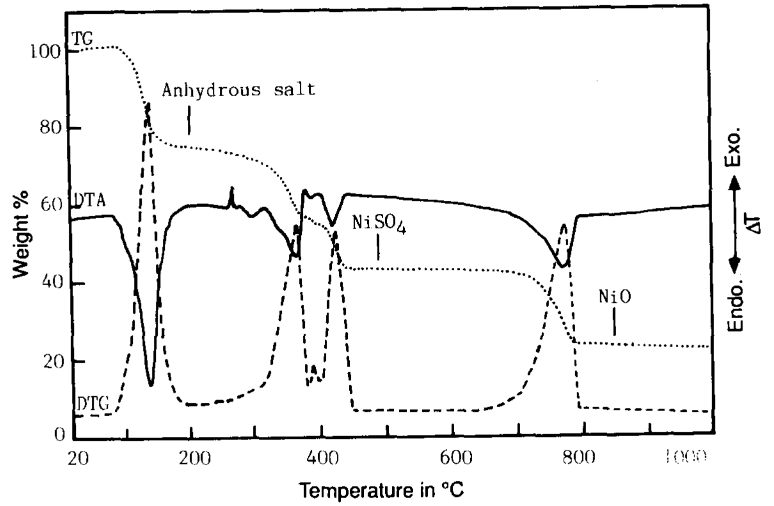

Fig. 4. TG, DTG and DTA curves of $(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$.

The second stage (from approx. 220 to approx. 450°C) is associated with the thermal decomposition of the anhydrous double salts to their respective metal sulphates. All the anhydrous double salts are stable up to about 220°C. The second decomposition stage takes place in three or four consecutive steps in which the gradual removal of $(NH_4)_2SO_4$ occurs. The DTA peaks show that during this stage, the thermal decomposition of the anhydrous double sulphates is very complex and proceeds via intermediates which were almost impossible to isolate because of the very small temperature differences between the steps. The solid decomposition

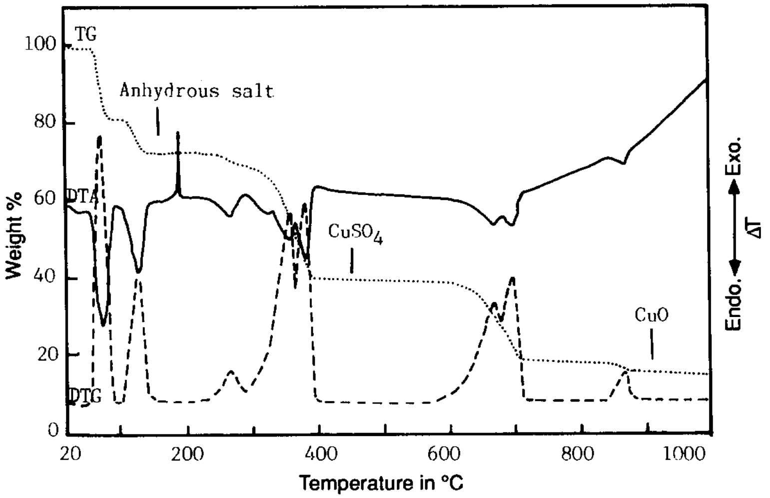

Fig. 5. TG, DTG and DTA curves of $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$.

Table 1
Thermoanalytical results (TG, DTG, DTA) for the double ammonium sulphates

Stage	Temperature range in °C	DTG_{max} in °C	Phase transition temp. in °C	Weight loss in % Exp.	Calcd.	Solid decomposition product	Colour
$(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$							
1	55–162	83	216	27.10	27.63	$(NH_4)_2Mn(SO_4)_2$	White
2	227–443	–		29.88	33.76	$MnSO_4$	White
3	706–935	835		20.27	20.05	Mn_2O_3	Black
$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$							
1	60–175	106	212	27.58	27.55	$(NH_4)_2Fe(SO_4)_2$	Brown
2	223–445	–		22.95	21.23	$Fe_2(SO_4)_3$	Yellow
3	474–685	642		28.74	30.69	Fe_2O_3	Brown-red
$(NH_4)_2Co(SO_4)_2 \cdot 6H_2O$							
1	75–184	120	229	26.99	27.34	$(NH_4)_2Co(SO_4)_2$	Violet
2	235–422	–		31.69	33.42	β-$CoSO_4$	Pink
3	680–850	794		20.58	19.99	Co_3O_4	Black
$(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$							
1	85–210	142	272	26.33	27.36	$(NH_4)_2Ni(SO_4)_2$	Yellow
2	278–460	–		31.17	33.44	$NiSO_4$	Yellow
3	640–800	775		20.17	20.27	NiO	Black
$(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$							
1	58–100	79	195	18.12	18.02	$(NH_4)_2Cu(SO_4)_2 \cdot 2H_2O$	
	106–165	135		8.80	9.01	$(NH_4)_2Cu(SO_4)_2$	Yellow
2	220–405	–		32.60	33.04	$CuSO_4$	Grey
3	585–734	702		20.17	19.91	CuO	Black

product of the Fe(II) double salt was found to be $Fe_2(SO_4)_3$ rather than $FeSO_4$, due to the oxidation of Fe(II) to Fe(III). The solid decomposition product of the Co(II) double salt was β-$CoSO_4$. The calculated and determined weight losses for the second stage are in very good agreement with each other (Table 1). The thermal decomposition reactions in the second stage can generally be written

$$(NH_4)_2M(SO_4)(s) \rightarrow MSO_4(s) + (NH_4)_2SO_4(g)$$

The thermal decomposition of $(NH_4)_2SO_4$ is suggested to be

$$(NH_4)_2SO_4(s) \rightarrow NH_4HSO_4(s) + NH_3(g)$$

$$NH_4HSO_4(s) \rightarrow NH_3(g) + H_2O(g) + SO_3(g)$$

In the third stage (between approx. 480 and approx. 940°C), the metal sulphates decompose to their respective metal oxides. The oxidation of Mn(II) and Co(II) is observed during this stage and results in the formation of Mn_2O_3 and Co_3O_4 respectively. The thermal decomposition reactions of the third stage can be written

$$MSO_4(s) \rightarrow MO(s) + SO_3(g) \qquad \text{M is Ni, Cu}$$

$$Fe_2(SO_4)_3(s) \rightarrow Fe_2O_3(s) + 3SO_3(g)$$

$$2MnSO_4(s) + 0.5O_2(g) \rightarrow Mn_2O_3(s) + 2SO_3(g)$$

$$3CoSO_4(s) + 0.5O_2(g) \rightarrow Co_3O_4(s) + 3SO_3(g)$$

In order to discuss the thermal stability in the solid state, the initial decomposition temperatures of the hydrated and anhydrous double salts were taken for comparative purposes. Table 1 indicates that the thermal stability of both the hydrated and anhydrous double salts follows the same order. $Mn < Cu < Fe < Co < Ni$. The plot of the initial decomposition temperatures of the hydrated and anhydrous double salts against the corresponding reciprocal ionic radii exhibits some definite trends as shown in Fig. 6. The ionic radius of the divalent metal ions decreases from Mn to Cu [9]. It is clear that the thermal stability of the ionic double salts is a function of the radii of the divalent metal ions and increases as the radii decrease. However, the ammonium copper(II) sulphate double salt deviates from this general trend.

3.2. Decomposition kinetics

The first stage of decomposition (dehydration) of the double salts was chosen for detailed study. The kinetic parameters such as energy of activation E_a and order of reaction n were evaluated graphically by employing Jeres' modification [10] of the Freeman and Carroll method [11], applying the relation

$$[\Delta \ln(d\alpha/dT)]/\Delta \ln(1-\alpha)] = n - E_a[\Delta(1/T)/\Delta \ln(1-\alpha)]/R \qquad (1)$$

where E_a is the energy of activation, T the temperature in K, R the gas constant, $\alpha = (m_{int} - m)/(m_{int} - m_{fnl})$, and n is the order of reaction.

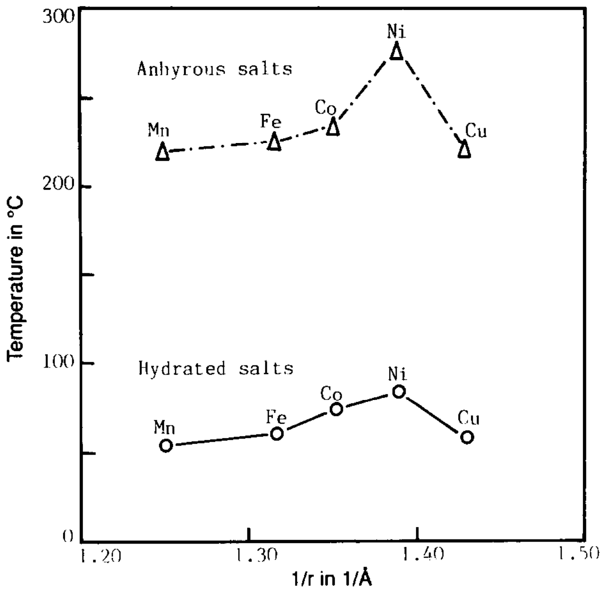

Fig. 6. Initial temperature of thermal decomposition of hydrated and anhydrous double salts vs. the reciprocal of the ionic radii.

Table 2
Kinetic data from Eq. (1) for the first decomposition stage of the double salts

Reaction	E_a in kJ mol^{-1}	n	r [a]
$(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O \xrightarrow{-6H_2O} (NH_4)_2Mn(SO_4)_2$	12.31	1	0.990
$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O \xrightarrow{-6H_2O} (NH_4)_2Fe(SO_4)_2$	19.75	1	0.985
$(NH_4)_2Co(SO_4)_2 \cdot 6H_2O \xrightarrow{-6H_2O} (NH_4)_2Co(SO_4)_2$	17.36	1	0.998
$(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O \xrightarrow{-6H_2O} (NH_4)_2Ni(SO_4)_2$	14.94	1	0.990
$(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O \xrightarrow{-4H_2O} (NH_4)_2Cu(SO_4)_2 \cdot 2H_2O$	18.68	1	0.999

[a] Correlation coefficient of the linear plot.

The kinetic parameters obtained by application of Eq. (1) to the thermoanalytical data are summarized in Table 2. A typical curve of $[\Delta \ln(\mathrm{d}\alpha/\mathrm{d}T)/\Delta \ln(1-\alpha)]$ against $[\Delta(1/T)/\Delta \ln(1-\alpha)]$ is shown in Fig. 7 for the double salt of Co(II). The slope of the plot gave the value of $-E_a/R$ and the order of decomposition reaction n was determined from the intercept. All the linear plots were evaluated by regression analysis, and the corresponding correlation coefficients r were calculated. It was found that the thermal dehydration of the double salts is first order and the values of the energy of activation for the thermal dehydration are 12.31, 19.75, 17.36, 14.94 and 18.66 kJ mol^{-1} for the Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) double salts respectively. The reaction order and energy of activation of the hydrated double salts of mono- and trivalent metals have not been reported in the

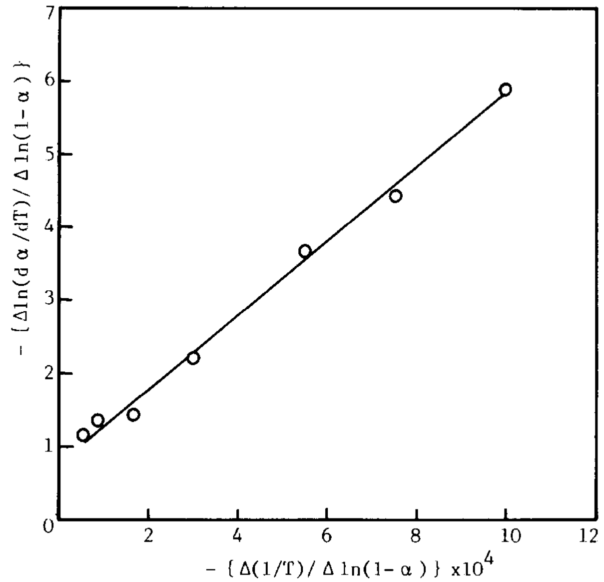

Fig. 7. Freeman–Carroll plot for the thermal dehydration process of $(NH_4)_2Co(SO_4)_2 \cdot 6H_2O$.

literature. However, from Table 2, it can be concluded that the thermal dehydration of those double salts also follows a low energetic process.

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