Journal of Thermal Analysis, Vol. 29 (1984) 121–129

REACTIONS BETWEEN AMMONIUM SULPHATE AND METAL OXIDES (METAL = Cr, Mn AND Fe) AND THERMAL DECOMPOSITION OF THE PRODUCTS

T. Nagaishi, S. Ishiyama, M. Matsumoto and *S. Yoshinaga*

DEPARTMENT OF INDUSTRIAL CHEMISTRY, KYUSHU SANGYO UNIVERSITY,
2-327, MARSUKADAI, HIGASHI-KU, FUKUOKA, JAPAN

(Received September 1, 1983)

The reactions between ammonium sulphate and three metal oxides (Cr_2O_3, MnO_2 and Fe_2O_3) were studied. It was confirmed by X-ray diffraction and chemical analysis that stable reaction intermediates were formed consecutively in the course of the reactions.

These were $(NH_4)_3M(SO_4)_3$ and $NH_4M(SO_4)_2$ for Cr_2O_3 and Fe_2O_3 and $(NH_4)_2Mn_2(SO_4)_3$ for MnO_2. The thermal decompositions of these intermediates and of the metal sulphates were carried out. The contracting-volume equation was valid for the decomposition of all the intermediates. The Arrhenius parameters were determined.

The investigation of the reactions of ammonium sulphate with various metal oxides is of great practical interest [1, 2]. In metallurgy, this reaction is frequently applied for the beneficiation of low-grade metal ores, as well as for the extraction of metal oxide from metal ores [3, 4]. The poisoning of metal oxide catalysts in the catalytic reduction of NO_x using ammonia gas has been attributed to sulphation of the catalyst used [5]. Sahoo [6, 7] studied the sulphation of various metal oxides with ammonium sulphate to obtain equilibrium and kinetic data. Little attention has been paid to the formation of stable reaction intermediates during the sulphation of metal oxides with ammonium sulphate, though the case of aluminium oxide was reported by these authors [8].

The aim of this paper is to clarify the reaction between ammonium sulphate and metal oxides (metal = Cr, Mn and Fe), and to discuss the decomposition pathways and the kinetics of the reaction intermediates.

Experimental

Materials used

Ammonium sulphate, chromium(III) oxide, manganese(IV) oxide and iron(III) oxide, obtained from Nakai Chemicals, were homogenized by sieving below 149 μm. The purities of these compounds were above 99%.

Preparation of stable intermediates

Each reaction intermediate produced in the reactions between ammonium sulphate and metal oxides was prepared on the basis of the thermal analysis of the mixture. The separation of a product from the reactant was performed as described earlier [8], except for the chromium oxide–ammonium sulphate system. For this system, a mixture of chromium oxide with ammonium sulphate molar ratio 1:10 was heated to 380° to produce insoluble $(NH_4)_3Cr(SO_4)_3$, which was separated from unreacted ammonium sulphate by dissolving the heat-treated mixture in water. It was assumed that the total amount of chromium oxide had reacted with ammonium sulphate. For $NH_4Cr(SO_4)_2$ and $Cr_2(SO_4)_3$, mixtures with the same molar ratio were heated to 470° and 600°, respectively, and separated by the above-mentioned procedure. All of these reaction intermediates were identified by both X-ray diffraction and chemical analysis of metal ions, ammonium ions and sulphate ions.

Thermal analysis and X-ray diffraction

The apparatus used in this experiment was described earlier [9].

Results and discussion

Cr_2O_3–$(NH_4)_2SO_4$

There are four mass loss regions, as seem from Fig. 1(b). The DTA curve was omitted since no thermal change was observed clearly, probably due to the mixture ratio used for this system. It was confirmed from X-ray diffraction that the reaction products were $(NH_4)_3Cr(SO_4)_3$ at 350°, $NH_4Cr(SO_4)_2$ at 500°, $Cr_2(SO_4)_3$ at 600° and Cr_2O_3 at 700°. The reaction scheme for this system, may be deduced on the basis of X-ray diffraction as follows:

$$6\,(NH_4)_2SO_4 + Cr_2O_3 = 2\,(NH_4)_3Cr(SO_4)_3 + \text{gaseous products } (\sim 300°) \quad (1)$$

$$(NH_4)_3Cr(SO_4)_3 = NH_4Cr(SO_4)_2 + \text{gaseous products } (\sim 400°) \quad (2)$$

$$2\,NH_4Cr(SO_4)_2 = Cr_2(SO_4)_3 + \text{gaseous products } (\sim 500°) \quad (3)$$

$$Cr_2(SO_4)_3 = Cr_2O_3 + \text{gaseous products } (\sim 610°) \quad (4)$$

The observed mass losses for reactions (1) and (4), 1.4% and 8.4%, respectively, agreed with the calculated ones (1.6% and 8.0%, respectively), though those for reactions (2) and (3) did not. This fact suggested that the temperature range over which reaction (2) occurred slightly overlapped that for reaction (3). The stable reaction intermediates $(NH_4)_3Cr(SO_4)_3$, $NH_4Cr(SO_4)_2$ and $Cr_2(SO_4)$ were prepared for thermal analysis by the method described in the Experimental section.

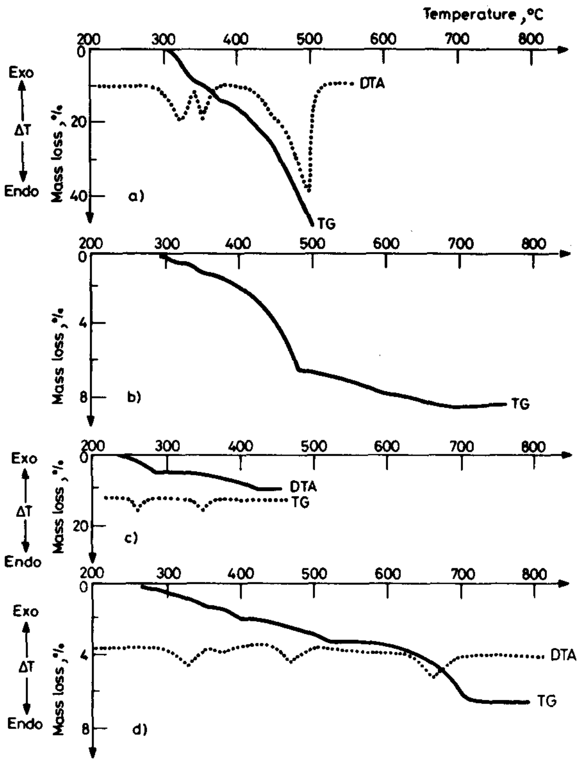

Fig. 1 DTA and TG curves of various mixtures in air (heating rate = 10 deg/min). (a) pure $(NH_4)_2SO_4$, (b) $(NH_4)_2SO_4:Cr_2O_3 = 1:10$ (molar ratio), (c) $(NH_4)_2SO_4:MnO_2 = 1:4$, (d) $(NH_4)_2SO_4:Fe_2O_3 = 1:12$

The materials obtained did not contain any impurities such as reactants or byproducts, as confirmed by X-ray diffraction and by chemical analysis of chromium ions, ammonium ions and sulphate ions.

MnO_2--$(NH_4)_2SO_4$

Figure 1(c) shows the DTA and TG curves for this system. There are two endothermic peaks, at 260° and 350°, corresponding to two mass loss regions. The mixture ratio was chosen so that the ammonium sulphate reacted totally with the MnO_2, since MnO_2 decomposes at around 500°. This was verified by comparison with Fig. 1(a), the thermal analysis of ammonium sulphate. From X-ray diffraction, it was shown that the reaction products were $(NH_4)_2Mn_2(SO_4)_3$ at 300° and $MnSO_4$ at 450°. The reaction scheme for this system may be given on the basis of these observations as follows:

$$3\,(NH_4)_2SO_4 + 2\,MnO_2 = (NH_4)_2Mn_2(SO_4)_3 + \text{gaseous products } (\sim 220°) \qquad (5)$$

$$(NH_4)_2Mn_2(SO_4)_3 = 2\ MnSO_4 + \text{gaseous products } (\sim 350°) \qquad (6)$$

The theoretical mass losses based on reactions (5) and (6), 5.0% and 9.8%, agreed with the observed weight losses of 5.2% and 9.2%, respectively. Thermal analysis of this system was not carried out above 500°, since excess, unreacted MnO_2 decomposed and was oxidized in addition to the decomposition of $MnSO_4$. It should be noted that manganese(IV) ions were reduced to manganese(II) in the first reaction step. The stable reaction intermediates $(NH_4)_2Mn_2(SO_4)_3$ and $MnSO_4$ were prepared by the heat-treatment of this mixture at 280° and 380° for thermal analysis experiments. Identification and checking of the purities of the materials obtained were carried out by the same method as earlier. Each intermediate proved to be pure.

Fe_2O_3–$(NH_4)_2SO_4$

DTA and TG curves for the mixture of Fe_2O_3 and $(NH_4)_2SO_4$ (molar ratio 12:1) are shown in Fig. 1(d). Though the DTA trace is not so clear as that of TG, due to the mixture ratio, it seems to have four endothermic peaks, corresponding to four mass loss regions. The reaction products in the individual reaction steps were $(NH_4)_3Fe(SO_4)_3$ at 360°, $NH_4Fe(SO_4)_2$ at 400°, $Fe_2(SO_4)_3$ at 550° and Fe_2O_3 at 750°, identified by X-ray diffraction. The reaction scheme for this system may be given as:

$$6\ (NH_4)_2SO_4 + Fe_2O_3 = 2\ (NH_4)_3Fe(SO_4)_3 + \text{gaseous products } (\sim 270°) \qquad (7)$$

$$4\ (NH_4)_3Fe(SO_4)_3 + Fe_2O_3 = 6\ NH_4Fe(SO_4)_2 + \text{gaseous products } (\sim 380°) \qquad (8)$$

$$2\ NH_4Fe(SO_4)_2 = Fe_2(SO_4)_3 + \text{gaseous products } (\sim 400°) \qquad (9)$$

$$Fe_2(SO_4)_3 = Fe_2O_3 + \text{gaseous products } (\sim 600°) \qquad (10)$$

The observed mass losses were 1.4% for reaction (7), 2.1% for reactions (7) + (8), 3.4% for reactions (7) + (8) + (9), and 6.5% for reactions (7) + (8) + (9) + (10), in agreement with the calculated cumulated weight losses of 1.3%, 1.9%, 3.5% and 6.5%, respectively. Nakamura [5] studied the same mixture, but at a molar ratio very different from ours, and suggested reaction (7), (9), (10) and (8') instead of (8).

$$\begin{aligned}&(NH_4)_2Fe(SO_4)_3 = \\ &\quad = NH_4Fe(SO_4)_2 + 4\ NH_3 + 3\ SO_2 + 6\ H_2O + N_2\ (\sim 360°) \qquad (8')\end{aligned}$$

This may be caused by the different mixture ratios used in the two experiments. The stable reaction intermediates $(NH_4)_3Fe(SO_4)_3$, $NH_4Fe(SO_4)_2$ and $Fe_2(SO_4)_3$ were prepared for thermal analysis by heat-treatment of the same mixture at 360°, 400° and 550°, respectively. Each of the intermediates was proved to be pure by X-ray diffraction and chemical analysis.

Thermal analysis of $(NH_4)_3M(SO_4)_3$ (*M* = Cr *and* Fe)

Figure 2 shows the DTA and TG curves, which have three endothermic peaks, corresponding to three weight loss regions. From X-ray diffraction and weight loss measurement on TG, it was revealed that the decomposition of $(NH_4)_3M(SO_4)_3$ occurred in three steps, involving reactions (i), (ii) and (iii) in Table 1.

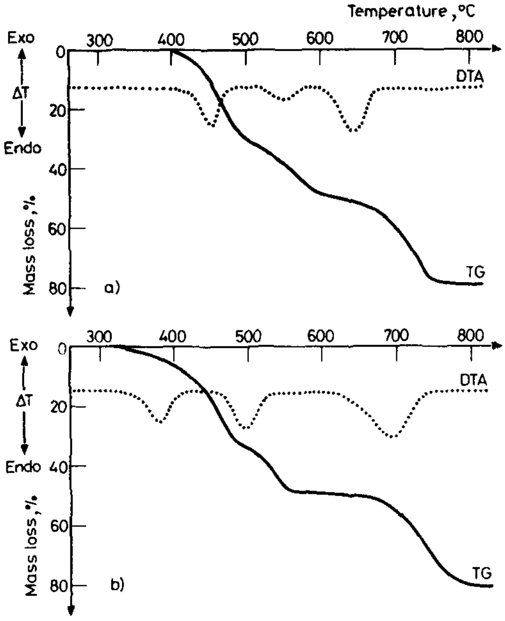

Fig. 2 DTA and TG curves of reaction intermediates. (a) $(NH_4)_3Cr(SO_4)_3$, (b) $(NH_4)_3Fe(SO_4)_3$

Thermal analysis of $NH_4M(SO_4)_2$ (*M* = Cr *and* Fe)

The DTA and TG curves of $NH_4M(SO_4)_2$ are shown in Figs (3(a) and (c). As expected, the decomposition of $NH_4M(SO_4)_2$ was expressed by reactions (ii) and (iii) in Table 1, as confirmed by X-ray diffraction and weight loss measurement on TG.

Thermal analysis of $(NH_4)_2Mn_2(SO_4)_3$

Figure 3(b) shows the TG curve, which has two weight loss regions. The decomposition pathway was expressed by reactions (iv) and (v) in Table 1, as confirmed by the above-mentioned method.

Thermal analysis of $M_2(SO_4)_3$ (*M* = Cr *and* Fe) *and* $MnSO_4$

Figure 4 shows the DTA and TG curves of the metal sulphates. As decomposition product, metal oxide was recognized. The decomposition pathway was expressed by reaction (iii) or (v) in Table 1; this was supported by the weight loss measurements.

Table 1 Summary of decomposition pathways for the intermediates deduced from X-ray diffraction and weight loss measurements

Reaction	M	Reaction temp. at which weight loss begins, °C	Mass loss, %	
			obs.	calculated
(i) $(NH_4)_3M(SO_4)_3 = NH_4M(SO_4)_2 + G. P.$	Cr	400	32.4	33.5
	Fe	310	33.3	33.2
(ii) $2\ NH_4M(SO_4)_2 = M_2(SO_4)_3 + G. P.$	Cr	532	25.0	25.1
	Fe	440	26.6	24.8
(iii) $M_2(SO_4)_3 = M_2O_3 + G. P.$	Cr	632	58.0	61.2
	Fe	640	60.0	59.8
(iv) $(NH_4)_2Mn_2(SO_4)_3 = 2\ MnSO_4 + G. P.$	–	420	32.0	30.4
(v) $3\ MnSO_4 = Mn_3O_4 + G. P.$	–	850	48.9	49.5

G. P. = gaseous products

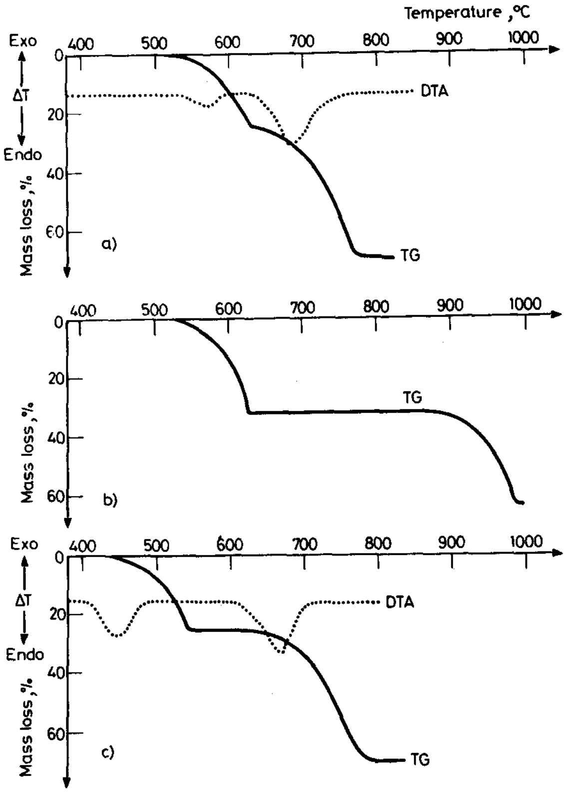

Fig. 3 DTA and TG curves of reaction intermediates. (a) $NH_4Cr(SO_4)_2$, (b) $(NH_4)_2Mn_2(SO_4)_3$, (c) $NH_4Fe(SO_4)_2$

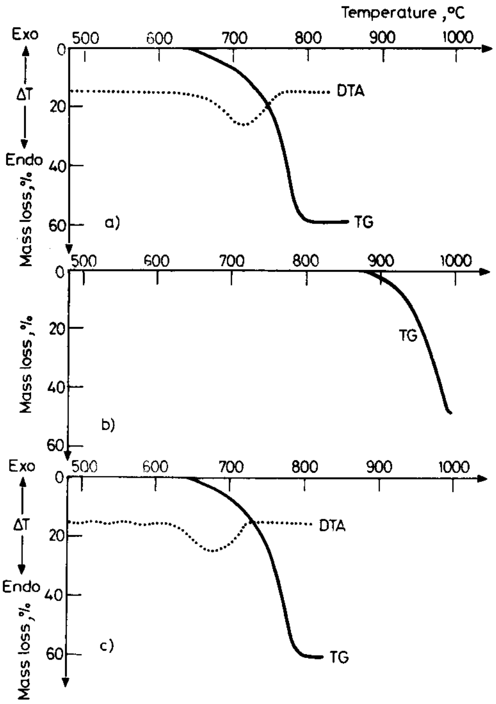

Fig. 4 DTA and TG curves of reaction intermediates. (a) $Cr_2(SO_4)_3$, (b) $MnSO_4$, (c) $Fe_2(SO_4)_3$

Decomposition kinetics

Kinetic measurements on the decomposition of $(NH_4)_3M(SO_4)_3$, $NH_4M(SO_4)_2$ and $M_2(SO_4)_3$ (M = Cr and Fe), expressed by reactions (i), (ii) and (iii), were carried out using the isothermal TG method. As concerns the kinetics of decomposition of the products, all obey the contracting-volume equation:

$$1-(1-\alpha)^{1/3}=kt$$

Arrhenius plots are shown in Fig. 5, including those for the Al salts [8]. The kinetic parameters and temperature ranges studied are listed in Table 2.

It is concluded that the intermediates of Fe are the most unstable, and have higher decomposition rates than for the intermediates of Al and Cr.

* * *

The authors are grateful to Dr. H. Osada and Mr. H. Nakamura, Department of Environmental Engineering, Kyushu Institute of Technology, for their helpful discussions.

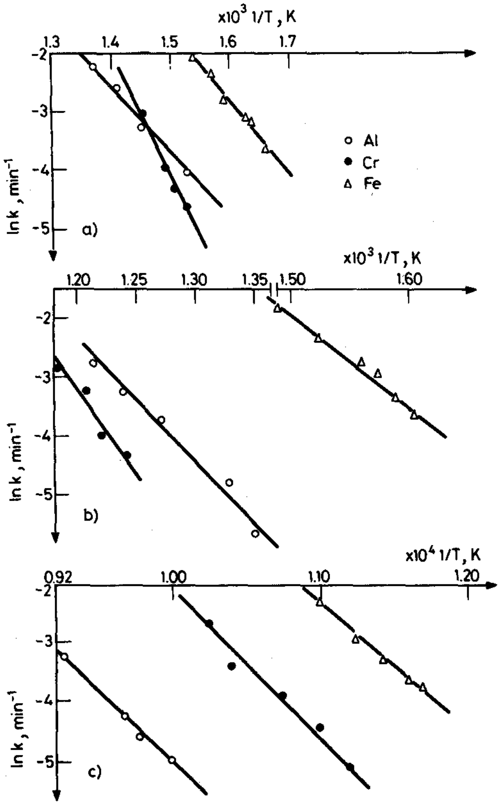

Fig. 5 Arrhenius plots of decomposition of the intermediates. (a) $(NH_4)_3M(SO_4)_3$, (b) $NH_4M(SO_4)$, (c) $M_2(SO_4)_3$

Table 2 Arrhenius parameters for the decomposition of the intermediates

Substances	M	*E*, kJ/mol	ln *A*	Temperature range studied, °C
$(NH_4)_3M(SO_4)_3$	Al	95.9	13.5	380–458
	Cr	193.9	29.9	382–413
	Fe	108.8	18.2	328–375
$NH_4M(SO_4)_2$	Al	177.9	23.3	467–550
	Cr	209.0	26.7	532–573
	Fe	130.2	21.4	350–395
$M_2(SO_4)_3$	Al	291.0	29.3	748–805
	Cr	215.3	24.3	620–704
	Fe	169.5	20.3	584–640

References

1 A. Saba, M. Hussein and E. Khairy, Egypt J. Chem., 16 (1973) 529.

2 E. Semin, I. Dmitiev, Yu. Zainlin and V. Strikov, Tr. Ural Politekh. Inst., 148 (1966) 11; C. A., 68 (1968) 108292q.

3 R. Chernov and I. Kouzum, Zh. Prikl. Khim., 47 (1974) 1910.

4 J. Feterman and S. Sun, Ext. Met. Aluminium, 1 (1963) 333.

5 H. Nakamura, Y. Hara and H. Osada, J. Chem. Soc. Japan, Chem. and Chem. Industry, (1980) 706.

6 P. K. Sahoo, S. K. Bose and S. C. Sircar, Thermochim. Acta, 31 (1979) 303.

7 ibid, 31 (1979) 315.

8 T. Nagaishi, S. Ishiyama, M. Matsumoto and S. Yoshinaga, J. Thermal Anal., 23 (1982) 201.

9 T. Nagaishi, J. Yoshimura, M. Matsumoto and S. Yoshinaga, ibid, 18 (1980) 501.

Zusammenfassung — Es wurden die Reaktionen zwischen Ammoniumsulfat und drei Metalloxiden (Cr_2O_3, MnO_2 und Fe_2O_3) untersucht. Durch Röntgendiffraktion und chemische Analyse wurde bestätigt, dass im Verlaufe der Reaktion stabile Zwischenprodukte gebildet werden. Es handelt sich dabei um $(NH_4)_3M(SO_4)_3$ und $NH_4M(SO_4)_2$ im Falle von Cr_2O_3 und Fe_2O_3 und um $(NH_4)_2Mn_2(SO_4)_3$ im Falle von MnO_2. Diese Zwischenprodukte und die Metallsulfate wurden thermisch zersetzt. Die Volumenkontraktionsgleichung war für die Zersetzung all dieser Zwischenprodukte gültig. Die Arrheniusparameter wurden bestimmt.

Резюме — Изучены реакции между сульфатом аммония и тремя окислани металлов Cr_2O_3, MnO_2 и Fe_2O_3. Химическим анализом и диффракцией рентгеновских лучей подтверждено, что в ходе реакций последовательно образуются устойчивые промежуточные продукты. В случае окислов трехвалентных хрома и железа, такими продуктами были $(NH_4)_3M(SO_4)_3$ и $NH_4M(SO_4)_2$, а в случае двуокиси марганца $(NH_4)_2Mn_2(SO_4)_3$. Проведено термическое разложение этих промежуточных продуктов и сульфатов этих металлов. Для реакций разложения всех промежуточных продуктов справедливым было уравнения объемного сжатия. Определены аррениусовские параметры.