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REACTION OF AMMONIUM SULPHATE WITH ALUMINIUM OXIDE

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The reaction between ammonium sulphate with aluminium oxide was studied. It was confirmed by X-ray diffraction and chemical analysis that three intermediate reaction products, $(NH_4)_3Al(SO_4)_3$, $NH_4Al(SO_4)_2$ and $Al_2(SO_4)_3$, are formed. The thermal decompositions of these three compounds were carried out. It has been shown that the same rate law is valid for them. The activation energies for $(NH_4)_3Al(SO_4)_3$, $NH_4Al(SO_4)_2$ and $Al_2(SO_4)_3$ are 95.9, 177.9 and 291.0 kJ/mol, respectively.

Generally, study of the reactions of ammonium sulphate with metal oxides is important from the standpoint of the poisoning and recycling of metal oxide catalysts in catalytic methods for the dry removal of NO_x and SO_x [1]. These have been applied not only for the extraction of metal oxide from metal ores, but also for the beneficiation of low-grade metal ores [2, 3]. Saba, Hussein and Khairy [4] studied the sulphatization of Fe_2O_3, MnO_2, a mixture of Fe_2O_3 with MnO_2 and local ferruginous manganese ores with ammonium sulphate, and discussed the reaction scheme on the basis of X-ray and analytical results.

The reaction of ammonium sulphate with aluminium oxide has mainly been investigated by Russian researchers [5—7], who established the optimum conditions for sulphatization. The present work is intended as a more detailed investigation of the progressive solid-state reaction between mixtures of ammonium sulphate and aluminium oxide, and of the thermal decompositions of the products, by thermal analysis.

Experimental

The starting materials $(NH_4)_2SO_4$ and Al_2O_3 used in the present study were obtained from Nakai Chemicals (Japan). They were homogenized by sieving below 200 mesh (particle size under 75 μm).

Three intermediate reaction products, $(NH_4)_3Al(SO_4)_3$, $NH_4Al(SO_4)_2$ and $Al_2(SO_4)_3$, which were identified by chemical analysis and X-ray diffraction in the course of the reaction between $(NH_4)_2SO_4$ and Al_2O_3, were prepared as follows; $(NH_4)_3Al(SO_4)_3$: a mixture of $(NH_4)_2SO_4 : Al_2O_3 = 1 : 4$ (molar ratio) is heated to 300° and kept for an hour at the same temperature. This sample is dissolved in water to remove the excess Al_2O_3 by filtering. The solution is then evaporated to a concentration which permits separation of the salt on cooling.

$NH_4Al(SO_4)_2$: the same mixture is heated to 400° and kept for 30 minutes at the same temperature. The separation process is the same as for $(NH_4)_3Al(SO_4)_3$. $Al_2(SO_4)_3$: the mixture is heated to 600°. The separation is the same as the abovementioned one.

The purities of the three materials obtained were checked by weighing the heattreated sample (assuming that the total amount of $(NH_4)_2SO_4$ can react with Al_2O_3) and by X-ray diffraction.

Chemical analysis of the reaction products was performed for NH_4^+, SO_4^{2-} and Al^{3+} [8].

The DTA and TG data on the mixtures of $(NH_4)_2SO_4$ with Al_2O_3, as well as on the reaction products, were obtained simultaneously with a Shimazu DT-2B thermal analyser apparatus, in air. Powder X-ray diffraction patterns were recorded with an X-ray diffractograph, using CuKα radiation.

Results and discussion

Figure 1 shows the DTA and TG traces for various mixtures of $(NH_4)_2SO_4$ with Al_2O_3. Each of the DTA traces of the mixtures displays four endotherms, at temperatures of 320, 380, 560 and 780°, respectively. The TG traces show four weight loss regions, corresponding to the DTA traces in the same temperature ranges. The effect of the decomposition of $(NH_4)_2SO_4$ [9] could be neglected due to excess addition of the oxide, though it was observed to a slight extent in Fig. 1(b) and (c). The product in each reaction step was identified on the basis of chemical analysis and X-ray diffraction for the $(NH_4)_2SO_4$ / Al_2O_3 mixture of molar ratio 1 : 4.

It was shown that the reaction products were $(NH_4)_3Al(SO_4)_3$ at 320°, $NH_4Al(SO_4)_2$ at 400°, $Al_2(SO_4)_3$ at 600°, and Al_2O_3 at 800°. Table 1 gives the results of chemical analysis of the mixtures heat-treated at various temperatures.

Table 1

Determination of the products formed at various temperatures by chemical analysis of NH_4^+, Al^{3+} and SO_4^{2-}

Product	Molar ratio			Chemical formula of the product
	NH_4^+	Al^{3+}	SO_4^{2-}	
at 320°	3.10	1.00	2.94	$(NH_4)_3Al(SO_4)_3$
at 400°	0.94	1.00	2.04	$NH_4Al(SO_4)_2$
at 600°		2.00	2.94	$Al_2(SO_4)_3$

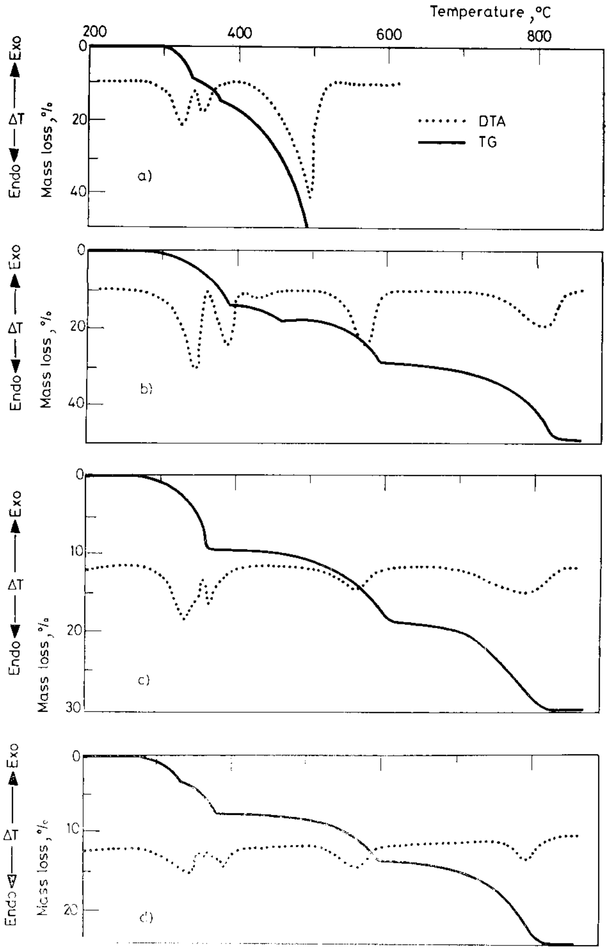

Fig. 1. DTA and TG traces of various mixtures of $(NH_4)_2SO_4$ with Al_2O_3 in air (heating rate = = 10°/min). (a) pure $(NH_4)_2SO_4$; (b) $(NH_4)_2SO_4$: Al_2O_3 = 1.8 : 1 (molar/ratio); (c) = 1 : 1.3; (d) = 1 : 4.0

On the basis of thermal analysis, supported by X-ray diffraction and chemical analysis of each reaction product formed at the different temperatures, the following reaction sequence may be proposed:

(1) $6\,(NH_4)_2SO_4 + Al_2O_3 = 2\,(NH_4)_3Al(SO_4)_3$ + gaseous products (~ 300°)

(2) $4\,(NH_4)_3Al(SO_4)_3 + Al_2O_3 = 6\,NH_4Al(SO_4)_2$ + gaseous products (~ 350°)

(3) $6\,NH_4Al(SO_4)_2 = 3\,Al_2(SO_4)_3$ + gaseous products (~ 500°)

(4) $2\,Al_2(SO_4)_3 = 2\,Al_2O_3$ + gaseous products (~ 650°)

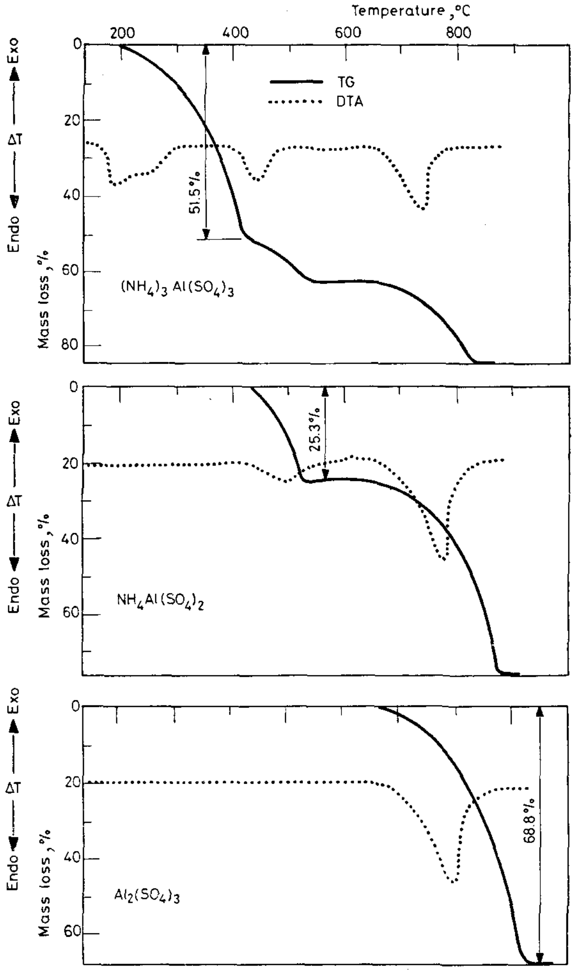

Fig. 2. DTA and TG traces of the three intermediate reaction products in air

The observed weight losses are 4.6% for reaction (1), 7.3% for reactions (1) + (2), 13.2% for reactions (1) + (2) + (3), and 23.9% for reactions (1) + (2) + (3) + (4). The cumulated weight losses calculated for reactions (1) to (4) are 5.3%, 7.2%, 13,3% and 24.5%, respectively. Quantitative analysis of gaseous products was not carried out, though ammonia and sulphur dioxide were detected. DTA and TG traces of the three intermediate reaction products are shown in Fig. 2. X-ray diffraction and the observed weight losses suggest the following reaction scheme:

(5) $6\,(NH_4)_3Al(SO_4)_3 = 4\,NH_4Al(SO_4)_2 + Al_2O_3$ + gaseous products, (~ 300°)

(6) $6\,NH_4Al(SO_4)_2 = 3\,Al_2(SO_4)_3$ + gaseous products (~ 430°)

(7) $2\,Al_2(SO_4)_3 = 2\,Al_2O_3$ + gaseous products (~ 700°)

The decomposition of $(NH_4)_3Al(SO_4)_3$ is described by the three equations (5), (6) and (7), that of $NH_4Al(SO_4)_2$ by the equations (6) and (7), and so on. The observed weight losses are 51.5% for reaction (5), 25.3% for (6) and 68.8% for (7), as compared with the calculated values of 52.6, 27.9 and 70.2%, respectively.

Physiak and Pacewska [10] reported the thermal decomposition of basic aluminium ammonium sulphate in vacuum. The decomposition scheme suggested by them is rather complex compared with ours, probably due to their starting material being different from ours. Figure 3 shows the α *vs.* t curves from isothermal weight loss experiments for $(NH_4)_3Al(SO_4)_3$ at four different temperatures between 380

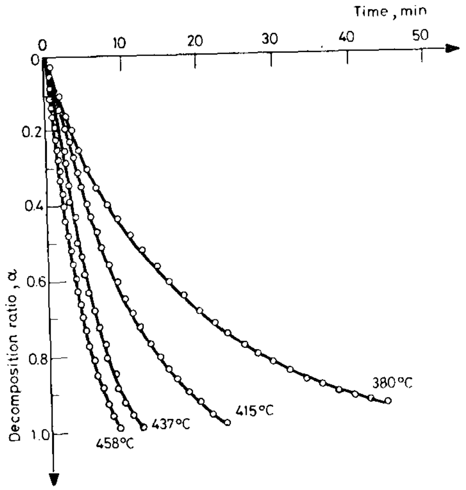

Fig. 3. Isothermal decomposition curves of $(NH_4)_3Al(SO_4)_3$ in air

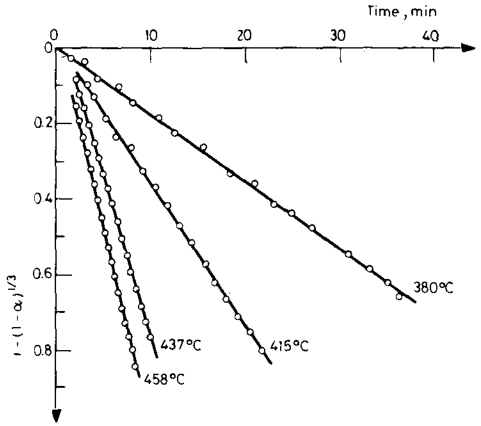

Fig. 4. Plot of contracting-volume equation for $(NH_4)_3Al(SO_4)_3$ *vs.* time

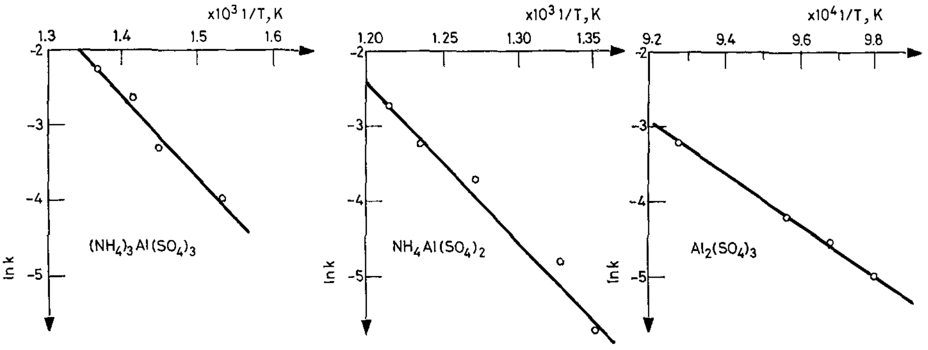

Fig. 5. Arrhenius plots of decomposition reactions of the three intermediate products

and 460°. The kinetics of the decomposition follows the contracting-volume equation (8),

$$1 - (1 - \alpha)^{1/3} = kt \tag{8}$$

Figure 4 shows the validity of Eq. (8), where the plots of $1 - (1 - \alpha)^{1/3}$ *vs.* t at various temperatures are straight lines. The same experiments were also performed for $NH_4Al(SO_4)_3$ and $Al_2(SO_4)_3$. The temperature range of study of $NH_4Al(SO_4)_2$ was from 460 to 550° and for $Al_2(SO_4)_3$ from 740 to 810°. The applicability of Eq. (8) was confirmed for these compound too. Arrhenius plots are shown in Fig. 5, from which the rate constants for decomposition reactions (5), (6) and (7) are given by $7.51 \times 10^5 \exp(-95900/RT)$, $1.3 \times 10^{10} \exp(-177900/RT)$ and $5.3 \times 10^{12} \exp(-291\,000/RT)$, respectively, where R is the gas constant (J/mol/K) and T is the absolute temperature (K).

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Zusammenfassung — Die Reaktion von Ammoniumsulfat mit Aluminiumoxid wurde untersucht. Durch Röntgendiffraktion und chemische Analyse wurde bestätigt, daß drei Zwischenprodukte $(NH_4)_3Al(SO_4)_3$, $NH_4Al(SO_4)_2$ und $Al_2(SO_4)_3$ gebildet werden. Die thermische Zersetzung der drei Verbindungen wurde durchgeführt. Es wurde gezeigt, daß für alle drei dasselbe Geschwindigkeitsgesetz Gültigkeit hat. Die Aktivierungsenergien für $(NH_4)_3Al(SO_4)_3$, $NH_4Al(SO_4)_2$ und $Al_2(SO_4)_3$ sind 95.9, 177.9 und 291.0 kJ/Mol.

Резюме — Изучена реакция между сульфатом аммония и окисью алюминия. С помощью рентгено-диффракционного анализа и химического анализа подтверждено образование трех промежуточных продуктов реакции: $(NH_4)_3Al(SO_4)_3$, $NH_4Al(SO_4)_2$ и $Al_2(SO_4)_3$. Проведено термическое разложение этих трех соединений, и установлено, что для соблюдается один и тот же закон скорости. Значения энергии активации соединений $(NH_4)_3Al(SO_4)_3$, $NH_4Al(SO_4)_2$ и $Al_2(SO_4)_3$, соответственно, равны 95.9; 177.9 и 291.0 кдж. моль$^{-1}$.