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THERMAL DECOMPOSITION OF ALUMINIUM-BEARING COMPOUNDS

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The thermal decomposition of aluminium sulfate, potassium aluminium sulfate, ammonium aluminium sulfate and alunite have been studied by dynamic thermogravimetry and X-ray diffraction. Specifically, the factors that affect the sulfate decomposition reaction have been investigated. The sulfate decomposition is found to be significantly influenced by the presence of an inert material such as potassium sulfate in the solid matrix.

This paper considers the aluminium sulfate decomposition behaviour starting with various aluminium-bearing materials such as aluminium sulfate dodecahydrate, aluminium potassium sulfate (potash alum), aluminium ammonium sulfate (ammonium alum) and alunite. Upon heating, these compounds all form anhydrous aluminium sulfate which then undergoes sulfate decomposition leading to various forms of alumina [1–5].

The decomposition consists of the following steps:

i) for aluminium sulfate dodecahydrate:

$$Al_2(SO_4)_3 \cdot 18H_2O \rightarrow Al_2(SO_4)_3 + 18\ H_2O_{(g)}$$

$$Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3\ SO_{3(g)}$$

ii) for potash alum:

$$KAl(SO_4)_2 \cdot 12H_2O \rightarrow KAl(SO_4)_2 + 12\ H_2O_{(g)}$$

$$2\ KAl(SO_4)_2 \rightarrow K_2SO_4 + Al_2(SO_4)_3$$

$$Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3\ SO_{3(g)}$$

iii) for alunite:

$$KAl_3(SO_4)_2(OH)_6 \rightarrow KAl(SO_4)_2 + Al_2O_3 + 3\ H_2O_{(g)}$$

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Then $KAl(SO_4)_2$ follows the same steps as in potash alum

iv) for ammonium alum:

$$AlNH_4(SO_4)_2 \cdot 12H_2O \rightarrow AlNH_4(SO_4)_2 + 12\,H_2O_{(g)}$$

$$2\,AlNH_4(SO_4)_2 \rightarrow Al_2(SO_4)_3 + 2\,NH_{3(g)} + H_2O_{(g)} + SO_{3(g)}$$

$$Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3\,SO_{3(g)}$$

When the starting material is potash alum or alunite, aluminium sulfate decomposition takes place in a solid matrix containing potassium sulfate as an inert material. Ammonium alum presents a different situation. This is due to the gaseous evolution stage (which produces ammonia, water and SO_3) preceding the sulfate decomposition. As a result, the physical features (e.g. porosity) in anhydrous aluminum sulfate produced from ammonium alum may be different from those produced from hydrated aluminium sulfate. Such variations are worthy of exploration in the modeling of reaction kinetics for gas-solid non-catalytic reactions.

These factors can, for example, affect the progress of sulfate decomposition by causing a change in the temperature range or the kinetic mechanism of the reaction. Sato et al. [2] observed the same temperature range (750–925°) for the sulfate decomposition starting with either reagent-grade aluminum sulfate or ammonium alum. However, the endothermic DTA peak maximum which was observed at 920° starting with aluminium sulfate, was shifted to 880° in the case of ammonium alum as starting material. They attributed the difference to the variation in the particle size produced during the preceding thermal transformations. In a related work by Johnson and Gallagher [1], it has been reported that freeze-dried ammonium alum decomposes faster then freeze-dried aluminium sulfate. They have also attributed this difference to the disruptive effect on physical structure by low temperature ammonium sulfate decomposition. Further, it was observed that the activation energies for sulfate decomposition starting with ammonium alum were higher than those starting with aluminium sulfate, by about ten percent.

Alunite has the formula which can be written in two generalized forms as:

$$M_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3$$

or

$$MAl_3(SO_4)_2(OH)_6$$

where M is potassium(K). When M is sodium(Na), the compound is known as natroalunite. By changing the proportion of K and Na, a range of alunitic compounds can be synthesized [6]. In such an alunite-natroalunite series, the potassium end-member is quite similar to potash alum and thus would be of interest for comparison. The differences lie in the relative abundance of elemental aluminium and the presence of water molecules. However, the kinetics of thermal decomposition of alunite have not been reported in the literature in any detail.

This study illustrates our experimental findings on the similarities and the differences in the sulfate decomposition of all these compounds and the influence of the nature of the solid matrix on the kinetics of the reactions.

Experimental procedures

Hydrated aluminium sulfate from Fisher Scientific Co. and reagent grade potash alum and ammonium alum from Aldrich Chemical Co. were used as samples. The formula weights for $Al_2(SO_4)_3 \cdot 18H_2O$, $KAl(SO_4)_2 \cdot 12H_2O$ and $NH_4Al(SO_4)_2 \cdot 12H_2O$ are 666.42, 474.39 and 453.3, respectively. Alunite was synthesized in the laboratory by the atmospheric reflux between aluminum sulfate and potassium sulfate as described in the literature [6]. A fine-grained powder was produced. The formula weight of alunite is 414.

Dynamic thermogravimetric experiments were conducted at 20 deg/min heating rate, in a flowing nitrogen atmosphere (60 ml/min) for all compounds using a DuPont 951 TGA modified as discussed elsewhere [7]. Typically, the sample size used was in the range from 12 to 16 mg. Powder X-ray diffraction analyses were performed using a Philips–Norelco diffractometer with Ni-filtered CuK radiation and the generator operating at 35 kV and 15 mA current.

Results and discussion

a) Thermogravimetric analysis

Figures 1 and 2 show the weight loss and derivative weight loss as a function of temperature for all the compounds studied. As can be seen from these figures, various stages of decomposition are distinguishable in different temperature zones for these compounds. Alunite appears to undergo gradual decomposition. The final weight loss values observed at 900° are 82% for aluminum sulfate, 69% for potash alum, 87% for ammonium alum and 48% for alunite. These correspond closely with the theoretical expectations (based on reactions described earlier) of 84.7%, 70.9%, 87.6%, 42%, respectively. The small discrepancies are probably due to variations in water content, as has been discussed elsewhere [7]. Potash alum shows the widest flat region (in the temperature range of 300–600°) in these curves, indicating a clear separation of the dehydration and sulfate decomposition stages.

In Fig. 2, which shows the variation of rate of weight loss versus temperature,

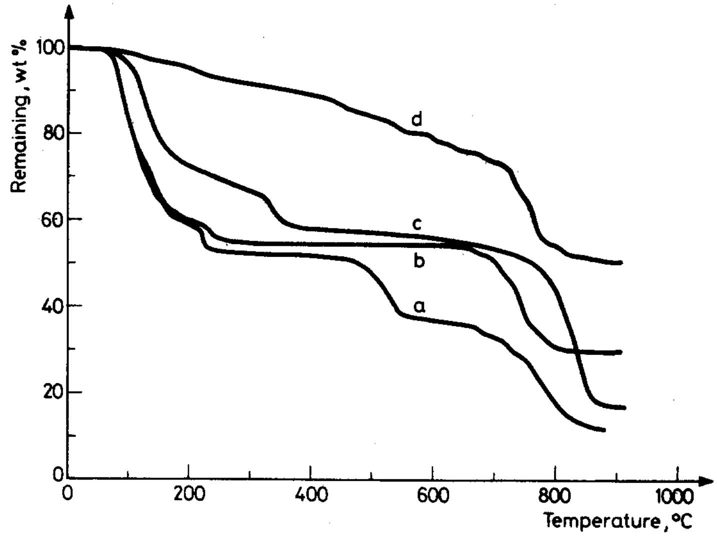

Fig. 1 Comparative TG behaviour at 20 deg/min heating rate (in flowing nitrogen atmosphere, 60 ml/min). (a) Ammonium alum; (b) Potash alum; (c) Aluminium sulfate; (d) Alunite

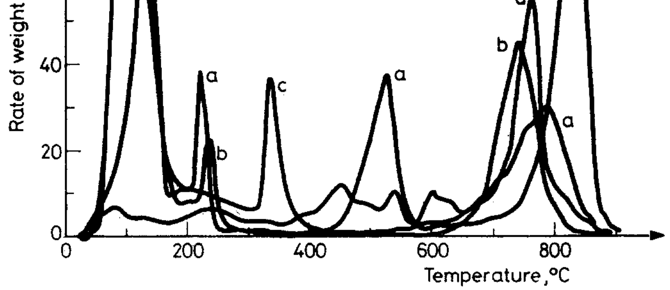

Fig. 2 Comparative DTG behaviour at 20 deg/min heating rate (in flowing nitrogen atmosphere, 60 ml/min). (a) Ammonium alum; (b) Potash alum; (c) Aluminium sulfate; (d) Alunite

each peak has been labeled by the corresponding compound number for clarity. In the figure, the four peaks for ammonium alum are clearly seen. Obviously, the additional peak (which is not seen in aluminum sulfate or potash alum) belongs to the release of ammonia, water and SO_3 between 400 and 600°. The curve for alunite shows that the dehydration does not take place with the same intensity as in the other compounds, probably due to the complex nature of its solid structure. The numerous small peaks in the temperature range from 50 to 650° can be attributed to dehydration, although doubts exist about the nature of the gaseous products corresponding to the peak at 600°. It is arguable, however, that the sulfate decomposition is only represented by the large peak between 640 and 900°. This premise is supported by X-ray analyses of alunite samples reported in the literature [9], which indicate complete absence of alumina formation until 650°.

It should be noted that the dehydration in potash alum and ammonium alum is completed at much lower temperatures, compared to aluminium sulfate. This can be seen by comparing curves c&b and c&a in Fig. 1 and Fig. 2. The second dehydration peak for potash alum and ammonium alum occurs at a temperature, which is at least 100° lower than that for aluminium sulfate. Another trend is seen among the sulfate decomposition peaks. The locations of these peaks suggest that the presence of potassium sulfate starting with potash alum or alunite, lowers the temperature for aluminium sulfate decomposition. The greater the amount of K_2SO_4, the lower is the aluminium sulfate decomposition temperature. Also, the peaks become broader as more of K_2SO_4 is present. These observations illustrate the influence of the presence of a non-reactive solid (K_2SO_4) domain in the matrix.

b) X-ray diffraction studies

In order to clearly identify the solid phases, powder X-ray diffraction analyses were performed on the samples obtained from TG experiments conducted at 20 deg/min upto 900°.

All of the samples displayed a pattern consisting of a broad background peak, rather than distinct peaks, confirming the formation of amorphous alumina at 900°. The angular range (Bragg diffraction angles) for the broad background (amorph halo) is 20 to 45° in all of the compounds. Formation of amorphous or irregularly shaped alumina has also been reported previously [4, 10]. In addition to the amorph alumina background, potash alum and alunite samples displayed sharper peaks corresponding to K_2SO_4. Alunite and ammonium alum were further analyzed at lower temperatures. The diffraction patterns confirmed the intermediate formation of anhydrous aluminium sulfate, as well as the temperature ranges for the sulfate decomposition reaaction.

c) Comparative kinetic evaluations

In a previous study, it was shown that the sulfate decomposition in aluminium sulfate can be described by a contracting disc model, with an activation energy of 235 kJ/mol [8]. It has been of interest to examine if the sulfate decomposition starting from different materials can still be described by the contracting disc model or is influenced by the differences in the solid matrix. As indicated above, the sulfate decomposition in the presence of K_2SO_4 starts at lower temperature.

Using the dynamic TG data and both the derivative and integral procedures [7, 8], the sulfate decomposition reaction was analyzed in the temperature range from 500° to 900° with aluminium sulfate and potash alum as starting materials. For ammonium alum and alunite as the starting materials, the analyses were conducted in the temperature ranges of 600–900° and 650–900°, respectively. These specific temperature ranges were identified from the location of the peaks corresponding to sulfate decomposition in Figures 1 and 2.

The results of these analyses, that have been discussed in detail elsewhere [7], do not provide exact information about the decomposition model applicable to each compound. Only minor discrimination in discarding a few models can be exercised without ambiguity. Nonetheless, it is observed that the favoured models are different for these compounds. The results clearly indicate that the phase boundary movement models are no longer valid when K_2SO_4 is present in the solid matrix (i.e. for potash alum and alunite). Instead, 3-dimensional diffusion or the homogeneous reaction models appear to describe the reactions better.

Conclusions

It has been demonstrated that the physical state of the sample has a major influence on the onset and progress of aluminum sulfate decomposition. The presence of inert K_2SO_4 matrix affects the onset, the progress and the kinetic mechanism of the decomposition significantly.

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Zusammenfassung — Mittels dynamischer Thermogravimetrie und Röntgendiffraktionsverfahren wurde der thermische Zerfall von Aluminiumsulfat, Kaliumaluminiumsulfat, Ammoniumaluminiumsulfat und Alaunstein untersucht. Es wurden insbesondere diejenigen Faktoren untersucht, die die Zersetzungsreaktion der Sulfate beeinflussen. Es konnte nachgewiesen werden, daß die Sulfatezersetzung durch die Gegenwart von inerten Materialien, z. B. von Kaliumsulfat in der Festkörpermatrix eindeutig beeinflusst wird.

Резюме — С помощью динамической термогравиметрии и рентгено-диффракционного анализа изучено термическое разложение сульфата алюминия, калийалюминий сульфата, аммонийалюминий сульфата и алунита. Детально исследованы факторы, затрагивающие реакцию разложения сульфата. Найдено, что разложение сульфата в значительной степени затрагивается присутствием в твердой матрице какого-либо инертного вещества, как например, сульфата калия.