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A HIGH-TEMPERATURE X-RAY AND THERMAL ANALYSIS STUDY OF SYNTHETIC DAWSONITE[1]

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ABSTRACT

DTA, TGA, and high-temperature X-ray analysis carried out on synthetic dawsonite [$NaAlCO^3(OH)_2$] from room temperature to 900°C show the decomposition of synthetic dawsonite to be more complex than previously reported for the natural mineral. Water and/or CO_2 remain in the material after the collapse of the dawsonite structure and are not completely evolved until 675°C. A hitherto unreported exotherm at 650°C is apparently associated with the crystallization of $NaAlO_2$.

INTRODUCTION

A previous study of the thermal decomposition of natural dawsonite [$NaAlCO_3(OH)_2$] by Beck (1950) using DTA methods showed a minor endotherm at 300°C associated with the loss of nonessential water and a major endotherm at 440°C in which all chemically bound water and carbon dioxide were evolved. No additional reactions were noted on the DTA curve and no related weight loss data were obtained.

Recently there has been considerable interest in synthetic dawsonite because of its use as the source material for sodium aluminate ($NaAlO_2$) which may be used as an absorbent for industrial flue gases. Our preliminary thermal studies of synthetic dawsonite (supplied by Grace Chemical Company) indicated that its decomposition was more complex than that described by Beck for the mineral. Therefore, a combined DTA, TGA, and high-temperature X-ray diffraction study of synthetic dawsonite was undertaken.

EXPERIMENTAL METHODS

DTA and TGA Methods. Samples of synthetic dawsonite were heated in independent DTA and TGA apparatus in which nearly identical conditions could be maintained. Heating rates were normally 10°C/min, with either air or argon atmosphere. The dawsonite was first crushed and sieved (retaining the −200 mesh fraction) in order to standardize conditions. Samples were randomly selected from the material and examined by X-ray diffraction to confirm homogeneity.

X-Ray Diffraction Methods. A high angle X-ray diffractometer was employed in the examination of the samples at room temperature; a high-temperature diffractometer attach-

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ment was used at elevated temperatures. CuKα radiation ($\lambda = 1.5418$ Å) was used in all diffraction experiments. The heating element of the high-temperature camera, which also acts as the sample holder, was constructed of platinum foil. The temperatures were determined with a Chromel-Alumel thermocouple placed in contact with the heater. All the high-temperature diffraction studies were carried out in air.

RESULTS

Figure 1 shows typical DTA and TGA curves for a sample of synthetic dawsonite heated in argon at a rate of 10°C/min.

The DTA curve is characterized by a broad asymmetrical endothermic peak at about 375°C. This endotherm is about 65°C below that of the major peak of the natural mineral. Since the heating rates in Beck's and our experiments are nearly identical, the cause for the endothermic peak position differences may be due to differences in crystallite size. Support for this hypothesis may be found in the DTA studies of antigorite by Callère and Hénin (1947) where the natural materials (which had larger crystallites) had higher reaction temperatures than corresponding synthetic materials.

The section of the TGA curve which parallels this endothermic reaction shows a slow weight loss from room temperature to about 200°C after which a rapid change in the rate of weight loss takes place up to approximately 400°C. The average calculated weight loss for several samples heated to 400°C was 35 percent compared to the expected weight loss of 43 percent assuming total evolution of water and carbon dioxide as reported by Beck for natural dawsonite. In fact the theoretical weight loss was not obtained until after the sample had undergone additional thermal reactions between 600 to 700°C. These reactions consisted of a very weak exotherm (650°C), followed by a shallow endotherm (675°C), with an associated weight loss at 675°C (Fig. 1).

The crystallization of $NaAlO_2$ at the exotherm-endotherm above was confirmed on the basis of room-temperature diffraction data from samples quenched from the locations shown by the numbers on the DTA curve (Fig. 1). No diffraction peaks were observed for samples located at points 1, 2, and 3, whereas those at 4 and 5 gave diffraction patterns for $NaAlO_2$.

Examination of the diffractometer tracings obtained from the high-temperature X-ray diffraction experiments revealed that the dawsonite structure collapses at 200°C and sodium aluminate ($NaAlO_2$) is well crystallized by 500°C. Several unidentified peaks were observed in the patterns taken at 225°C; namely, 5.15, 4.98, and 3.209 Å. Additional heating of this material resulted in a noncrystalline product at 350°C and this was confirmed by examining the quenched sample at room temperature after removing it from the heating element.

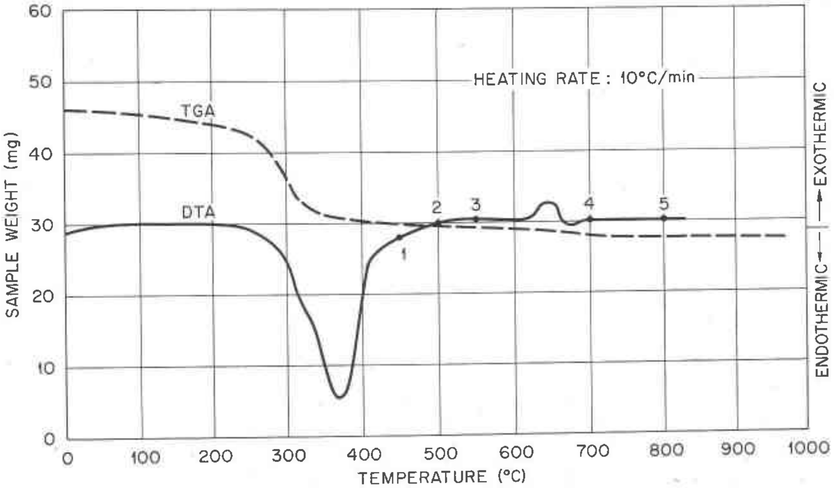

FIG. 1. Differential thermal analysis and thermogravimetric curves for synthetic dawsonite.

The differences in the temperature of crystallization of $NaAlO_2$ as observed in the high-temperature diffraction versus the DTA and TGA experiments is due to their heating methods. Unlike the thermal apparatus, the high-temperature X-ray camera is heated statically, that is, the temperature of the sample is raised stepwise and held at the given temperature for the time necessary for equilibration and the diffraction experiment (2 to 4 hr). This has the effect of lowering the reaction temperature relative to that of the continuous heating process.

CONCLUSIONS

The results of these experiments have shown that there is a temperature range in which noncrystalline material exists between the collapse of the synthetic dawsonite structure and the appearance of $NaAlO_2$. Furthermore our experiments suggest that some carbon dioxide and/or water is retained in the material following the major endotherm and preceding the crystallization of $NaAlO_2$.

REFERENCES

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