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OBSERVATIONS ON THE ROLE OF STRUCTURAL DISORDER IN THE THERMAL REACTIONS OF AMMONIUM HEXAVANADATE

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ABSTRACT

The thermal reactions of ammonium hexavanadate (AHV) were studied in inert, oxidizing and reducing atmospheres. It was found that the degree of structural order in the crystal lattice of AHV was an important factor which significantly influenced the course of the reaction.

INTRODUCTION

The thermal decomposition reaction of ammonium metavanadate (AMV) has been investigated by several research workers [1–9], and is well known to proceed as follows

$$\underset{\text{(AMV)}}{3(NH_4)_2O \cdot V_2O_5} \rightarrow \underset{\text{(AHV)}}{(NH_4)_2O \cdot 3V_2O_5} + 2H_2O + 4NH_3 \quad (1)$$

$$\underset{\text{(AHV)}}{(NH_4)_2O \cdot 3V_2O_5} \rightarrow 3V_2O_5 + H_2O + 2NH_3 \quad (2)$$

It has been shown that structural disorder in the AMV crystal has a marked effect on the decomposition reaction [1]. The crystal structure of AMV consists of zig-zag chains of distorted tetrahedra of oxygen around the vanadium. These tetrahedra are linked by their corners to form the chains. The NH_4^+ ions are located between these V–O groups in such a way that each NH_4^+ ion is surrounded by 10 O atoms. The decomposition of AMV involves scission of the V–O chains with the simultaneous evolution of NH_3

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and H_2O, followed by a rearrangement reaction and cross-linking of the V–O units to form AHV. It can therefore be expected that some degree of disorder will be built into the AHV crystal structure when it is formed via the decomposition of AMV.

It has also been shown that the surrounding atmosphere has a marked influence on the intermediate decomposition products as well as the final V_2O_5 product [4,5,7]. Various workers [4,5,7,10] suggested that catalytic decomposition of the evolved NH_3 on the surface of the V_2O_5 could cause some degree of reduction of V_2O_5.

It was therefore of interest to focus on the transition of AHV to V_2O_5, in order to assess the relative importance of the structural order/disorder in the AHV crystal and of the surrounding atmosphere during the decomposition reaction. For this purpose, three types of AHV crystals were prepared and the decomposition reaction was studied in oxidizing, inert and reducing atmospheres.

EXPERIMENTAL

Thermal analysis

A Stanton Redcroft STA 780 simultaneous thermal analyser with a platinum sample (135 cm^3) and reference cups was used to collect TG and DTA data. DSC studies were carried out using a Perkin–Elmer system 7/4 thermal analysis controller with a DTA 1700 differential thermal analyser operated in the DSC mode. Heating rates of 5 °C min^{-1}, a gas flow rate of 50 cm^3 min^{-1} and sample sizes of 20 to 30 mg were used.

X-ray powder diffraction studies

X-ray powder diffraction was used to identify the intermediate and final products using a Seifert MZ IV instrument with Cu $K\alpha$ radiation. Diffraction patterns were compared with those obtained from the ASTM powder diffraction files of the Joint Committee on Powder Diffraction Standards, except where otherwise indicated.

Materials and sample preparation

The AMV supplied by Riedel de Haën (analytical grade) was used as the starting material. To obtain AHV crystals with varying degrees of structural order, the commercially supplied AMV was subjected to different treatments.

AHV(1) with an ordered structure was prepared from solution according to the method described by Kelmers [11]. AHV(2) having a less ordered crystal structure than AHV(1) was prepared by the in situ thermal decomposition of AMV. AHV(3) having an even more disordered crystal structure was prepared by the in situ thermal decomposition of AMV with a highly disordered crystal structure, which was prepared according to the method suggested by Brown et al. [2].

RESULTS AND DISCUSSION

In this study, the starting material AHV was prepared for certain runs by the in situ thermal decomposition of commercial AMV, as well as AMV prepared according to the method described by Brown et al. [2]. For this reason thermogravimetric checks were run to confirm the formation of AHV as a stable intermediate in the various atmospheres to be used. A mass loss of 15.5% was obtained, as compared with the theoretical mass loss of 14.85% calculated for the thermal decomposition of AMV to AHV. An example of such a thermogravimetric curve, the decomposition of commercial AMV in a nitrogen atmosphere, is shown in Fig. 1. The X-ray powder diffraction pattern obtained for the AHV agreed with that published by Kelmers [11].

Decomposition in an inert atmosphere

The DSC curves for the decomposition of the various samples of AHV are shown in Fig. 2. The enthalpies of the reactions were determined and are

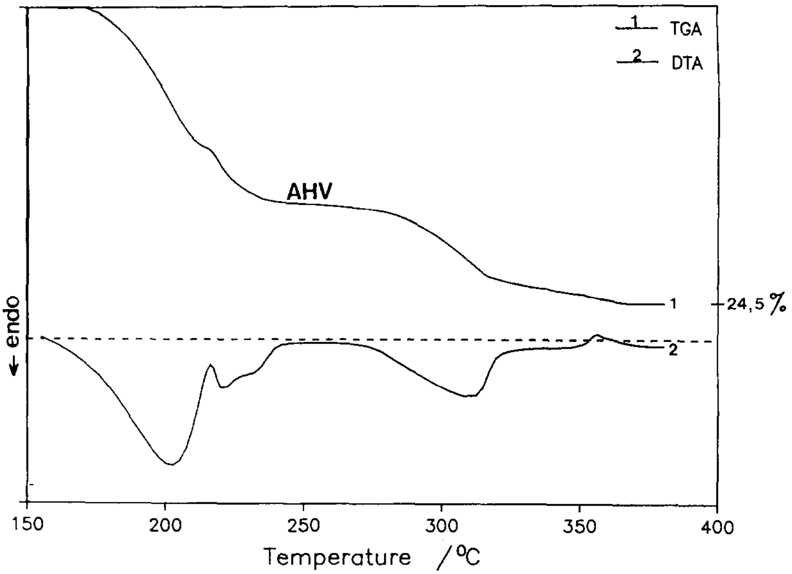

Fig. 1. Thermal decomposition of AMV in an inert (nitrogen) atmosphere. Heating rate 5 ° C min^{-1}.

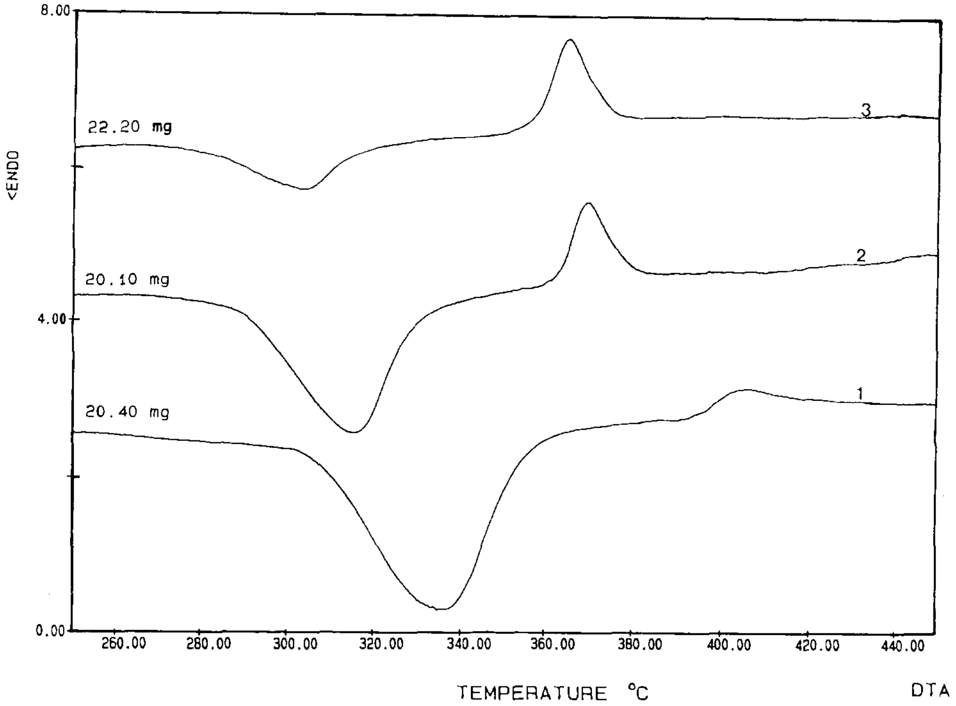

Fig. 2. DSC curves for the thermal decomposition of AHV in a nitrogen atmosphere.

given in Table 1, together with the mass losses as obtained from the TG experiments.

The endothermic process can be assigned to the transition of AHV to V_2O_5. This process involves a structural rearrangement as described above. The degree of disorder which is expected to be built into the crystal structure during decomposition will certainly give rise to some amount of lattice strain. Therefore, the decomposition of the less ordered AHV reactant must have a lower reaction enthalpy than that of its more ordered counterparts.

TABLE 1

Thermochemical data for the decomposition of AHV in an inert atmosphere

Sample [a]	Endothermic reaction		Exothermic reaction		Total mass loss (%) [b]
	Enthalpy (kJ mol^{-1} AHV)	Peak max. (°C)	Enthalpy (kJ mol^{-1} AHV)	Peak max. (°C)	
1	122.6	333	−7.2	405	9.1
2	83.1	314	−20.5	368	9.6
3	24.9	302	−23.3	364	11.1

[a] Degree of structural order: $3 < 2 < 1$ (sample 1 has the most ordered structural arrangement).

[b] Theoretical mass loss for AHV to $V_2O_5 = 8.7\%$.

This also explains the lower temperatures observed for the less ordered reactants.

The exothermic process which occurred between 350 °C and 420 °C for the various samples can be ascribed to the reduction of V_2O_5, caused by the

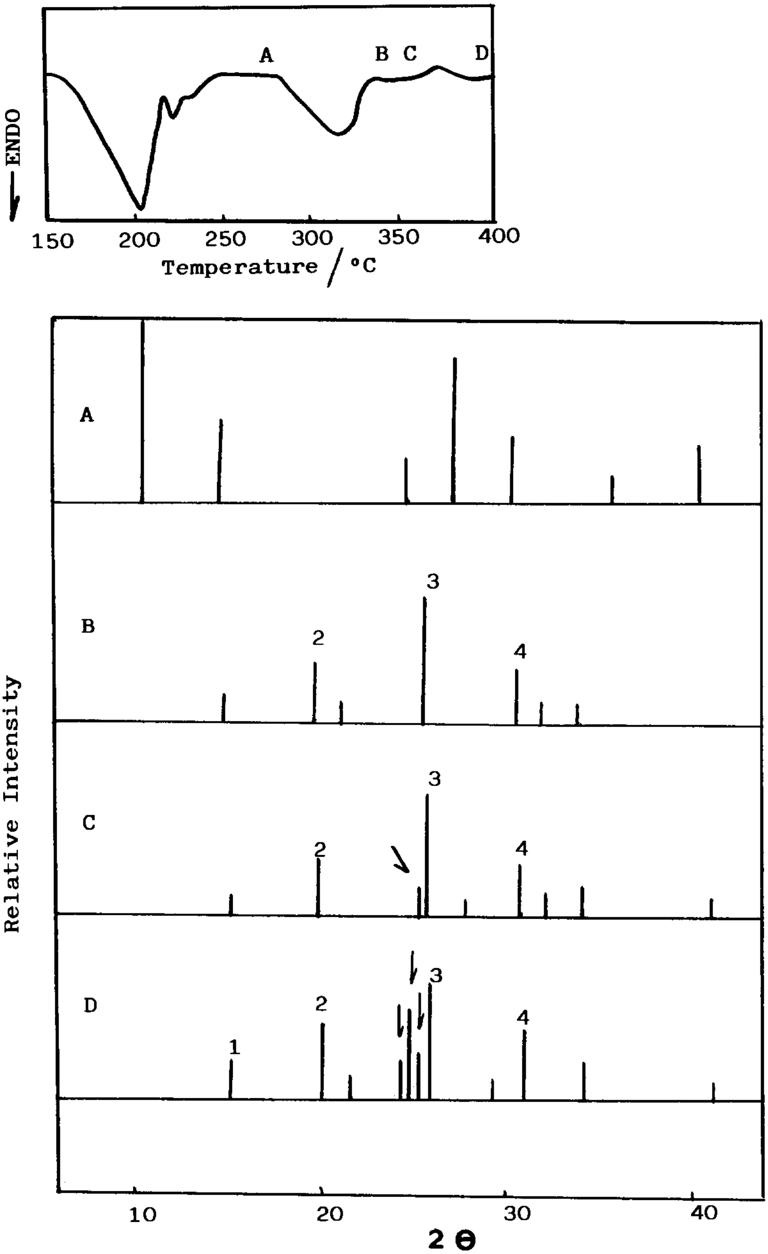

Fig. 3. X-ray powder diffraction of the intermediates during the thermal decomposition of AHV in nitrogen.

catalytic decomposition of ammonia on the surface of V_2O_5. X-ray powder diffraction patterns of samples taken at various stages of the reaction, as indicated in Fig. 3, confirmed this theory. Pattern A was mainly that of AHV, while pattern B was found to be that of V_2O_5 (the most prominent V_2O_5 lines are indicated by numbers 1–4). Patterns C and D indicated the presence of V_3O_7 and V_6O_{13} (the prominent lines are indicated by arrows).

The varying reaction enthalpies and mass losses observed for this process (see Table 1) can be ascribed to different degrees of reduction. A possible explanation would be that the V=O bonds in a disordered V_2O_5 structure are weakened as a result of strain, leading to different degrees of reduction for different degrees of disorder.

Decomposition of AHV in a reducing atmosphere

The DTA curves for the reaction of the different types of AHV crystals in a CO atmosphere are given in Fig. 4. The peaks which are observed at $T < 250\,^\circ C$ represent the decomposition of AMV. The peak observed between 300° and 380 °C represents mainly the thermal decomposition of AHV to V_2O_5. The peaks above 380 °C can be assigned to the reduction of V_2O_5 to V_2O_3 according to the reaction

$$V_2O_5 + 2CO \rightarrow V_2O_3 + 2CO_2 \qquad (3)$$

The DTA curves showed a shift towards lower temperature for both the decomposition and the reduction reaction in the more disordered crystal

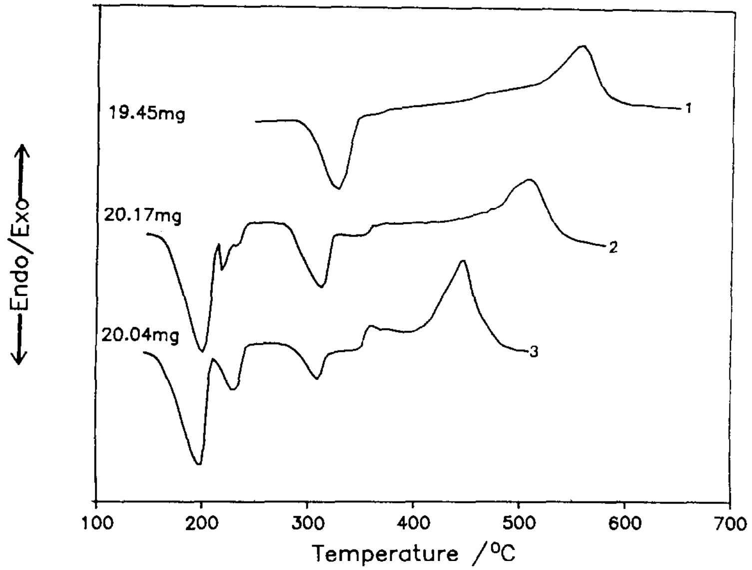

Fig. 4. DTA curves for the thermal decomposition of AHV in a carbon monoxide atmosphere.

structures. It is also clear that the formation of an intermediate, at approximately 350 °C, becomes more prominent in the more disordered structure. This may be due to the partial reduction of V_2O_5 and fits in with the theory that a disordered crystal structure of V_2O_5, as formed from the decomposition of a disordered AHV crystal, will be reduced more easily than a more ordered structural arrangement as a result of lattice strain.

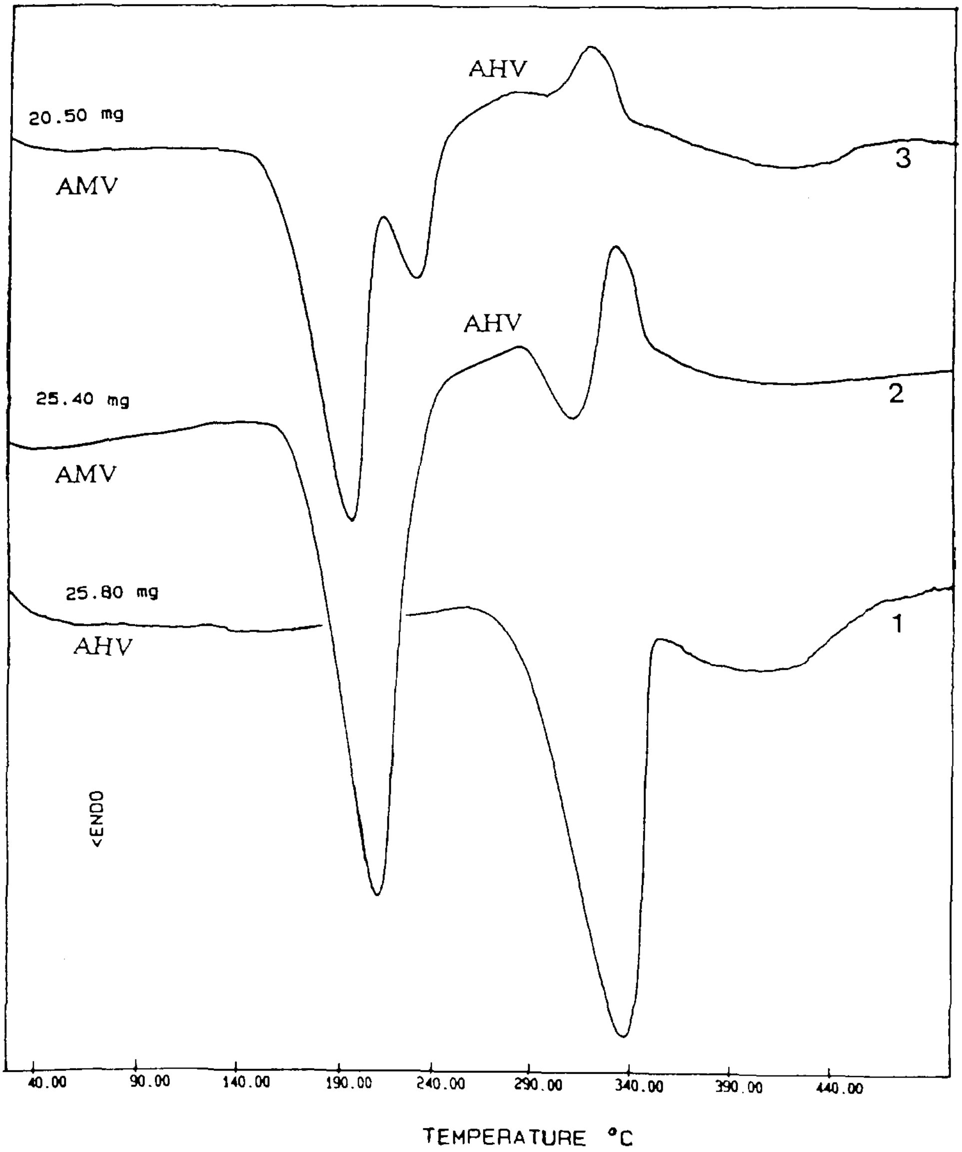

Fig. 5. DTA curves for the decomposition of AHV in an oxygen atmosphere.

Decomposition of AHV in an oxidizing atmosphere

The DTA curves for the decomposition of AHV samples 1–3 are shown in Fig. 5. It appears that two simultaneous processes are taking place, which are represented by an overlapping endo- and exotherm. In sample 1, the endothermic process is dominant, while in sample 3 the exothermic process is the dominant one. A total mass loss of 8.85% was observed for all of the samples and represents the endothermic thermal decomposition of AHV to V_2O_5 (cf. calculated value of 8.7%). The exothermic process could be a result of the oxidation of the reduction products of V_2O_5, which were formed by the catalytic decomposition of NH_3 as described above. The fact that the exothermic reaction is dominant in sample 3, the less ordered structural arrangement, may be explained in terms of the fact that the highly disordered AHV would require less energy to decompose than the ordered AHV. At the same time, the V_2O_5 decomposition product will be more readily reduced by the NH_3, and larger amounts of V_3O_7, V_6O_{13} and similar products may form, which, when oxidized, will account for the exothermic nature of the total reaction.

CONCLUSIONS

The above results indicated that the thermal decomposition of the AHV intermediate, as well as the reduction reactions of the V_2O_5 which is formed, are strongly influenced by the degree of structural order which exists in the AHV crystal. In general, a shift towards lower temperatures is observed for both the decomposition and the reduction reactions in a more disordered arrangement.

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