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THE GC STUDY OF THE THERMAL DECOMPOSITION OF AMMONIUM PARAMOLYBDATE TETRAHYDRATE IN A HYDROGEN ATMOSPHERE

WANG JIN YONG

Department of Chemistry, Nanjing Normal University, Nanjing 210024 (China)

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ABSTRACT

The GC study of the thermal decomposition of ammonium paramolybdate tetrahydrate (APM) in the solid state in a hydrogen atmosphere is reported. The evolved gas (EG) curve shows that the compound decomposes in four distinct steps within the experimental temperature range 60–640 °C. After the first dehydration step, the compound decomposes with evolution of NH_3 and H_2O in two successive steps leading to the formation of MoO_3. The last step is the reduction of MoO_3 to MoO_2.

INTRODUCTION

The thermal decomposition of APM has been investigated by various thermal analysis techniques [1–4], such as TG and DTA in atmospheres other than hydrogen. The present work, conducted in a hydrogen atmosphere using gas chromatography in combination with X-ray powder diffraction (XR) and IR spectroscopy as well as chemical analysis, gave thermal decomposition results for APM which differ from those previously obtained.

EXPERIMENTAL

Material

The $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ obtained was AnalaR and was used without further treatment.

Thermal analysis

The special heater designed for the study of the decomposition of the sample and the EG-analysis equipment employed and its operating conditions were essentially the same as those described by Xin et al. [5].

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The intermediate solid products (ISP) for the following analyses were taken at 170 °C, 260 °C, 360 °C and 630 °C, the process being stopped when each successive full water band appeared on the EG curve.

Chemical analysis

Mo was determined by a gravimetric method using lead acetate and the NH_3 content was determined by the Kjeldhal method.

IR spectra

IR spectra (4000–400 cm^{-1}) were recorded with a FTIR IFS-48 Bruker spectrometer at room temperature using KBr discs.

X-ray powder diffraction

X-ray diffraction patterns were obtained on a D/Max-rC diffractometer using Cu $K\alpha$ radiation.

RESULTS AND DISCUSSIONS

The EG curve for the thermal decomposition of APM in the temperature range 60–640 °C in a hydrogen atmosphere is shown in Fig. 1, in which a clear four-step decomposition can be observed. The result was reproducible under the experimental conditions.

The first water band, between 60 °C and 170 °C with a peak temperature of 150 °C corresponds to the first decomposition step. The colour of the ISP at 170 °C was still white. The IR measurement (see Fig. 2b) and chemical analysis for this ISP confirmed that the decomposition was a dehydration.

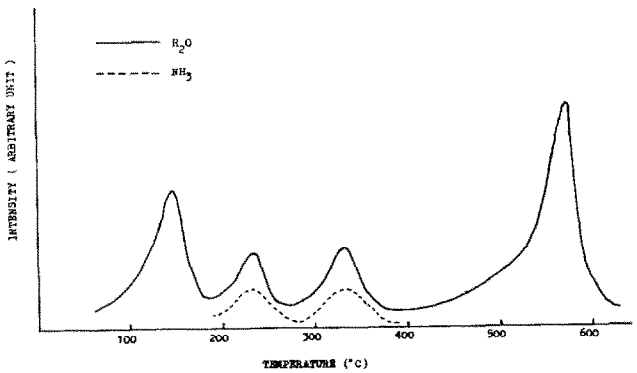

Fig. 1. EG curve for APM in a hydrogen atmosphere.

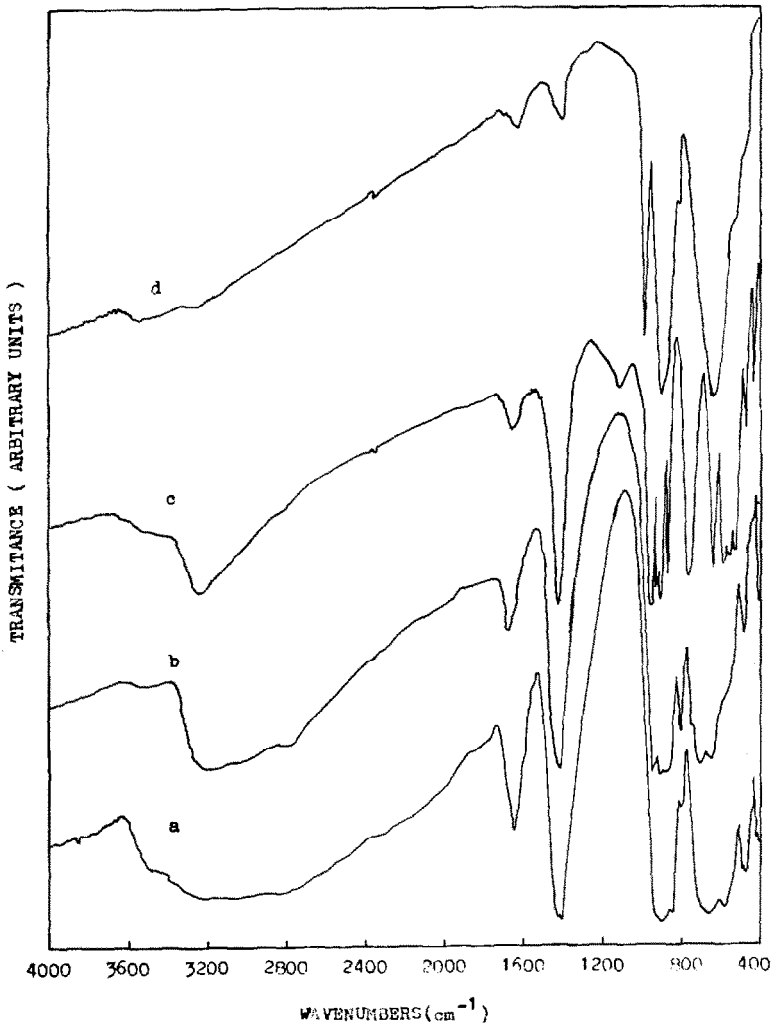

Fig. 2. IR spectra of APM and its decomposition products obtained in a hydrogen atmosphere: a, APM; b, 170 °C; c, 260 °C; d, 360 °C. Recording temperature 25 °C.

The results obtained in the earlier investigations [1–4] differ from the present one in that both H_2O and NH_3 were released at this stage, leading to the breakdown of the APM structure.

As the temperature gradually increased, an ammonium band began to appear while the second water band was developing. This is the second decomposition step, which took place in the temperature range 180–260 °C. The anhydrous compound changed from white to grey. The ISP at 260 °C was $(NH_4)_2O \cdot 4MoO_3$, according to the IR (see Fig. 2c), XRD and chemical analyses. However Iso et al. [2] and Manabe et al. [3] reported that $2(NH_4)_2O \cdot 8MoO_3$ was formed at this stage.

On further heating, more NH_3 and H_2O were released. Evolution of structural NH_3 and H_2O stopped at around 360 °C indicating completion of the third decomposition step. The areas beneath the ammonia bands indicated that the quantities evolved at these two steps were roughly in a ratio of 2 : 3. The ISP at 360 °C was deep blue in colour and was found to be orthorhombic MoO by XRD analysis, its IR spectrum being shown in Fig. 2d. Both the previous and present work might suggest the only thermal decomposition ISP of APM at this stage is MoO_3, regardless of the atmosphere used or the mechanism of the decomposition. But it is not clear why Mo^{VI} in APM does not undergo any reduction in the presence of a reducing agent as powerful as H_2 when it is quite easily reduced by some other reducing agents such as $SnCl_2$ and ascorbic acid in aqueous solution.

When the temperature rose still higher, a fourth water band appeared and on the EG curve. This is the final decomposition step, the reduction of MoO_3 by H_2 to monoclinic MoO_2, demonstrated by XRD analysis of the final solid product, the colour of which was black. The decomposition steps of APM in a hydrogen atmosphere can be summarised by the following equations

$$(NH_4)_6Mo_7O_{24} \cdot 4H_2O \rightarrow (NH_4)_6Mo_7O_{24} + H_2O$$

$$(NH_4)_6Mo_7O_{24} \rightarrow (NH_4)_2O \cdot 4MoO_3 + NH_3 + H_2O$$

$$(NH_4)_2O \cdot 4MoO_3 \rightarrow MoO_3 + NH_3 + H_2O$$

$$MoO_3 \xrightarrow{H_2} MoO_2 + H_2O$$

ACKNOWLEDGMENT

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