Journal of Thermal Analysis, Vol. 16 (1979) 201–204

PREPARATION OF THE VANADIUM OXIDE V_6O_{13}

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(Received March 15, 1978)

Based on thermogravimetric studies of thermal decomposition of NH_4VO_3 a method is proposed for obtaining V_6O_{13} from NH_4VO_3 by heating it at 500–550° in a stream of purified nitrogen.

Several methods have been suggested for the preparation of the vanadium oxide V_6O_{13} [1–5]. Recently Yankelevich and co-workers [6] reviewed them and found two of them the most interesting: calcination of NH_4VO_3 in a stream of SO_2 or of an inert gas at 400–500° and reduction of V_2O_5 in a stream of SO_2 at 650°. As the disadvantage of the first method, however, they list the simultaneous with V_6O_{13} formation of $(NH_4)_2O.\ 2\ VO_2.\ 5\ V_2O_5$ and as the disadvantage of the second method – its protractedness and high expense of SO_2. As result of their own experiments Yankelevich and co-workers [6] proposed a new method based on the reduction of dry hydrated V_2O_5 by SO_2 at 650°. The hydrated V_2O_5 is prepared through precipitation from an NH_4VO_3 solution using HNO_3 and drying the product at 120° for 6–10 hours. The output of 70% V_6O_{13} is claimed after 1.5-hour reduction with SO_2, increasing up to 86% after a 9-hour reduction. The above concentrate of V_6O_{13} can be further enriched through treatment with boiling water and boiling solution of NaOH with the output of V_6O_{13} 75–80%.

The first stage of the proposed method is still lengthy and involves the inconvenient use of SO_2 gas. Also, as was shown by Šatava [7], reduction by SO_2 leads already at the temperature of 500–600° to a partial formation of VO_2 and this oxide cannot be removed in the subsequent stage of leaching by NaOH solution as proposed by Yankelevich et al. [6]. It seemed therefore useful to investigate the possibility of using instead of the SO_2 reduction a simpler method of thermal decomposition of NH_4VO_3 in a stream of nitrogen. Šatava [7] pointed out that V_6O_{13} can be obtained through the thermal decomposition of NH_4VO_3 in the CO_2, Ar, or N_2 atmosphere at 500° or in the SO_2 atmosphere at 450°. He gave, however, thermoanalytic curves only for the CO_2 and SO_2 atmospheres. In those experiments he used 1 g samples and applied heating rate of 360°/hr. He did not consider, however, the critical role of the mass of the sample, of its layer thickness, and of the heating rate on the kinetics and the mechanism of the thermal decomposition reaction of NH_4VO_3 and of its subsequent decomposition products and therefore he was unable to choose the optimum conditions for the reduction process leading to the formation of a relatively pure V_6O_{13}, showing a sufficiently long plateau on the TG curves, and resulting in a possibility of its isolation for preparative purposes.

Experimental

Thermal decomposition of NH_4VO_3 (Glavkhimreaktiv, pure) was studied in nitrogen atmosphere using a Chevenard type thermobalance. The preparation's purity was checked by determining the contents of the tetravalent vanadium (titrating with a 0.05 N $KMnO_4$ solution), sodium contents using the flame photometric method, and admixtures of heavy metals (iron and copper), magnesium and silicon semiquantitatively using a medium-dispersion quartz spectrograph ISP–22. The results are shown in Table 1.

Table 1

Impurity	% Contents
V^{IV}	undetectable
Na	0.016
Si	0.010
Mg	0.001
Cu	0.001
Fe	0.001

The preparation was ground in an agate mortar before the experiments and the average crystal size of the unground (10 μm) and of the ground (5 μm) preparation were determined under a microscope with a micrometric eyepiece.

Compressed commercial nitrogen, purified from oxygen in a column with a solution of sodium hyposulphite with an addition of sodium anthraquinone-β-sulphonate [8], passed through a quartz tube in which a quartz rod, located on the thermobalance beam, supported a porcelain crucible with the sample.

Results and discussion

Based on the results of this author's previous studies [9–13] on the impact of heating rate and of the thickness of layer of the substrate on the mechanism of thermal decomposition of NH_4VO_3 as well as on the results of Šatava's [7] thermogravimetric experiments on its decomposition in CO_2 and NH_3 and Brown and Stewart's [14] results on its isothermal decomposition in Ar (12 mg samples, final product at 270–300°: V_2O_5) and in NH_3 (12 mg samples, final product at 340–360°: VO_2) – the experimental conditions for thermogravimetric studies of thermal decomposition of NH_4VO_3 in nitrogen could be properly chosen. In order to enable a gentle reduction (leading to the formation of V_6O_{13} but not of VO_2) of the thermal decomposition products by the self-released NH_3 gas a sufficiently thick sample had to be heated with a relatively low heating rate.

The results of an experiment so designed are shown in Fig. 1. The experimental parameters chosen are described in the caption. The first stage of the decomposition ends at about 240° with a well developed plateau of 15.2% weight loss which could indicate a hypothetical intermediate compound of the formula $4(NH_4)_2O \cdot 2\,VO_2 \cdot 11\,V_2O_5$ (15.4% stoichiometric weight loss) but this hypothesis requires further study. In any case this intermediate product can be identified with an analogous intermediate compound of Šatava [7] (although his plateau for that compound was less distinctive), shown by X-ray analysis to be different from ammonium trivanadate. The product of the second stage of decomposition at about 400° can be assumed to be ammonium vanadyl vanadate $(NH_4)_2O \cdot 2\,VO_2 \cdot 5\,V_2O_5$ which is consistent with the results of Šatava [7]. The final product of decomposition (weight loss of 25.3%) shows a long plateau from 440° to 650°, at which temperature the experiment was interrupted, and can be identified as mainly V_6O_{13} (stoichiometric weight loss of 26.8%) which is again consistent with Šatava's results [7] and his X-ray analysis identification of this product.

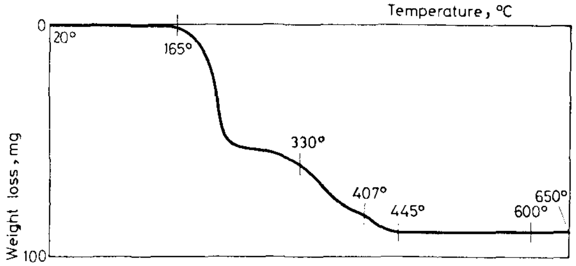

Fig. 1. TG curve of NH_4VO_3 in the nitrogen atmosphere. Sample weight: 355.1 mg. Heating rate: 150°/hr. Layer thickness: 222 mg/cm^2 or 1.89 mmol/cm^2. Thermobalance sensitivity: 1.84 mm/mg. Original diagram reduced 3 times

Based on a 25.3% weight loss with respect to NH_4VO_3 the output of V_6O_{13} at 450–500° can be calculated as 67%, the remainder being V_2O_5. The shape and length of the V_6O_{13} plateau (Fig. 1) indicate a complete decomposition of $(NH_4)_2O \cdot 2\,VO_2 \cdot 5\,V_2O_5$ at lower temperatures. Thermal decomposition of NH_4VO_3 in a stream of purified nitrogen at 500–550° (this temperature being reached slowly) can therefore be recommended as the first stage in the process of obtaining V_6O_{13}, thus avoiding the use of SO_2 and the danger of the contamination of the product by the simultaneously formed VO_2. This first stage can be followed by treatment of the product with boiling water and boiling solution of NaOH as proposed by Yankelevich et al. [6] to remove V_2O_5.

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