

## Thermal behaviour of $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$ prepared by hydrothermal crystallization<sup>1</sup>

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### Abstract

Pure samples of  $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$  were prepared by hydrothermal crystallization of amorphous ammonium vanadate hydrate in the presence of LiOH solution. By changing the conditions of the hydrothermal treatment, crystallites differing by one order in size resulted. The ammonium hexavanadate thus prepared was thermally investigated by simultaneous TG and DTA, as a function of heating rate under a constant stream of different gases.

### INTRODUCTION

The recovery of vanadium from vanadium-containing ores involves a step in which ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) is thermally decomposed. The decomposition carried out in air yields vanadium pentoxide ( $\text{V}_2\text{O}_5$ ), which is widely employed either as a catalyst or as a precursor for vanadium-bearing products [1]. When the decomposition is performed under various atmospheres, the formation of intermediate vanadates with poorly defined compositions takes place [2–6]; ammonium hexavanadate(V),  $(\text{NH}_4)_2\text{V}_6\text{O}_{12}$ , has been identified as an intermediate product when the thermal treatment is carried out in air in an open system [2]. The conflicting results reported in the literature are related to the fact that during the decomposition both  $\text{NH}_4\text{VO}_3$  and  $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$  lose ammonia and water to form  $\text{V}_2\text{O}_5$ . In this case, in fact, a possible redox reaction takes place between the oxidizing vanadium(V) and the reducing

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ammonia which depends on the different conditions of the thermal decomposition [2, 3, 7].

From a practical point of view, the knowledge of the reaction mechanism under non-equilibrium conditions and at atmosphere pressure is fundamental to the selective formation of  $V_2O_5$  with specific characteristics such as texture, structure and specific surface area.

This paper focuses on both the synthesis and thermal behaviour of pure ammonium hexavanadate prepared either by hydrothermal crystallization of amorphous ammonium vanadate, in the presence of LiOH solutions, or by direct precipitation from  $NH_4VO_3$ -containing solutions. The thermal behaviour was studied under non-equilibrium conditions in different gaseous environments at atmosphere pressure, and as a function of the heating rate.

## EXPERIMENTAL

Several methods for the synthesis of ammonium hexavanadate have been proposed [8–11]. A pure, well-crystallized sample, with some crystals having approximate dimensions of  $0.03 \times 0.03 \times 0.06 \text{ mm}^3$ , was synthesized by Range et al. [11]. In our case two methods of synthesis were adopted. In the first, the product was prepared by acidification of a hot aqueous solution of reagent-grade  $NH_4VO_3$  [9]. The best result was achieved by adding dilute  $H_2SO_4$  (1 g of  $H_2SO_4$  and 9 g of distilled water) to a boiling solution.  $(NH_4)_2V_6O_{16}$  was also synthesized by hydrothermal crystallization of the amorphous red powder obtained by adding ammonia to a cold, acidified solution of  $NH_4VO_3$ . The crystallization experiments were carried out in LiOH solutions, with the molar ratio  $X_{Li}$  ( $Li/Li + V$ ) ranging between 0.1 and 0.4. The solid/water ratio of the corresponding suspensions was kept constant at 1/40. The hydrothermal treatments were performed in rotating sealed Teflon containers and the reaction time was usually 7 days. The temperatures were 60, 85, 110 or  $140^\circ\text{C}$ , respectively. After reaction, the products were washed to eliminate excess LiOH, and characterized by chemical analysis for  $V_2O_5$ ,  $NH_3$  and  $Li_2O$ . X-ray powder diffraction (XRD) patterns were recorded using a Philips diffractometer with  $Cu K\alpha$  radiation. Simultaneous TG and DTA measurements were carried out on 20 mg samples using a Stanton apparatus model 780 and  $\alpha\text{-Al}_2\text{O}_3$  as reference sample. Different heating rates of 1, 10 or  $40^\circ\text{C min}^{-1}$  were applied under a constant flow of dry  $N_2$ , Ar or  $O_2$ .

## RESULTS AND DISCUSSION

An orange-yellow powder was obtained on adding dilute  $H_2SO_4$  to the boiling aqueous solution of  $NH_4VO_3$ . This was analysed for vanadium(IV) content by dissolving it in a concentrated alkali and titrating the

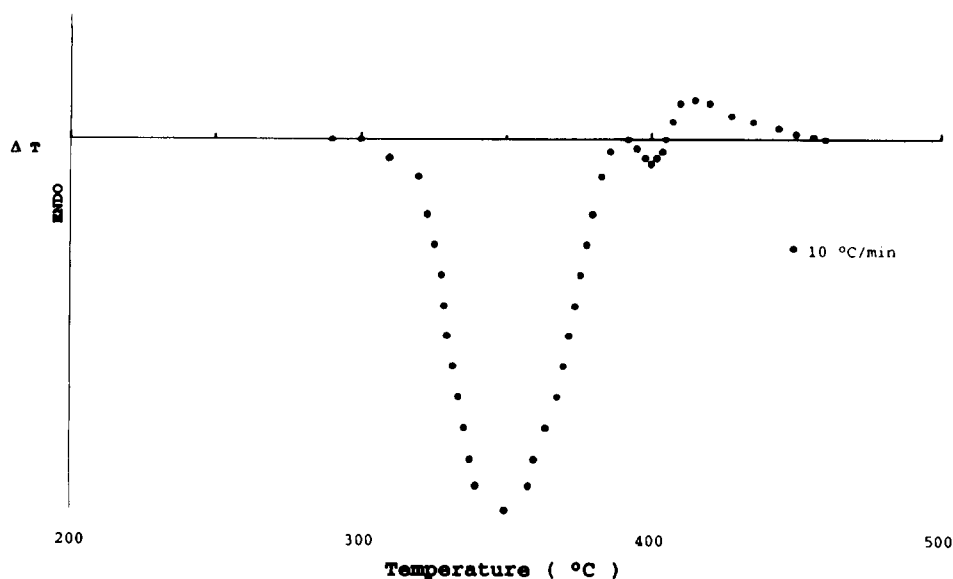


Fig. 1. DTA curve of  $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$  prepared by acidification of aqueous solution of  $\text{NH}_4\text{VO}_3$ .

corresponding solution with a 0.05 N  $\text{KMnO}_4$  solution. No trace of tetravalent vanadium was found. The X-ray pattern of the product is consistent with Levanto's results and his identification of  $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$  [10]. When analysed in simultaneous DTA–TG in a stream of pure, dry  $\text{N}_2$  at a heating rate of  $10^\circ\text{C min}^{-1}$ , the sample shows an endothermic peak at  $345^\circ\text{C}$ , followed by a small endothermic one at  $400^\circ\text{C}$ , and a small exothermic peak at  $410^\circ\text{C}$  (Fig. 1). The decomposition ends at about  $400^\circ\text{C}$  with a 10.0% weight loss with respect to the stoichiometric value of 8.7%.

Pure ammonium hexavanadate samples were also synthesized by hydrothermal crystallization of an appropriate amorphous vanadium-containing precursor. In this case, the presence of ammonia in the composition of the precursor is necessary. After dissolution of  $\text{NH}_4\text{VO}_3$  in a hot  $\text{HNO}_3$  solution, a red amorphous precipitate was obtained by slow addition of ammonia to the resulting cooled solution. Alternatively, the precursor was also prepared by  $\text{HNO}_3$  addition to a solution obtained by dissolving  $\text{NH}_4\text{VO}_3$  in a hot solution of  $\text{NaOH}$ .

The low crystallinity of the two precursors thus prepared is shown in the X-ray diffraction patterns of Fig. 2. The presence of ammonia in the composition of the precursor can be observed in the TG curves of Fig. 3. Comparing the two curves, the ammonia-containing precursor presents an additional weight loss at higher temperatures (curve (a)) due to the evolution of ammonia during heating. With this precursor, pure, well-crystallized samples of  $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$  were obtained by hydrothermal

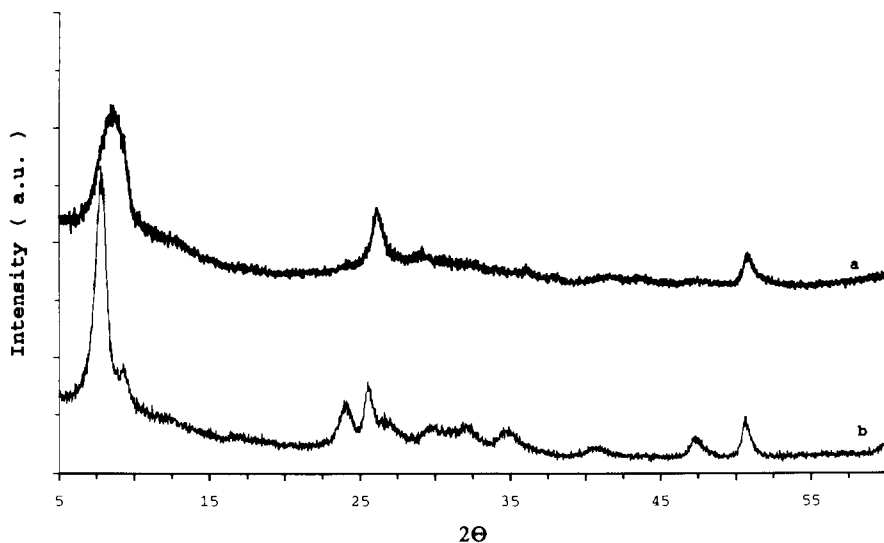


Fig. 2. X-ray diffraction patterns of two amorphous vanadium-containing precursors. Curve (a), sample obtained using ammonia as precipitant agent; curve (b), sample precipitated with  $\text{HNO}_3$  solution.

crystallization at temperatures ranging between 60 and  $120^\circ\text{C}$  in the 0.1–0.3 range of  $X_{\text{Li}}$ . Both  $\text{LiOH}$  concentration and temperature affect the crystal size and the yield of the product. In particular, the crystal sizes increase by increasing both the temperature and the molar ratio  $X_{\text{Li}}$  of the hydrothermal treatment, while the yield decreases by increasing the molar ratio. These results suggest a typical dissolution–precipitation mechanism in the product formation.

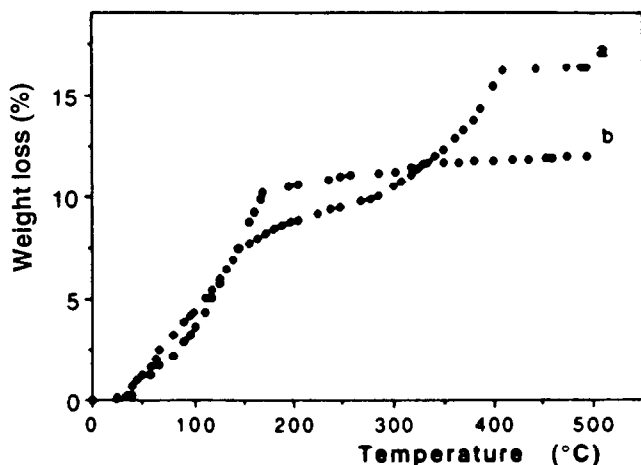


Fig. 3. TG curves of samples reported in Fig. 2.

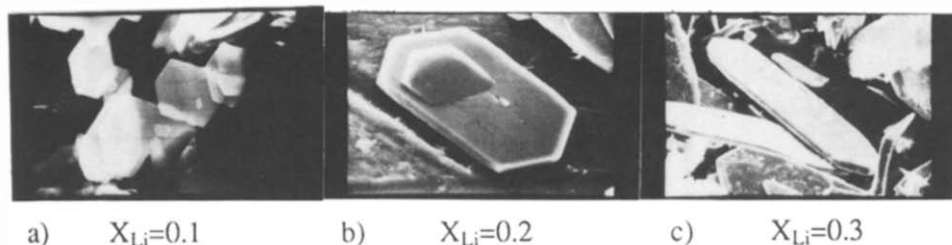


Fig. 4. SEM micrographs of  $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$  samples crystallized at  $110^\circ\text{C}$  using different molar ratios  $X_{\text{Li}}$ : (a) 0.1; (b) 0.2; (c) 0.3. Original magnifications: (a)  $2000\times$ ; (b)  $1200\times$ ; (c)  $370\times$ .

The effect of the concentration of LiOH on the crystal size of samples hydrothermally synthesized at  $110^\circ\text{C}$  is shown by the SEM micrographs in Fig. 4. It can be seen that the pseudo-hexagonal crystals of  $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$  differ by one order in size on increasing the concentration of crystallization agent. The approximate dimensions increase from  $0.03 \times 0.025 \times 0.0015$  to  $0.30 \times 0.15 \times 0.015 \text{ mm}^3$  on increasing  $X_{\text{Li}}$  from 0.1 and 0.3. This involves a shift in the corresponding endothermic peak of the main decomposition step of  $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$ . With a constant heating rate of  $10^\circ\text{C min}^{-1}$ , a minimum of  $345^\circ\text{C}$  and a maximum value of  $361^\circ\text{C}$  can be observed (Fig. 5). An analogous behaviour was observed with constant  $X_{\text{Li}}$  values and increasing temperatures of hydrothermal treatment.

No significant differences in the chemical composition of differently synthesized samples have been observed. The following average weight percents were found:  $\text{V}_2\text{O}_5 = 90.8$  (91.3);  $\text{NH}_3 = 5.88$  (5.69);  $\text{H}_2\text{O} = 3.12$  (3.01) with the theoretical values in parentheses.

A sample hydrothermally synthesized at  $110^\circ\text{C}$  with a molar ratio equal to 0.15, was studied by TG, with different heating rates under a constant flow of various gases such as  $\text{N}_2$ ,  $\text{O}_2$  and Ar. The corresponding TG curves, obtained at three different rates under  $\text{N}_2$ , are reported in Fig. 6. In

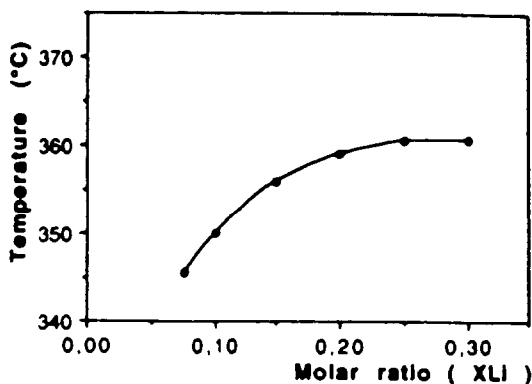


Fig. 5. Decomposition peak temperature of  $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$  samples crystallized at  $110^\circ\text{C}$  as a function of the concentration  $X_{\text{Li}}$  of the crystallization agent.

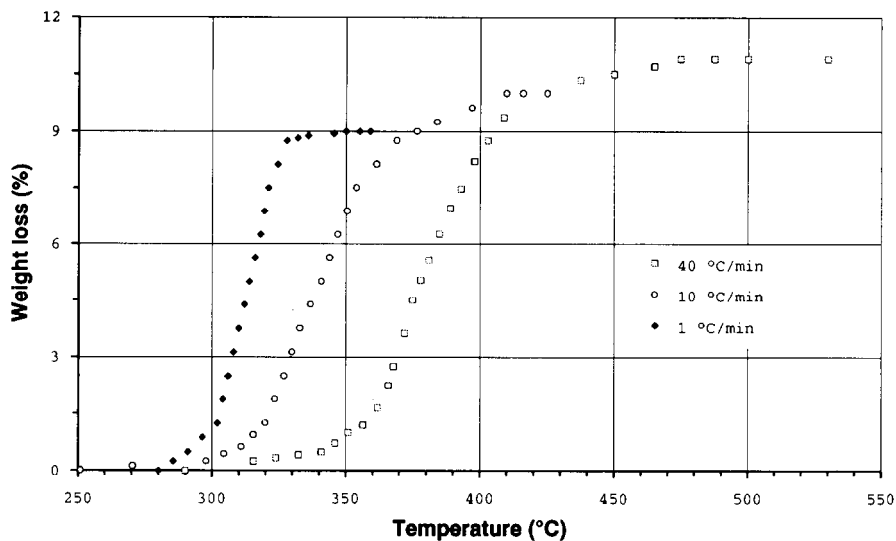
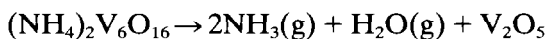
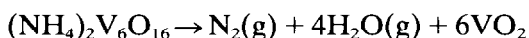


Fig. 6. Effect of heating rate on the weight loss and decomposition temperature of an  $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$  sample crystallized at  $110^\circ\text{C}$  with  $X_{\text{Li}} = 0.15$ .

addition to the expected shift in the peak temperature of the thermal decomposition, a marked increase in weight loss can also be observed. With a heating rate of  $1^\circ\text{C min}^{-1}$ , a stoichiometric value was found (8.7%) that corresponds to the decomposition reaction:



At high heating rate (10 to  $40^\circ\text{C min}^{-1}$ ), a redox reaction between the evolved ammonia and the corresponding solid product of decomposition [2] must be considered. The redox reaction



is characterized by a greater weight loss than that of the previous reaction.

The partial reduction of pentavalent to tetravalent vanadium is confirmed from the X-ray diffraction patterns of two specimens decomposed in TG at low and high heating rates, respectively (Fig. 7). The slowly heated specimen contains only  $\text{V}_2\text{O}_5$ , while in the rapidly heated sample, a mixture of  $\text{V}_2\text{O}_5$  and  $\text{V}_3\text{O}_7$  [12] is indicated. It should be noted that the nature of the flowing gas has little influence on the nature of the decomposition products. This behaviour can mainly be explained in terms of the heating rate. When the heating is slow, the decomposition of  $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$  takes place at a minimum temperature and corresponds to negligible ammonia decomposition with consequent negligible redox reaction. However, a noticeable increase in the thermal decomposition temperature during rapid heating favours the redox reaction, with a consequent increase in the weight loss. The DTA curves of the two corresponding specimens, heated at 1 and

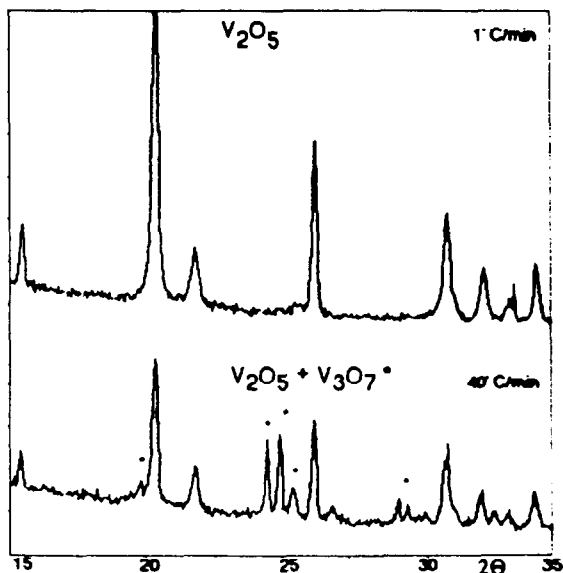


Fig. 7. X-ray diffraction patterns of the decomposition products of  $(NH_4)_2V_6O_{16}$ , reported in Fig. 6, heated at 1 and  $40^\circ C \text{ min}^{-1}$ .

$10^\circ C \text{ min}^{-1}$ , support this (Fig. 8). The small thermal peaks following the main endothermic one are absent in the slowly heated specimen. Thus, the small endothermic peak may be assigned to the decomposition of ammonia and the small exothermic peak to the redox reaction. Such behaviour explains the formation of pure  $V_2O_5$  in slowly heated specimens. However,

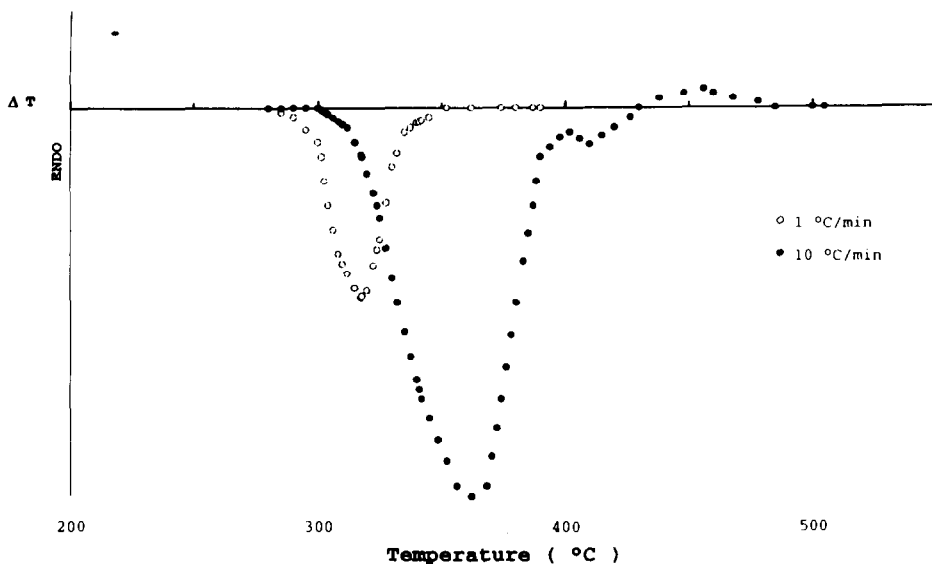


Fig. 8. DTA curves of specimens listed in Fig. 6.

with constant decomposition temperature (350°C) and gas flow, the ammonia evolved from the decomposition of  $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$  does not change significantly with the nature of the flowing gas. A practically constant value of  $\text{NH}_3$  (4.4%) was found compared to the stoichiometric value of 5.7% considering  $\text{V}_2\text{O}_5$  as the final decomposition product. When the decomposition is carried out at the same temperature and without a stream of flowing gas the evolved ammonia drastically drops to a value of 1.4%. In any case, even by increasing the decomposition temperature, the rate and the nature of gaseous stream, the evolved  $\text{NH}_3$  never corresponded to pure  $\text{V}_2\text{O}_5$  or, alternatively, to pure  $\text{VO}_2$ .

## CONCLUSIONS

Pure, well-crystallized samples of  $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$ , characterized by a noticeable range of crystal sizes, have been synthesized by hydrothermal crystallization of amorphous ammonium vanadate in the presence of  $\text{LiOH}$  solutions. By changing the conditions of the hydrothermal treatment, pseudo-hexagonal platelets, up to approximately 0.30 mm long, were obtained.

The thermal decomposition behaviour of the product, investigated under dynamic conditions by simultaneous TG–DTA under a constant stream of various gases, mainly depends on the heating rate. The consequent decomposition temperature determines the extent of the redox reaction between ammonia and the solid decomposition products. Adopting a very low heating rate, the formation of pure  $\text{V}_2\text{O}_5$  may also be obtained under a stream of an inert gas.

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