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THERMAL DECOMPOSITION OF AMMONIUM METAVANADATE *

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ABSTRACT

Ammonium metavanadate is subjected to thermal treatment in the range 180—550°C and structural and surface area changes are studied by X-ray diffraction and N_2 adsorption. DTA and TGA show the existence of a large endotherm (260°C) possibly composed of several stages, and a much smaller one (340°C) which is responsible for evolution of the molecule of water associated with the V_2O_5 initially formed. Three exotherms also appear and explanations for their presence are given. The phases formed, as well as the specific surface areas, are determined for the products obtained in a vacuum and in the presence of water vapour, and changes in surface areas are related to the phase transformations and dehydration of the products formed during thermal treatment.

INTRODUCTION

The main source of production of vanadium pentoxide is the roasting of NH_4VO_3 recovered from the hydrometallurgical treatment of some vanadium-containing ores. Although there have been a number of investigations on this roasting process [1—4], there is no general agreement on the actual course of the reaction under various atmospheres. The formation of intermediate vanadates has been reported [5—9] but only the XRD pattern for the trivanadate is quoted [5,9], and the sequence of decomposition is yet not well defined.

In spite of the studies on the effect of oxidising, inert and reducing atmospheres on the decomposition process [5,9], investigation of the important role of the presence of water vapour during thermal treatment on the structure of the solid products is still lacking. However, the rate of recombination of the products to form NH_4VO_3 has been studied over a wide range of partial pressures of NH_3 and H_2O vapour [8]. On the other hand the oxide forms of the *d*-metals are generally good catalysts for H_2 and H_2—D_2 reactions and it has become increasingly clear that knowledge of the microstructure of catalysts is of essential importance for complete understanding of their function. In this respect, scarcely any work has been performed.

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In the present investigation an attempt was made to clarify the sequence of formation of the decomposition products under vacuum and in some other atmospheres, and to investigate the changes in the specific surface area, with the textural and structural changes accompanying the decomposition.

EXPERIMENTAL

The ammonium metavanadate used was a product of Germed Veb Jenapharm of 99% purity with the following percentage of trace impurities: insoluble ammonium salts 0.02%, chloride 0.05%, sulphate 0.01%, iron 0.01% and alkali metals (Na and K) 0.3%.

Differential thermal analysis (DTA) was done with α-alumina as inert standard, a programmed temperature controller "Ether" transitrol type 994/2 to permit a linear rate of heating of 12°C min^{-1}, and a Cambridge recorder Model B for recording the temperature difference.

TG analysis was done on a silica spring balance of the McBain Bakr type with a sensitivity of 30 cm g^{-1}, for 350 mg of the material. The curves were obtained by heating the salt in air (a), vacuum (v) and atmospheres of 15.5 mm Hg of water vapour from ambient temperature to 600°C at a controlled linear rate of 10°C min^{-1} in air and 5°C min^{-1} in the other atmospheres.

X-ray diffraction patterns were obtained for samples treated in a vacuum and in the presence of 15.5 mm Hg of water vapour with a Philips diffractometer and Ni-filtered Cu radiation. The *d*-distances and relative intensities were calculated and compared with data in the ASTM cards [10,11].

Decomposition products were obtained by heating at 180—550°C for 5 h in the presence of the above-mentioned atmospheres. These will be designated by the letter V with the suffix denoting the type of prevailing atmosphere, and the decomposition temperature indicated in parentheses: $V_{15.5}(350)$ indicates ammonium metavanadate decomposed in the presence of 15.5 mm Hg of water vapour at 350°C.

Adsorption—desorption isotherms of nitrogen at —195°C were determined by conventional volumetric gas adsorption. Surface areas were calculated by the BET method taking 16.2 Å^2 as the molecular area of adsorbed nitrogen.

RESULTS AND DISCUSSION

Differential thermal analysis

Endothermic peaks

Differential thermal analysis of ammonium metavanadate indicated the presence of two distinct endothermic peaks, a large one centered at 260°C with a shoulder on either side (at 230°C and 275°C), followed by a small but distinct peak located at 340°C. The shape of the large endothermic peak showed that the decomposition is complex and involves several stages (Fig. 1). Taniguchi and Ingraham [9] obtained an intermediate product at

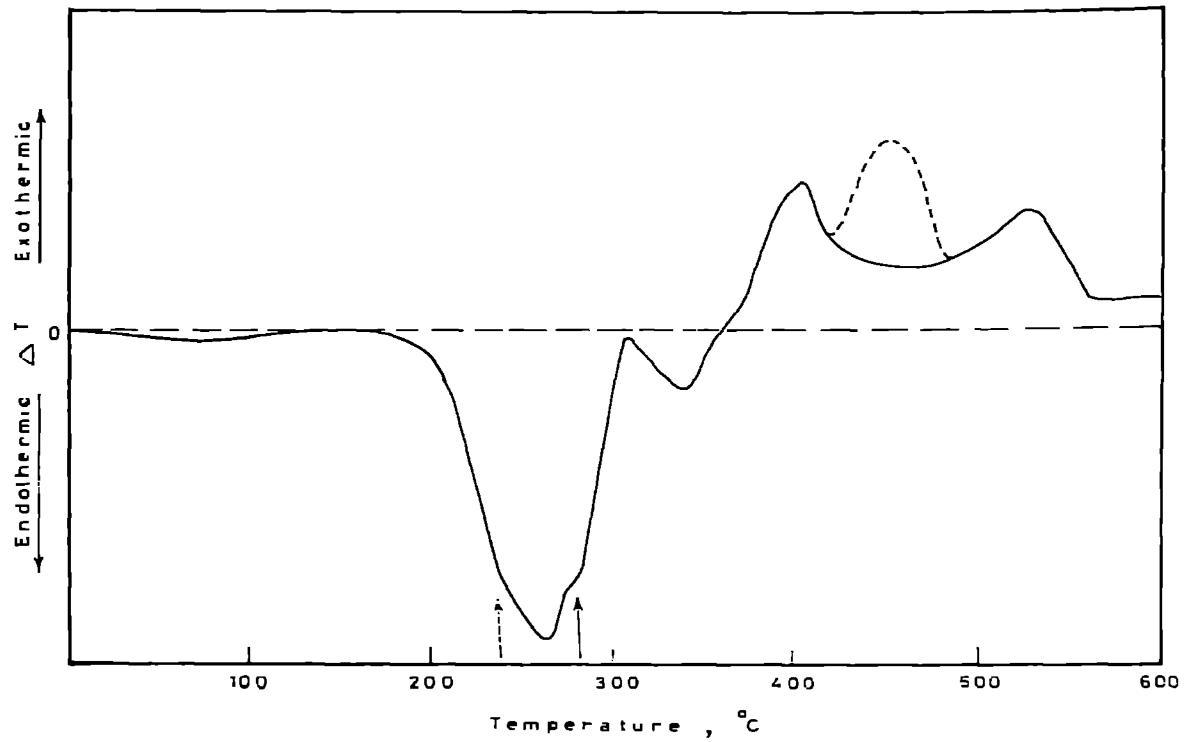


Fig. 1. Differential thermal analysis of ammonium metavanadate.

220°C characteristic of the trivanadate $(3V_2O_5 \cdot O(NH)_4)_2)$, whereas Lamure and Colin [7] showed that this intermediate is preceded by the divanadate $(2V_2O_5 \cdot O(NH_4)_2)$ at a lower temperature of ca. 175°C when a very low heating rate (25° h^{-1}) was used, in accordance with the decomposition steps

$$12(NH_4)VO_3 \rightarrow 3(2\ V_2O_5 \cdot O(NH_4)_2) + 6\ NH_3 + 3\ H_2O \tag{1}$$

$$3(2\ V_2O_5 \cdot O(NH_4)_2) \rightarrow 2(3\ V_2O_5 \cdot O(NH_4)_2) + 2\ NH_3 + H_2O \tag{2}$$

Further decomposition of the trivanadate was believed [9] to give V_2O_5 at 300°C. However, the product obtained in the present investigation at 300°C, as observed from XRD (see below) was not vanadium pentoxide but its hydrated form:

$$3\ V_2O_5 \cdot O(NH_4)_2 \rightarrow 3\ V_2O_5 \cdot H_2O + 2\ NH_3 \tag{3}$$

Steps (1)–(3) are manifested in the shoulder at 230°C, the peak apex at 260°C, and the shoulder at 275°C, respectively. The small endothermic peak observed at 340°C is therefore responsible for the evolution of the water molecule

$$3\ V_2O_5 \cdot H_2O \rightarrow 3\ V_2O_5 + H_2O \tag{4}$$

which is in accordance with the conclusions drawn from TG and XRD analysis, which are discussed later.

Exothermic peaks

At higher temperatures and just after the small endothermic peak at 340°C, an exothermic peak was obtained at 410°C, which results from reduction of the vanadium from the pentavalent to a lower valency state, as determined in previous investigations [5,9,12]:

$$6\,V^{5} + 2\,e \rightarrow 6\,V^{4.66}$$

and/or (5)

$$6\,V^{5} + 4\,e \rightarrow 6\,V^{4.33}$$

XRD data showed that the samples possess formulae between $VO_{2.33}$ (V_6O_{14}) and $VO_{2.17}$ (V_6O_{13}), which shows the vanadium to possess a valency between 4 and 5 [13].

Following this exotherm, a second exotherm was obtained at 440°C which did not reproduce itself with the same intensity each time the experiment was repeated; this exotherm proved to result from the catalytic decomposition of ammonia on the surface of the oxide. The same effect was noticed by Taniguchi and Ingraham [9]. It was also noted that this peak disappears when sufficient time is given for the ammonia gas to diffuse out of the closed DTA cell.

By raising the temperature to 520°C, a third exotherm was obtained which is due to further reduction [12] of the oxide formed at 410°C to the tetravalent state, as has been shown from XRD analysis.

Thermogravimetric analysis

Thermogravimetric analysis of ammonium metavanadate was carried out in the presence of air, in a vacuum, and in 15.5 mm Hg of water vapour. The thermograms show the decomposition to commence at a temperature >150°C and exhibit three main steps: (a) the first at about 50%; (b) the second at 66—70% (depending on the prevailing atmosphere); and (c) the third which terminates at 100% decomposition (Fig. 2). These three steps

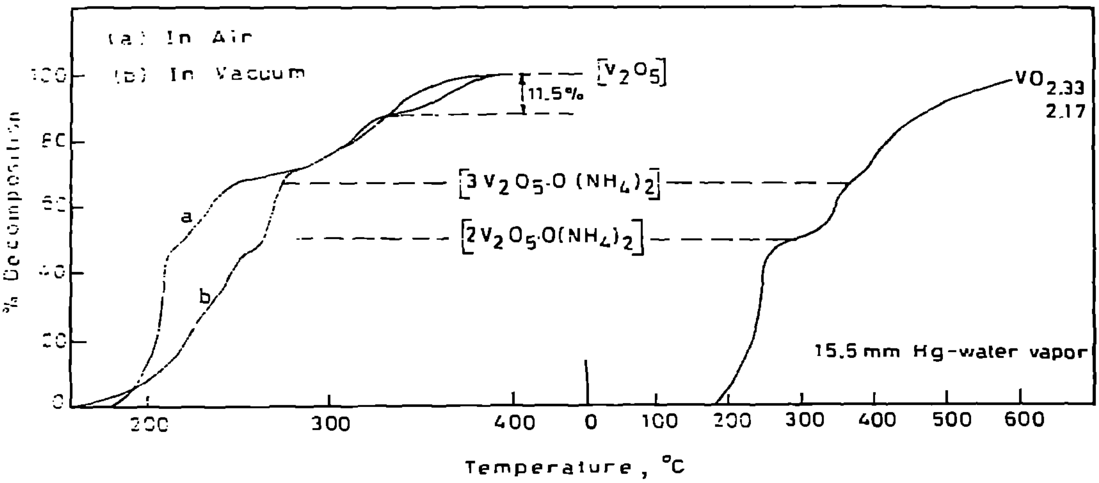


Fig. 2. Thermogravimetric curves of ammonium metavanadate under different atmospheres.

result, as mentioned before, from decomposition of the ammonium metavanadate initially to the divanadate [7], followed possibly by the second step which forms the trivanadate [5,7,8], and finally V_2O_5 is produced. V_2O_5, however, was not obtained in the presence of water vapour (see below).

Though the nature of the prevailing atmosphere affects the decomposition temperature leading to the di- and trivanadates, the general shape of the curves is not affected and the two steps are always present. However, the atmosphere affects the last decomposition step markedly — conversion of the trivanadate to V_2O_5. Though a continuous loss in weight was observed for decomposition in the presence of air, which gave rise to a one-step process, heating under vacuum produced another step at 88.5% decomposition which indicates that the decomposition of the trivanadate has taken place in two steps as described by eqns. (3) and (4). In such a case the molecule of water evolved should comprise 11.5% of the total percentage decomposition. Actually, one molecule of water would form 2.56% of the total loss of 22.56% (compared to the starting material):

$$12(NH_4)VO_3 \rightarrow 6\ V_2O_5 + 12\ NH_3 + 6\ H_2O \qquad (\text{loss} = 22.26\%)$$

Accordingly, it appears that on decomposition of the trivanadate, ammonia evolves first followed by water; each step is magnified by vacuum treatment, since the evolved gases are rapidly removed, which otherwise might be adsorbed (chemisorbed) on the solid substrate. This conclusion is also favoured by the XRD analysis.

It is worth mentioning that the decomposition was completed at ca. 400° C in the presence of air, or in a vacuum, but was extended to 600° C in the presence of water vapour.

X-ray analysis

Heating under vacuum

Further XRD experiments were done on the samples heated under vacuum and in the presence of water vapour in order to investigate both transitions of the metavanadate, and the effect of duration of heating at selected temperatures.

Figure 3 shows the patterns obtained by heating in a vacuum for 5 h at various temperatures. The duration of 5 h was chosen because it is the time for which the various samples used for surface area investigations were heated (see below).

Heating at 180° C and 230° C for 5 h led to one and the same product, which is brown, and which gave the pattern of the trivanadate. The indication gained from DTA, TG, and kinetic measurements [14] is that heating at 150° C is insufficient to bring about the transformation. However, in practice heating at 180° C for only 1 h gave a different pattern (Fig. 4b) which proved to be that of the divanadate (orange-yellow). Obviously at 180° C the divanadate is formed first, which later on changes to the trivanadate just by prolonging the heating time.

On heating at 230° C, even though the pattern obtained was that of the trivanadate, there was a shift in several lines by about 0.6 Å from that

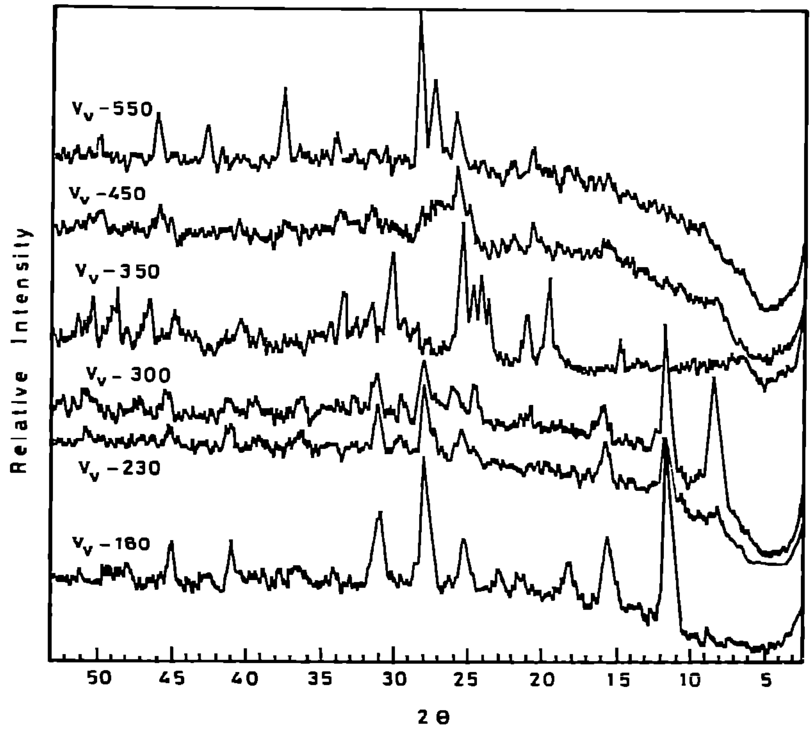


Fig. 3. X-ray diffraction patterns for the decomposition products of ammonium metavanadate produced in a vacuum.

reported in the literature [9], which is a reflection of a strained lattice and denotes the early stage of a further transformation. It is thus concluded that heating at 180°C and 230°C for 5 h actually represents initiation of the formation and the decomposition, respectively, of the trivanadate, to an extent which depends on the heating time.

Heating the salt at 300°C in a vacuum showed the appearance of a new and strong band at a *d*-distance of 10.80 Å and a weaker one at 10.75 Å (together with several other less intense lines). The pattern shown in Fig. 3 is that for the monohydrate $3\ V_2O_5 \cdot H_2O$ from TG and DTA. Heating at the slightly higher temperature of 350°C gave the pattern of V_2O_5.

Heating at 450°C in a vacuum for 5 h gave a pattern with lines which do not coincide with any known oxides of vanadium. From DTA results, reduction of the pentavalent oxide takes place at about 410°C and the vanadium was assigned a valency between 4.66 and 4.33. The reduction of vanadium oxides to lower oxidation states by thermal treatment has been reported by other investigators [5,9,12,16].

The pattern for the sample heated at 550°C under vacuum was mainly that of VO_2.

Heating in the presence of water vapour

The presence of water vapour (15.5 mm Hg) during thermal treatment retarded decomposition of the metavanadate even at temperatures as low as 180°C (IR results in this laboratory also support this conclusion). This

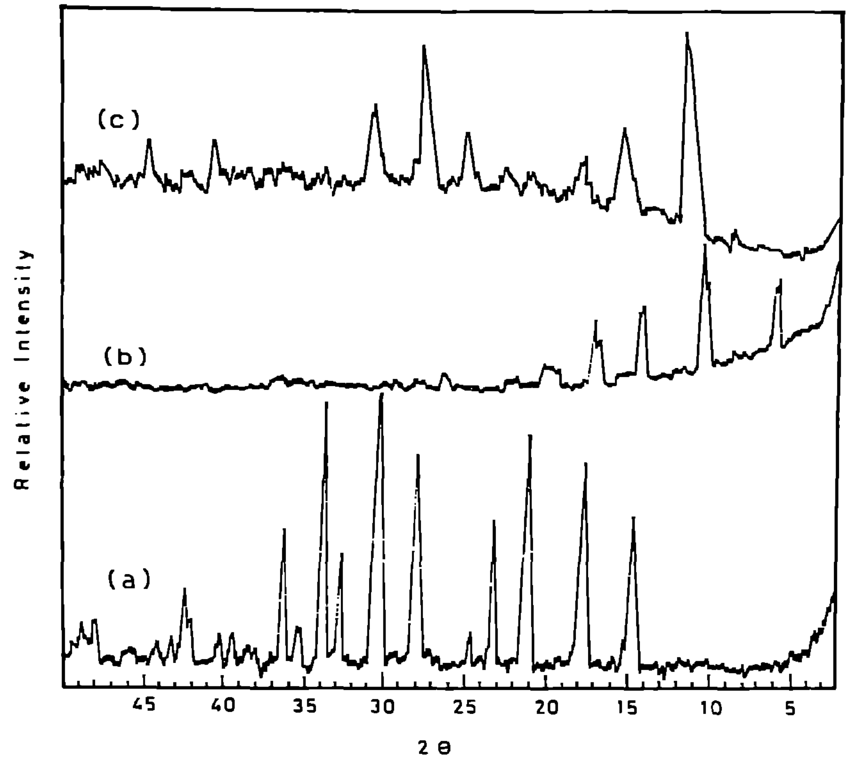


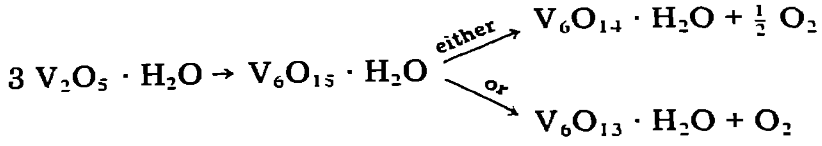
Fig. 4. X-ray diffraction of ammonium metavanadate heated at (a) 150°C for 5 h, (b) 180°C for 1 h, and (c) 180°C for 5 h.

retardation is probably due to chemisorption [14,16] of the water molecules on the surface of the material, thereby delaying its decomposition which then requires a higher energy of activation [14]. The product obtained by heating at 180° for 5 h was mainly ammonium metavanadate containing traces of the trivanadate, and the sample heated at 230°C proved to be ammonium trivanadate with well defined bands and improved crystallinity (Fig. 5). The well defined structure was also obtained by heating in a vacuum at 180°C.

Heating the salt at 300°C in the presence of water vapour yielded a product similar to that obtained at 230°C in a vacuum, i.e. ammonium trivanadate.

The pattern obtained at 350° was similar to that obtained in a vacuum at 300°C, namely the monohydrate.

Raising the temperature above 350°C appeared to bring about the reduction of the pentavalent vanadium while retaining the molecule of water, as observed for the sample heated at 450°C:



$$3\,V_2O_5\cdot H_2O \rightarrow V_6O_{15}\cdot H_2O \begin{array}{l} \xrightarrow{\text{either}} V_6O_{14}\cdot H_2O + \frac{1}{2}\,O_2 \\ \xrightarrow{\text{or}} V_6O_{13}\cdot H_2O + O_2 \end{array}$$

New sharp bands appear at 9.12, 8.05 and 7.285 Å, which disappear at

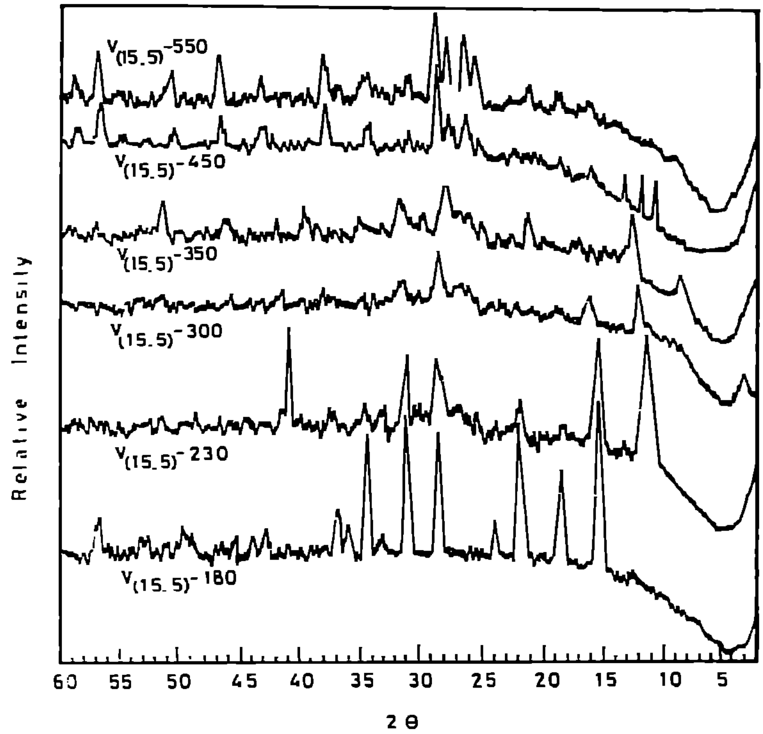


Fig. 5. X-ray diffraction patterns for the decomposition products of ammonium metavanadate produced in the presence of 15.5 mm Hg of water vapour.

550°C. These lines are probably due to the hydrated form of the oxide at 550°C. It appears surprising that the reduction process is preferred over the dehydration at 450°C, but the presence of high water vapour pressure seems to inhibit the latter, though in some cases [12] both processes take place simultaneously.

TABLE 1

Specific surface areas, and phases formed during the thermal treatment of ammonium metavanadate

Heating temperature (°C)	In vacuum		In water vapour (15.5 mm Hg)	
	Phases formed	$S_{\mathrm{BET}}^{\mathrm{N_2}}$ ($m^2\,g^{-1}$)	Phases formed	$S_{\mathrm{BET}}^{\mathrm{N_2}}$ ($m^2\,g^{-1}$)
180	$3V_2O_5 \cdot O(NH_4)_2$	89.6	$(NH_4)VO_3$	127.3
230	$3V_2O_5 \cdot O(NH_4)_2$	107.5	$3V_2O_5 \cdot O(NH_4)_2$	127.3
300	$3V_2O_5 \cdot H_2O$	95.1	$3V_2O_5 \cdot O(NH_4)_2$	142.1
350	V_2O_5	146.0	$3V_2O_5 \cdot H_2O$	127.1
450	$V_2O_{4.66}$ $V_2O_{4.33}$	150.0	$V_6O_{14} \cdot H_2O$ $V_6O_{13} \cdot H_2O$	94.8
550	V_2O_4	140.0	V_6O_{14} V_6O_{13}	214.3

Specific surface area

Full adsorption—desorption cycles of nitrogen were obtained for the decomposition products heated at 180—550°C, both in a vacuum and in the presence of water vapour. The isotherms obtained for the vacuum samples are all type II of Brunauer's classification, and they all form closed hysteresis loops, except the 550°C sample which is completely reversible. The isotherms obtained for the products heated in the presence of water vapour are in between types II and III of Brunauer's classification and are all reversible.

Specific surface areas were evaluated from the adsorption isotherms. The results are summarized in Table 1, and are graphically presented in Fig. 6. The variation of the specific surface area with temperature of thermal treatment is interesting, since it is almost completely dependent on the phase changes which accompany the thermal treatment.

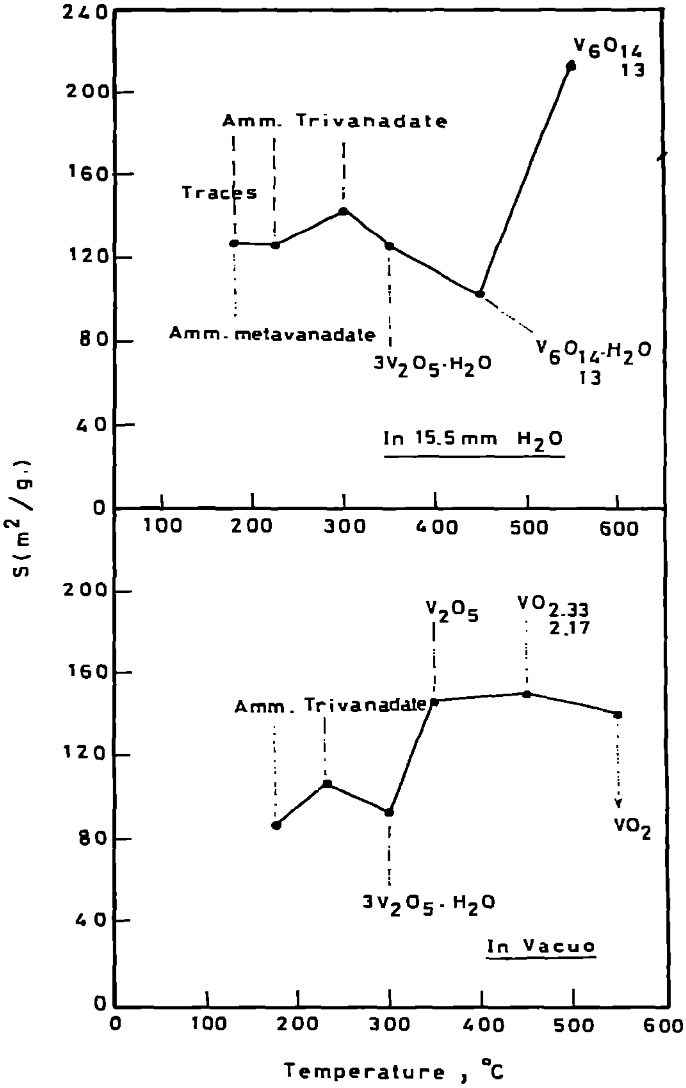


Fig. 6. Variation of specific surface area with decomposition temperature.

SUMMARY

Heating in a vacuum at 180—230°C leads to an increase in area. At both temperature limits the trivanadate is formed; the higher surface area at the higher temperature is due to the higher rate of decomposition at this temperature [14], which leads to a product of smaller crystallite size and hence higher surface area.

In the presence of water vapour the same effect is obtained but in a higher temperature range, namely 230—300°C. At 180°C, metavanadate is the predominant phase, and its transformation to the trivanadate (at 230°C) leads to no increase in surface area.

Heating in a vacuum at 300°C leads to formation of the monohydrate ($3\ V_2O_5 \cdot H_2O$), and brings about a decrease in the surface area. The same affect is obtained by heating in water vapour, but at a higher temperature, namely 350°C rather than 300°C. Further heating in a vacuum causes dehydration of the monohydrate and V_2O_5 is formed at 350°C, accompanied by an increase in the surface area.

Heating in water vapour beyond 350°C leads to the formation of another hydrate, namely $V_6H_{14} \cdot H_2O$ and/or $V_6H_{13} \cdot H_2O$ and this is accompanied by further decrease in area. Heating in a vacuum beyond 350°C leads to the reduction step discussed earlier, to form $VO_{2.33}$—$VO_{2.17}$ at 450°C, and VO_2 at 550°C. This is accompanied by a slight increase, followed by a slight decrease, in area.

In contrast, heating in water vapour beyond 450°C leads to dehydration of the compound, $V_6H_{\substack{14\\13}} \cdot H_2O$, formed at 450°C, and this dehydration is accompanied by an increase in surface area.

To sum up these area changes, note that an increase in area usually accompanies two processes, namely thermal activation of the trivanadate, and dehydration of the salt hydrate formed. On the other hand formation of a salt hydrate is normally accompanied by a decrease in area. Heating in a vacuum leads to the appearance of these area changes at a lower temperature range compared to heating in water vapour.

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