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SURFACE PROPERTIES OF THERMALLY DECOMPOSED AMMONIUM METAVANADATE UNDER VARIOUS ATMOSPHERES

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ABSTRACT

Adsorption of nitrogen was measured on the decomposition products of ammonium metavanadate produced by heating in the presence of air, oxygen and water vapour (4.6 mm Hg). The products were identified by X-ray diffraction. No reduction of the vanadium pentoxide is observed by heating in air in the temperature range 350—450°C, whereas in oxygen or water vapour (4.6 mm Hg) a crystalline product close to V_2O_5 is produced, possessing two characteristic lines at *d*-distances of 3.520 and 3.325 Å — this product appears to exist in the hydrated form in the latter atmosphere. Changes in surface area are related to both the phase transformations and the extent to which it is accomplished.

Pore structure studies reveal the products to possess characteristic pore widths which do not permit capillary condensation to take place.

A method of correcting the reference data is introduced for shifts of ~10% between S_{BET} and S_t areas — a significant criterium for pore analysis.

INTRODUCTION

Vanadium pentoxide, like other oxides of the d-metals, is generally a good catalyst for H_2 and H_2—D_2 reactions [1] and also for oxidation processes [2]. It is usually produced by the roasting of ammonium metavanadate and is markedly affected by the nature of the prevailing atmosphere during the decomposition process [3—5].

Most previous studies concentrated on the role of the surrounding atmosphere on the type of products obtained [3—5] and on the kinetics and mechanism of the decomposition process [3,5—7], but their effect on the surface texture of the catalyst received little attention [8,9].

In the present investigation both the structural and textural properties of the decomposition products of ammonium metavanadate are investigated on products prepared in the presence of air, oxygen and low water vapour pressure using XRD and nitrogen adsorption.

The methods usually applied [10,11] to detect porosities in solids require a non-porous reference material which should be of the same nature as the sample under test. Several non-porous reference materials are reported in the literature but how far their nature matches that of the material under test [11,12] is a question not yet fully answered. In this investigation a reliable method of testing the suitability of the reference material to be employed in the analysis is also presented.

EXPERIMENTAL

The ammonium metavanadate used was supplied by Veb Jenapharm (Germed) and had a purity of 99%. Decomposition products were obtained by heating in the temperature range 180—550°C for 5 h in the presence of air, oxygen and 4.6 mm Hg water vapour. In a previous investigation, decomposition in the presence of 15.5 mm Hg water vapour was reported [8]. The products will be denoted by the letter V, with the subscript indicating the type of prevailing atmosphere and the decomposition temperature (°C) noted between parentheses, viz, V_O (450) indicates ammonium metavanadate decomposed in the presence of oxygen at 450°C.

X-Ray diffraction patterns were obtained for the above decomposition products by means of a Philips diffractometer using Ni-filtered Cu-radiation. The *d*-distances and relative intensities were calculated and compared with data in the ASTM cards [13,14].

Adsorption—desorption isotherms of nitrogen at —195°C were determined by a conventional volumetric gas adsorption apparatus.

RESULTS AND DISCUSSION

X-Ray

X-Ray diffraction patterns were obtained for samples heated in the presence of air (static), oxygen (flowing) and 4.6 mm Hg water vapour pressure (static).

Heating in the presence of air gives rise to products almost identical with those obtained in vacuo [8] at temperatures $\leqslant$350°C, but of better crystallinity. Thus at 180 and 230°C the trivanadate [$3\ V_2O_5 \cdot O(NH_4)_2$] is obtained which decomposes at 300°C to give the monohydrate [$(3\ V_2O_5) \cdot H_2O$]. At 350°C the oxide V_2O_5 is produced with traces of the monohydrate; the latter disappears at higher temperatures, producing V_2O_5 of a well-defined crystalline structure. It is of significance to mention in this connection that no reduction of the pentavalent oxide took place, in contrast to the results previously obtained in this laboratory by heating in vacuo or in the presence of high water vapour pressure (15.5 mm Hg) [8], and the results obtained by other investigators [3,4,15,16].

Heating in the presence of oxygen retards the decomposition of NH_4VO_3 as compared with that produced in the presence of air. Figure 1 shows the patterns obtained by heating in oxygen for 5 h at various temperatures. No decomposition is observed at 180°C, although differences in band intensities are observed compared to that of the parent NH_4VO_3 [14]. TG and kinetic measurements [17] indicated that heating at 180°C produces no decomposi-

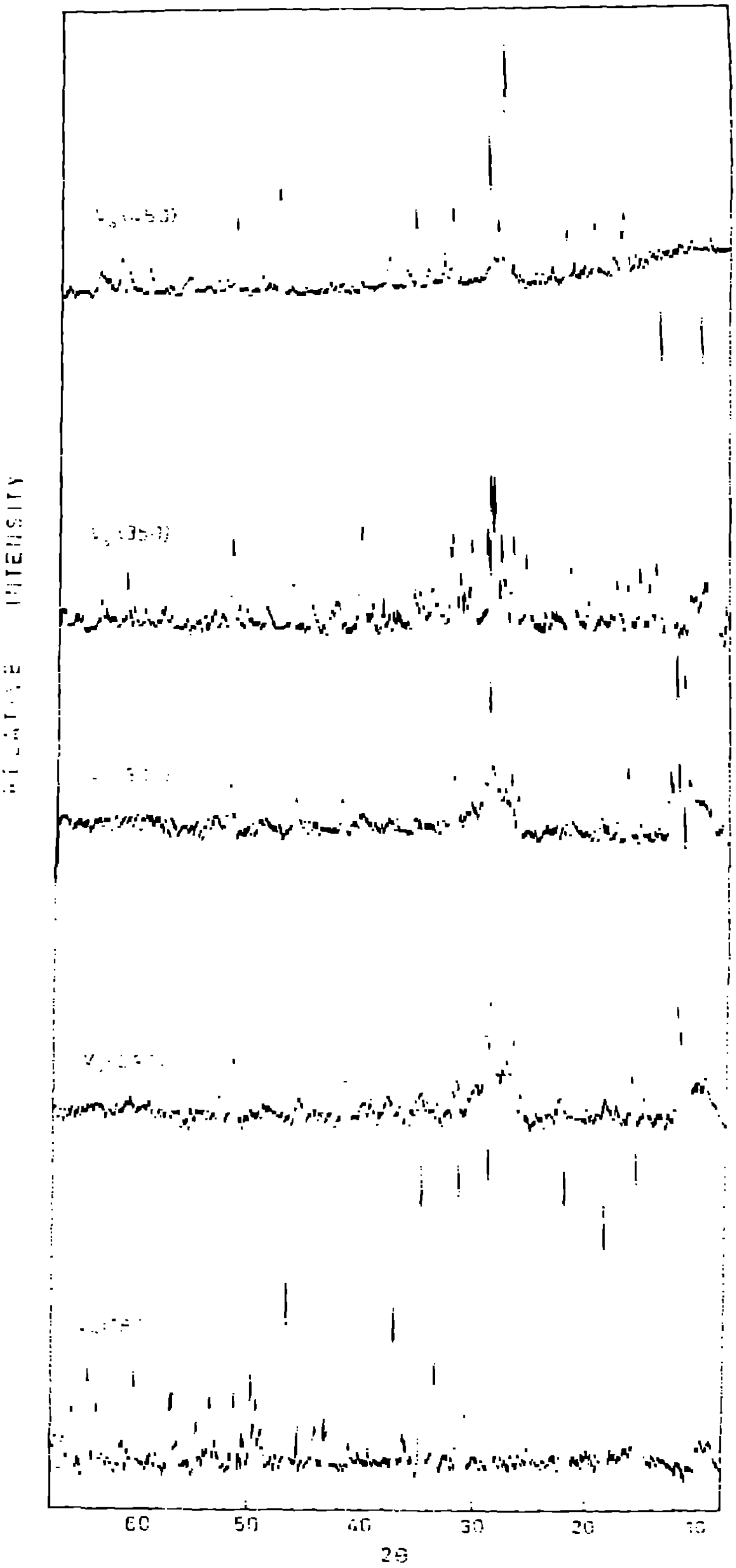

Fig. 1. X-Ray diffraction patterns for the decomposition products of ammonium metavanadate produced in the presence of oxygen.

tion. At 230° C ammonium trivanadate is obtained, as also observed by Taniguchi and Ingraham [3].

Heating the solid at 300° C gives rise to a mixture of the trivanadate and monohydrate. Complete decomposition to the monohydrate is achieved at 350° C, where a well crystallized product is obtained in contrast to that previously produced in vacuo [8] at 300° C which possessed a less-defined crystal structure.

At 450° C a crystalline product resembling V_2O_5 is produced having most of its *d*-distances close to those of V_2O_5 but in some cases with intensities different from those reported [13,14]. The two most intense lines situated at *d*-distances of 3.520 and 3.325 Å are slightly different from those of V_2O_5 together with others of lower intensities situated at 4.980, 4.500 and 2.970 Å. This pattern did not coincide with any of the lower oxides of vanadium or V_2O_5 which was expected to be the product [4]. At 550°C the pattern retains the main lines observed at 450° C but those of lower intensities are not distinguished.

When heating is effected in the presence of water vapour, an important parameter, namely the water vapour pressure, proved to be of significance, especially at high temperatures. In the present investigation low water vapour pressure is applied (4.6 mm Hg), the presence of which retards the decomposition of the metavanadate at 180° C. This retardation is probably due to the chemisorption of the water molecules on the surface of the material [9.17], thereby delaying its decomposition which should then require a higher energy of activation [17]. The product obtained is mainly ammonium metavanadate with traces of the trivanadate which becomes the predominant component at 230° C.

Heating the salt at 300° C produces several broad bands together with some well-defined ones. It is difficult to assign a definite structure to this product as it appears to be composed of several decomposition products, in contrast to that obtained under high water vapour pressure [8] which was mainly composed of the trivanadate. At 350° C the monohydrate becomes dominant. Raising the temperature to 450° C produces a solid which gives an XRD pattern corresponding to that produced in the presence of oxygen but with some additional weak bands which may correspond to a hydrated form. This pattern is quite different from that produced at the same temperature under 15.5 mm Hg water vapour. XRD of products obtained in the presence of 15.5 mm Hg is reported elsewhere [8]. Figure 2 shows the patterns obtained by heating at 300 and 450° C in the presence of 4.6 mm Hg water vapour.

Heating under the above atmospheres does not give rise to products similar to those obtained in vacuo or under high water vapour pressure. In the latter cases a process of reduction took place in the temperature range 350—450° C, whereas in the present situation heating in the presence of air produces V_2O_5, and in oxygen or low water vapour pressure a solid of structure close to V_2O_5 is produced, believed to be in the hydrated form under the latter condition.

Since heating in the presence of air definitely produces V_2O_5, it would be hard to expect heating in oxygen or low water vapour pressure to cause a

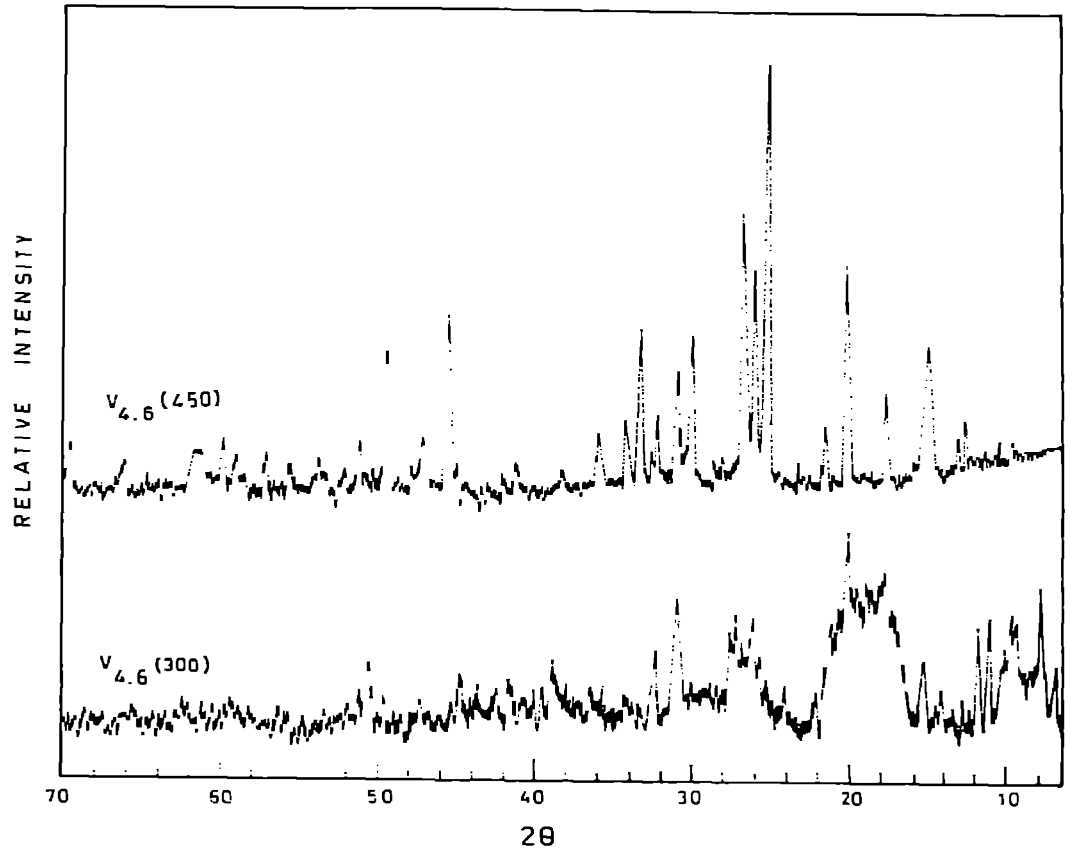

Fig. 2. X-Ray diffraction patterns for the decomposition products of ammonium metavanadate produced in the presence of 4.6 mm Hg water vapour at 300 and 450°C.

change to lower oxidation states. Moreover, the reduction of V_2O_5 under different conditions [4,18], in vacuo or in high water vapour pressure [8], brings about the belief that V_2O_5 so formed is not stable enough and further heating causes some rearrangement which results in a reduction process to proceed under favourable conditions. In the present case, no reduction is observed, but rearrangement takes place to give a more stable structure of V_2O_5. This stable form might represent another phase of V_2O_5. The existence of more than one phase in other oxides of vanadium has also been reported [19,20].

Surface area

The adsorption isotherms of nitrogen obtained for products treated in the presence of air, oxygen or water vapour (4.6 mm Hg) are near type II and are all reversible. In some cases the isotherms show an initial linear region which extends to intermediate relative pressures [e.g. $V_O(450)$]. The samples are characterized by possessing BET C-constants <3.5 but >2.5 and represent isotherms on the border between type III and type II (marked by an asterix in Table 1). The isotherms obtained under 15.5 mm Hg are given elsewhere

TABLE 1

Surface characteristics of the decomposition products of ammonium metavanadate produced in the presence of different atmospheres

Treatment temp. (°C)	In air			In oxygen			In 4.6 mm Hg water vapour			In 15.5 mm Hg water vapour		
	BET C-constant	S_{BET} ($m^2\ g^{-1}$)	S_t ($m^2\ g^{-1}$)	BET C-constant	S_{BET} ($m^2\ g^{-1}$)	S_t ($m^2\ g^{-1}$)	BET C-constant	S_{BET} ($m^2\ g^{-1}$)	S_t ($m^2\ g^{-1}$)	BET C-constant	S_{BET}[c] ($m^2\ g^{-1}$)	S_t ($m^2\ g^{-1}$)
180	3.50	164.5	157.3	3.70	159.0	156.0	3.27[a]	102.9	—	2.9[a]	127.3	—
230	4.33	101.1	102.0	3.40[a]	226.0	—	2.59[a]	141.1	—	3.5	126.0	118.0 125.0[b]
300	3.06[a]	168.5	—	8.50	171.8	172.0	4.60	118.8	118.0	3.1[a]	142.1	—
350	3.37[a]	112.96	—	3.50	247.0	247.0	4.10	125.0	124.0	3.6	127.1	128.0
450	4.33	252.69	251.7	2.90[a]	290.0	—	3.15[a]	252.3	—	3.8	93.7	84.0 92.0[b]
550	4.10	142.05	143.0	3.20[a]	236.6	—	3.46	280.5	280.0	3.5	214.3	209.0

[a] Evaluated as in ref. 21 for the sake of comparison.

[b] Corrected t-curve employed.

[c] Taken from ref. 8.

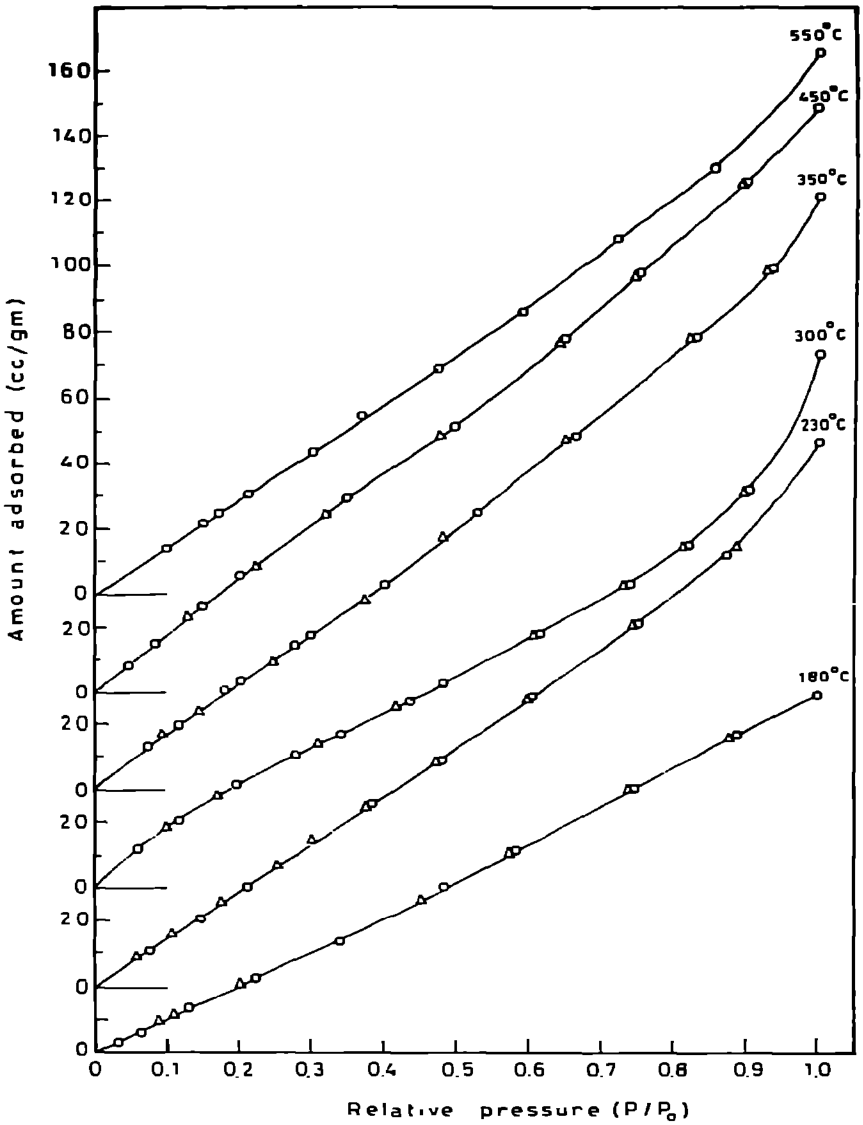

Fig. 3. Adsorption—desorption isotherms of nitrogen on the decomposition products of ammonium metavanadate produced in an atmosphere of oxygen. ○, Adsorption; △, desorption.

[8]. A typical set of isotherms is shown in Fig. 3 for the adsorption of nitrogen on products treated in the presence of oxygen.

Specific surface area values were obtained from the N_2 isotherms by the application of the BET equation in its normal range of applicability and by adopting the value of 16.2 Å for the molecular area of nitrogen. In the case of samples possessing a BET C-constant below 3.5, the area is obtained, for the sake of comparison with the other samples, by assuming an approximate value for C and locating $(P/P_0)_m$ from which the monolayer capacity is obtained [21], although they are still not to be considered reliable.

Table 1 summarizes the specific surface areas and BET C-constants for the

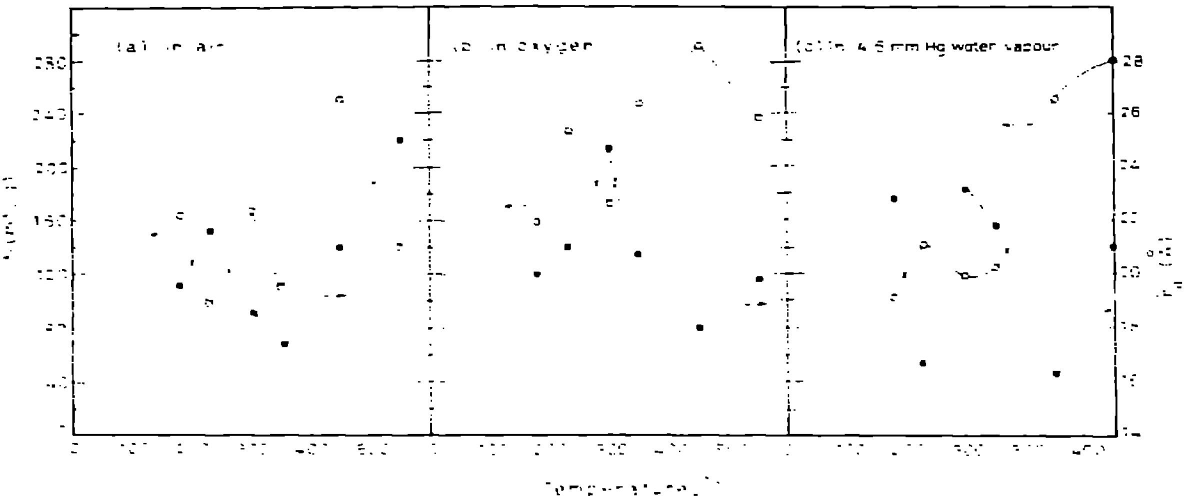

Fig. 4. Plots of surface area vs. temperature (———) and average pore radius vs. temperature (— — —) from N_2 adsorption on the decomposition products of ammonium metavanadate produced under various atmospheres.

samples treated under the different atmospheres. also including those obtained in the presence of 15.5 mm Hg water vapour [8].

The variation of area with decomposition temperature (Fig. 4) is not only a function of the phase composition [8], but also depends on the extent of decomposition of that phase. At 180°C similar areas are obtained in the presence of both air and oxygen, whereas in the presence of 4.6 mm Hg water vapour the area is reduced about 35% despite the common feature of the retarding effect upon decomposition produced by the last two atmospheres. The adsorption (chemisorption) of the polar water molecules [9,17] from the vapour phase during thermal treatment seems responsible for this decrease in area where it attacks those sites possessing enhanced adsorption potentials — namely, those located at the entrances of the narrower pores — rendering them inaccessible to the nitrogen molecules. This receives support from values of average pore radii, as will be discussed later.

Complete conversion to the trivanadate causes an increase in area, as observed at 230°C for products obtained in the presence of oxygen and water vapour and as previously reported [8] for products treated under vacuum. Heating in air at this temperature forms the trivanadate and commences the formation of the monohydrate. During this stage of transformation a decrease in area is observed, as is also found by heating in the presence of oxygen or water vapour (4.6 mm Hg) at 300°C.

Heating in air at 300°C or oxygen and 4.6 mm Hg water vapour at 350°C leads to the formation of the monohydrate, which brings about an increase in area and not a decrease, as was reported [8] for treatment in vacuo or under higher water vapour pressure. However, the increase in area produced in the presence of 4.6 mm Hg water vapour is quite small, pointing to the significance of the role of chemisorbed water even at this relatively high temperature.

Conversion of the monohydrate to the oxide V_2O_5 or further subsequent products is accompanied by an increase in area (as, for example, heating at 450° C). If this transformation is conducted slowly, as in the presence of air, an initial decrease in area is observed at 350° C (V_2O_5 + monohydrate). It appears that upon the evolution of the last traces of water a more open structure is formed through the widening of narrow entrances ("necks") to these pores. This will be seen to be the case from data on average pore radii (see Fig. 4).

Finally, heating at 550° C in the presence of air or oxygen results in a decrease in area. In the presence of 4.6 mm Hg water vapour a small increase in area is observed, resulting from the dehydration of the oxide hydrate formed at 450° C. From TG experiments carried out in the presence of 4.6 mm Hg water vapour, the product at 450° C is actually found to retain a small fraction of water. These area changes may be summarised as follows

(1) an increase in area usually accompanies (a) thermal activation of the trivanadate, (b) decomposition to the monohydrate and oxide hydrate, (c) complete dehydration of the monohydrate and oxide hydrate;

(2) a decrease in area is observed upon (a) incomplete transformation, and (b) sintering of the oxide.

V_l—t *and* N_s—N_R *plots*

In detecting the porosities of the various decomposition products investigated, the t-method of de Boer and co-workers [10] is commonly applied. In such plots the tested sample should invariably possess the same nature as the reference solid material and the BET C-constant is used to indicate such identity, being confirmed by the fulfillment of the criteria of the agreement between S_{BET} (specific area from BET equation) and S_t (specific area from V_l—t plots) values [12]. However, in many cases investigated in this laboratory, a deviation, reaching ~10% in some cases, was observed between S_{BET} and S_t. An alternative method of testing for the suitability of using the reference data is that proposed by Mikhail and Cadenhead [22], known as the N_s—N_R plot. In this method, if the initial experimental points up to a monolayer fall on a straight line passing through the origin with a slope of 1, then the indication is that the reference data can safely be used to analyze the material investigated. The choice of the reference through the identity of the BET C-constant is still valid as a preliminary step. In the present investigation the reference data of Mikhail et al. [23] are employed and the t-curve of the reference with BET C-constant 5—6 was successfully applied to samples having their C-constant in this approximate range. Figure 5 represents a typical example of such N_s—N_R plots (curves a) together with their corresponding V_l—t plots (curves b) for nitrogen adsorption on the decomposition products of NH_4VO_3 obtained in the presence of air. The initial part of the N_s—N_R plots for all samples with BET C-constant >3.5 gave a slope of 1 except for the samples heated in the presence of 15.5 mm Hg water vapour heated at 230 and 450° C, whose slopes deviated slightly from unity (Fig. 6). In all cases where a slope of 1 is obtained, good agreement was observed between S_{BET} and S_t (Table 1).

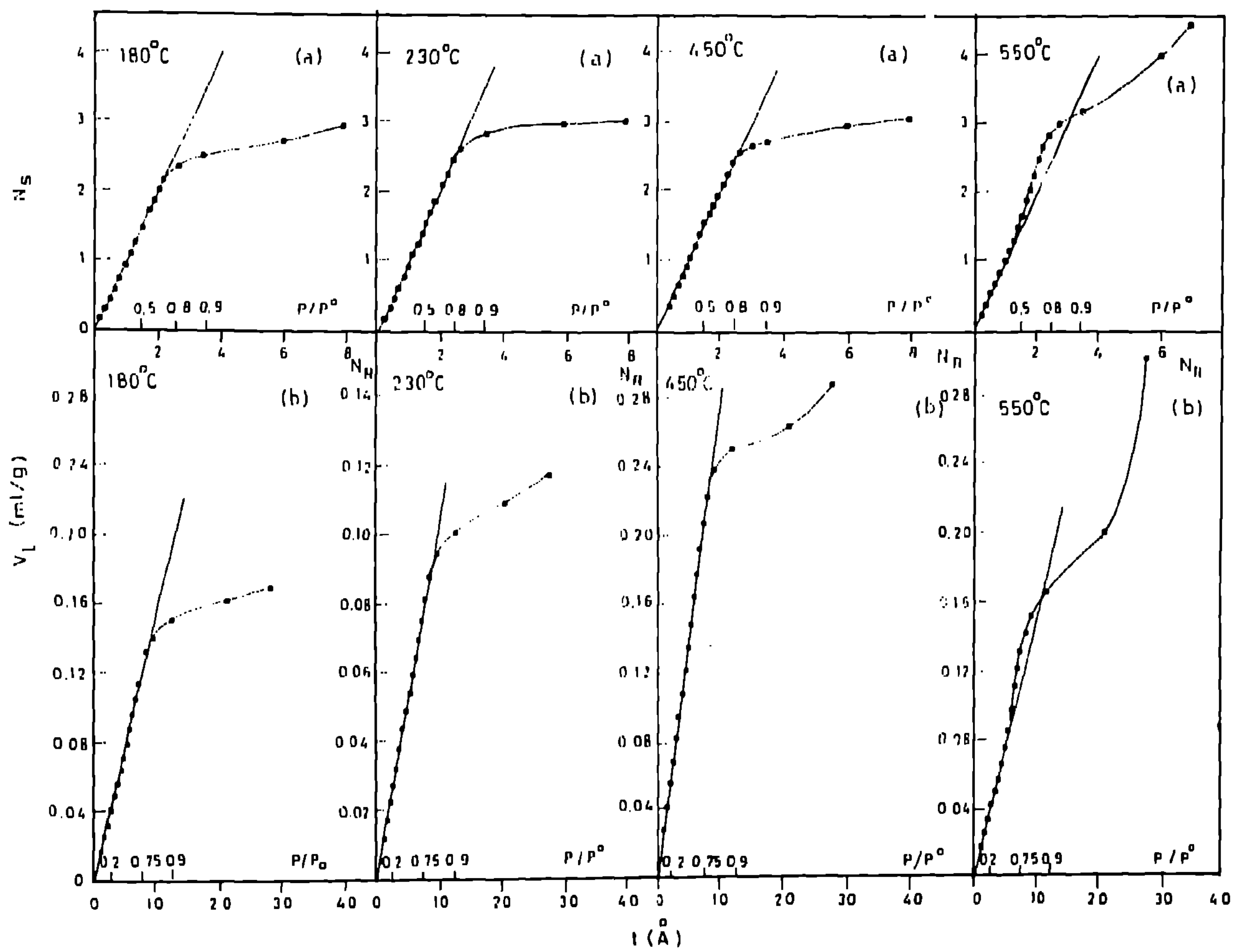

Fig. 5. (a) N_s—N_R and (b) V_l—t plots for nitrogen adsorption on the decomposition products of NH_4VO_3 produced in the presence of air.

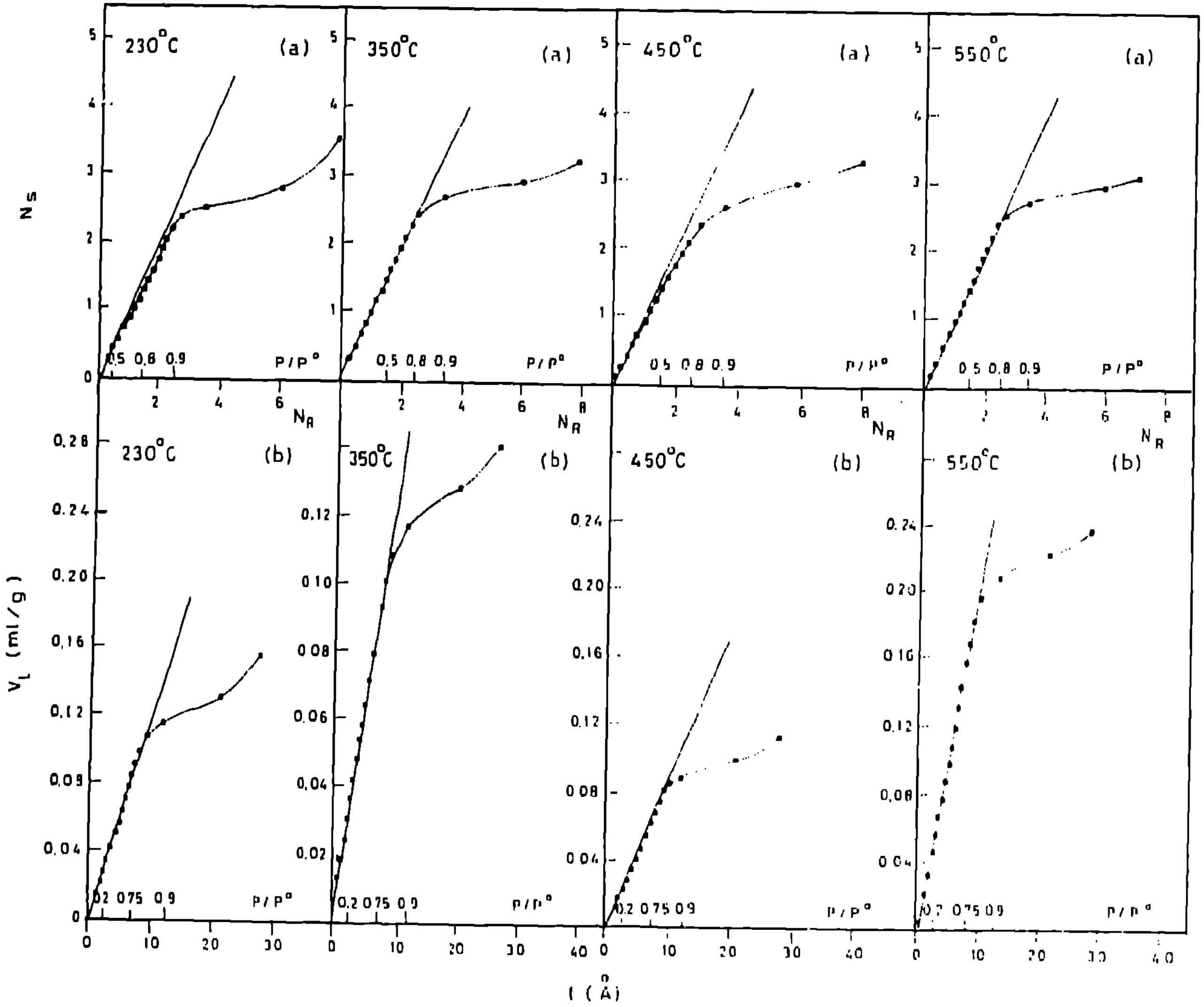

Fig. 6. (a) N_s—N_R and (b) V_l—t plots for nitrogen adsorption on the decomposition products of NH_4VO_3 produced in the presence of 15.5 mm Hg water vapour.

In cases where the initial experimental points fall on a straight line passing through the origin but with a slope different from 1, two cases may be considered. If the deviation from unity is major, say more than 10%, this points to the unfitness of the reference data which should then be changed. On the other hand, if the deviation from unity is little, say within 10%, then the same reference could be used but after introducing a certain correction, since such variations (~10%) may arise from differences in the packing of the adsorbate molecule on the reference (non-porous) and tested (porous) solid substrate. In this respect the adsorbed molecules may lose some of their internal degrees of freedom, especially that for vibrational motion where a variation of ca. 10% in bond length can result in a diatomic molecule such as N_2.

Identity of nature between the tested and reference material implies that the frequency of oscillations of adsorbed molecules should be the same on both solids and is expected to be of the same order as the frequency of vibration of the molecules or ions of the adsorbent lattice [24,25]. The C-constant, as derived from the BET equation, has neglected the effect of frequencies of oscillations by assuming those for the first and higher layers to be equal; therefore C-constants so evaluated could not be taken as more than a rough guide to the chemical nature of the solid. If the oscillations of the molecular vibrations are the same on the reference and tested samples, it would imply that the frequency of vibration of the molecules or ions of the adsorbent and reference solid will also be of the same order. Thus deviations in the N_s—N_R slopes within 10% appear to result from differences in the frequency terms. In such a case the reference data are corrected within this limit to match the same conditions as the tested sample. This is achieved by multiplying the reference data (N_R) by the slope from the N_s—N_R plot, which is 0.93 for the two samples previously mentioned. Table 2 gives the corrected N_R data which when applied in the N_s—N_R plots of these two samples give a slope of 1. This allows correction of the t-curves which are then reproduced from these corrected N_R values (N_{R_c}), and which allows more reliable V_l—t plots to be reproduced, with much better agreement between S_t and S_{BET} areas. This procedure was applied for samples $V_{15.5}$ (230) and V_{15} (450), S_t becoming 125.0 and 92.0 m^2 g^{-1}, being now comparable with S_{BET} which is 126.0 and 93.7 m^2 g^{-1} for the two samples, respectively.

From these plots it is noticed that most of the samples give straight lines up to t-values of 8—10 Å ($P/P_0 \geqslant 0.75$) similar to that produced on the surfaces of non-porous adsorbents, followed by a downward deviation at higher values. Such plots could be produced by solids having a parallel plate pore structure whose pore width does not permit capillary condensation to take place. The downward deviation at high t-values results from the limited adsorption of nitrogen at saturation and not necessarily indicating microporosity. However, samples obtained by heating in the presence of air at 550°C and in oxygen at 300°C exhibit an initial upward deviation at $V/V_m > 1.5$ ($t \approx$ 5—6 Å) but decreases its slope beyond a t-value of 9—10 Å. In these cases the pores widen ($r_H \sim$ 12 Å), as revealed from the average pore radii (Fig. 4) and permit capillary condensation to take place. In some cases

TABLE 2

Number of layers (N_R) of nitrogen formed on a non-porous solid (vermiculite) [23] with a BET C-constant of 5—6, together with the corrected values (N_{R_c})

P/P_0	N_R	N_{R_c}
0.05	0.200	0.184
0.10	0.375	0.347
0.15	0.551	0.508
0.20	0.720	0.665
0.25	0.858	0.792
0.30	0.974	0.899
0.35	1.124	1.037
0.40	1.299	1.199
0.45	1.475	1.362
0.50	1.599	1.476
0.55	1.700	1.569
0.60	1.799	1.661
0.65	1.949	1.799
0.70	2.098	1.937
0.75	2.251	1.985
0.80	2.449	2.260
0.85	2.779	2.565
0.90	3.599	3.322
0.95	6.099	5.628
1.00	7.909	7.301

an upward deviation occurs at $P/P_0 > 0.9$, resulting from capillary condensation, which may be intergranular condensation.

Variations of total average hydraulic radii (V_l 0.95/S_{BET}) assuming parallel plate idealization with both the specific area and decomposition temperature (Fig. 4) show that in most cases increase of area is accompanied by pore narrowing, whereas pore widening always accompanies its decrease. However, in the case of samples $V_a(450)$ and $V_{4.6}(550)$, widening of the pores from 8.7 and 8.1 Å to 10.5 Å for both treatments is associated with increase in area. This would possibly result from the presence of constrictions in the pores which deprive a fraction of an "internal area" to be measured. Upon thermal treatment to higher temperatures, widening of the pores themselves and of their mouths takes place, thus exposing a larger area to be measured.

The presence of various atmospheres during thermal treatment is seen from Fig. 4 to invariably affect the pore structure, depending on the extent of decomposition at temperatures below 300°C and also the dehydration accompanied by the phase change of the vanadium pentoxide at higher temperatures.

REFERENCES

1 K.S. De and F.S. Stone, Nature (London), 194 (1962) 570.
2 A.K. Ostern, Chem. Ker Ztg., 63 (1962) 49.

3 M. Taniguchi and T.R. Ingraham, Can. J. Chem., 42 (11) (1964) 2467.
4 V. Satava, Collect. Czech. Chem. Commun., 24 (1959) 2172.
5 M.E. Brown, L. Glesser and B.V. Stewart, Prog. Vac. Microbalance Tech., 2 (1973) 125.
6 Jerzy Trau, Rocz. Chem., 36 (1962) 1365.
7 J. Lamure and G. Colin, C. R., 258 (26) (1964) 6433.
8 S.A. Selim, Ch.A. Philip and R.Sh. Mikhail, Thermochim. Acta, 36 (1980) 287.
9 B.N. Rybakov and V.A. Strashnova, Zh. Prikl. Khim. (Moscow), 47 (1) (1974) 199.
10 B.C. Lippens, B.C. Linsen and J.H. de Boer, J. Catal., 3 (1964) 32. B.C. Lippesn and J.H. de Boer, J. Catal., 4 (1965) 319.
11 K.S.W. Sing, in P.W. Everett and R.H. Otterwill (Eds.), Surface Area Determination, Butterworths, London, 1970.
12 R.Sh. Mikhail and F. Shebl, J. Colloid Interface Sci., 34 (1) (1970) 65.
13 J.V. Smith (Ed.), X-Ray Powder Data File and Index to X-ray data File, Am. Soc. Testing Mater., Philadelphia, 1961.
14 Powder Diffraction Data, Joint Committee on Powder Diffraction Standards Associateship at the National Bureau of Standards, Swathmore, PA, 1st edn., 1976.
15 J. Bernard and F. Theohold, C. R., 256 (23) (1963) 4916.
16 E. Gellis, C. R. 258 (19) (1964) 765.
17 Ch.A. Philip, M.Sc. Thesis on Thermal Decomposition of Ammonium Metavanadate, Ain Shams University, 1978.
18 A.A. Barakov and P.V. Geld, Fiz. Khim. Osnovy Proizv. Jr. S-oi Kouf, (1959) 157—167.
19 P.V. Geld, S.I. Aly Amooski and I.I. Matvenko, Fiz. Met. Metalloid, Akad. Nauk S.S.S.R., 9 (1960) 315.
20 A. Magneli, S. Anderson, S. Asbrink, S. Wastman and B. Bohlmoberg, U.S. Dep. Commer., Office Tech. Serv., PB. Rep. 145, 923 (1961).
21 S.G. Gregg and K.S.W. Sing, Adsorption, Surface Area and Porosity, Academic Press, London, 1967, p. 96.
22 R.Sh. Mikhail and D.A. Cadenhead, J. Colloid Interface Sci., (1976) 55 (2).
23 R.Sh. Mikhail, N.M. Guindy and S. Hanafi, Egypt. J. Chem., Special Issue "Tourky", 1973, p. 53.
24 J.H. de Boer, The Dynamical Character of Adsorption, Oxford University Press, London, 1953, p. 34.
25 D.H. Everett, Proc. Chem. Soc., (1957) 38.