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The Catalytic Synthesis of Ammonia over Vanadium Nitride Containing Oxygen

II. Order–Disorder Transition Revealed by Catalytic Behavior

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The anomalous behavior revealed in the temperature dependence of the catalytic activity of vanadium nitride for the ammonia synthesis reaction mentioned in Part I of this series has been thoroughly examined, and an attempt made to elucidate this behavior by conducting high-temperature X-ray diffraction and magnetic susceptibility investigations. From the results it is concluded that no bulk phase change involving a rearrangement of the vanadium atoms in the lattice occurs between 20° and 770°C, and the anomalous behavior found in the temperature dependence of the magnetic susceptibility is attributed to the presence of small quantities of V_2O_3 in the samples. The anomaly in the catalytic activity, however, is readily explained in terms of an order–disorder transition; it is suggested that at temperatures below about 470°C ordering of oxygen and nitrogen atoms in the lattice occurs. Through the transition to the disordered state, the catalytic activity increases approximately threefold. Hysteresis in the temperature dependence of the activity through the transition region is revealed.

INTRODUCTION

As mentioned in Part I of this work (*1*), anomalous behavior in the temperature dependence of the catalytic activity of samples of vanadium nitride, prepared from NH_4VO_3 and containing substantial quantities of oxygen in the lattice, is indicative of a slow phase change. Many workers have investigated the influence of phase changes on heterogeneous reactions following the discovery of Tamman and Siebel (*2*) that the oxidation rate of Fe-Ni alloys undergoes a discontinuous change at the α–γ transformation temperature. The effect of first order transitions on the ammonia decomposition reaction has been reported by Fishbeck and Salzer (*3*) (over Fe, at 900°C), Koyano (*4*) (over Fe/Ni alloys) and Toyoshima and Horiuti (*5*) (over Fe in the region where the transition occurs to the nitride phases). In all cases, the activity of the allotropes was found to differ, and in the last case a stable hysteresis in the rate of ammonia decomposition through the transition region was reported.

EXPERIMENTAL

The catalysts and the apparatus used for the activity determinations were the same as those described in Part I.

An apparatus was constructed for the determination of the temperature dependence of the magnetic susceptibilities of samples of vanadium nitride used as ammonia synthesis catalysts. The Gouy method was used, the Gouy tube (Supremax glass, 7-mm OD) being suspended from an arm of a Sartorius air-damped semimicrobalance, refined for electrodynamic balancing using the technique of Hilal and Fredericks

(*6*), between the poles of an electromagnet (pole gap 1 inch, capable of producing a field of about 15,000 oersted in the gap). The furnace consisted of a 10-mm ID Supremax glass tube, with a noninductively wound heating element, the temperature being measured and controlled by means of a thermocouple situated a few millimeters below the lower end of the Gouy tube. Corrections for the buoyancy and diamagnetism of the Gouy tube were obtained experimentally, and deionized, air-free water was used for calibration (taking the susceptibility per gram at 20°C to be 0.72 $\times 10^{-6}$). The Gouy tube was evacuated to about 10^{-5} Torr and sealed off for each run.

RESULTS

Anomalous Catalytic Behavior

After preliminary experiments had revealed that anomalous behavior occurred in the temperature dependence of the activity of vanadium nitride, prepared at 1100°C, for the ammonia synthesis reaction, the following runs were carried out using a fresh 1100°C sample, weighing 8.1 g. The activity was measured in a 3 hydrogen:1

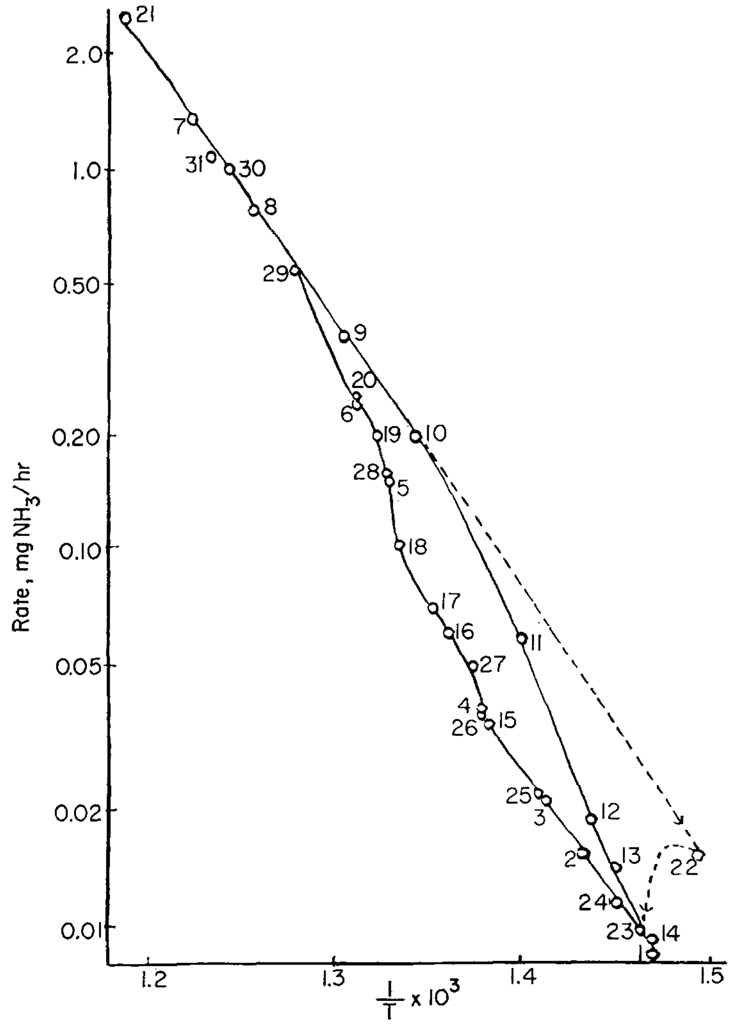


FIG. 1. Arrhenius plot for the ammonia synthesis over VN prepared at 1100°C; readings are numbered in their chronological order of determination.

nitrogen gas mixture, at 25 atm and flow rate of 4.5 liters (NTP)/hr, increasing the temperature in steps; precautions were taken to ensure that a steady rate of ammonia formation was attained in the reactor at each temperature by taking readings repeatedly for 4 to 10 hr, or longer where necessary, after each temperature change.

In the Arrhenius plot in Fig. 1 the readings are numbered in the order of their determination. The first four readings lie on a straight line, and in each case a steady rate of ammonia production was rapidly attained; however, on heating to 479°C the activity was found to increase continuously for a prolonged period, finally reaching a steady value after about 30 hr (Fig. 2). The resulting activity (point 5, Fig. 1) was well above the straight line through points 1 to 4. The heating curve was carried on to 545°C without further change in activity with time. The reactor temperature was then dropped in stages to 397°C, the run being continued for 5 to 35 hr at each temperature until a steady state was reached. At 441°C (point 11) and 422°C (point 12), a decrease in activity was observed with time (Fig. 3); it is possible that the decrease at 422°C was due to incomplete equilibrium at 441°C.

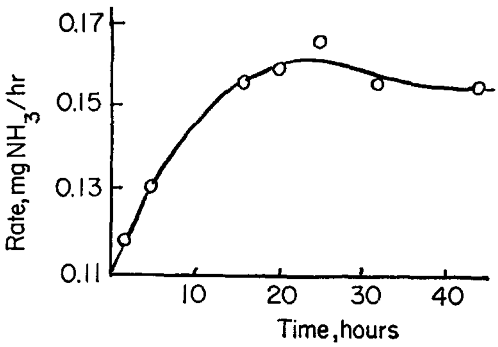


FIG. 2. Anomalous increase in activity on heating to 479°C.

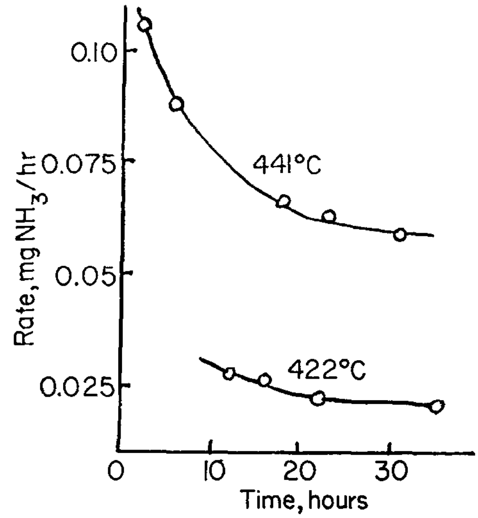


FIG. 3. Anomalous decrease in activity on cooling to temperatures shown.

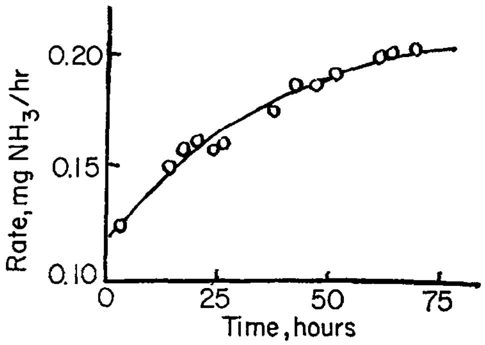


FIG. 4. Activity change in heating to 484°C.

An attempt was then made to establish more accurately the temperature at which the transition from the lower to the higher activity form occurred. The temperature was increased to 451°C, and then raised in steps of 5° to 10°, to 489°C, again continuing the run at each temperature until equilibrium was reached. At 460°C a slight time dependence of the activity was revealed, the equilibrium value lying a little above that expected, and at 484°C the activity increased markedly with time, taking about 70 hr to reach equilibrium (Fig. 4). The reactor was then heated to 569°C (point 21), maintained at this temperature for 3 days, and rapidly cooled to 388°C, at which temperature the activity remained perfectly stable (i.e., time-independent) for a further 30 hr; the reading (point 22) lies on the line extrapolated through the high-temperature readings. However, on heating to 407°C the activity, after showing an initial increase, began to drop, taking some 50 hr to reach the equilibrium value shown (point 23). The ensuing heating curve showed the same pattern as that previously found, the largest change occurring at 480°C and taking about 50 hr to reach equilibrium.

From the Arrhenius plot it is seen that the apparent activation energy for the ammonia synthesis reaction is, within experimental error, unchanged above and below the transition region (407–452°C, 32.1 kcal/mole; 470–569°C, 32.2 kcal/mole). The change in activity was therefore due to a change in the pre-exponential factor of the Arrhenius equation, the ratio of the pre-exponenetial factors at high and low temperatures being 3.0.

A second sample of VN, prepared at 1100°C, was sintered at 1100°C in ammonia for 3 days after being pelleted. The temperature dependence of the activity was observed in analogous manner to that described above and the Arrhenius plot (Fig. 5) showed a similar pattern to that of the unsintered catalyst, except that reproducibility in the low-temperature region was very poor, and the apparent activation energy through the high-temperature region was markedly higher, 35.2 kcal/mole. The transition occurred (on heating) between 460° and 515°C, in good agreement with the unsintered sample.

X-Ray Analysis

The above results could possibly be due to the catalyst undergoing a bulk phase transition, and efforts were therefore made to determine whether VN exists in a differ-

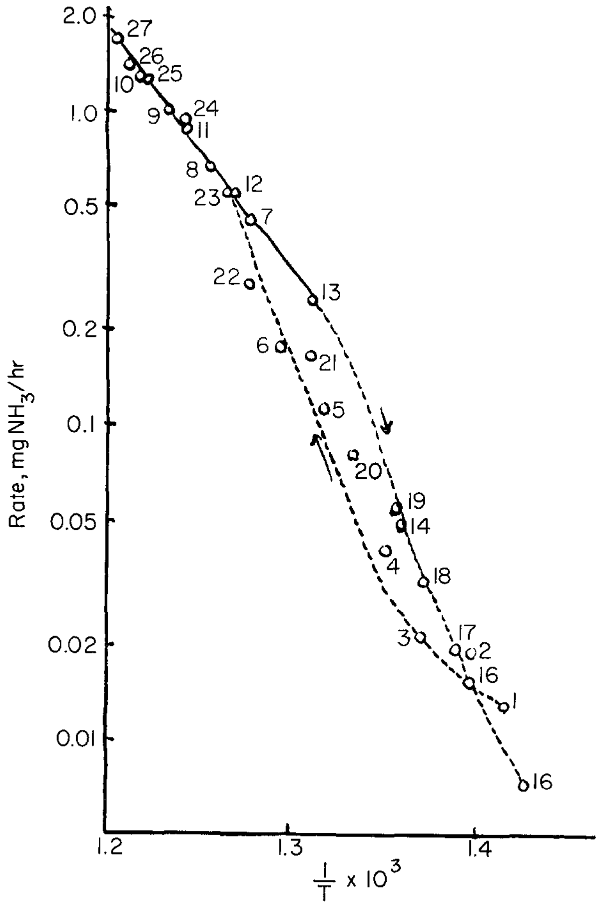


FIG. 5. Arrhenius plot for activity of sintered sample of VN; readings are numbered sequentially.

ent structural form at higher temperatures from that existing at room temperature. Two samples of VN, prepared at 1100°C, were heated in ammonia to 400° and 520°C, respectively, maintaining each sample at its respective temperature for 3 days. They were then rapidly cooled and subsequent X-ray diffraction patterns revealed no observable change from the normal patterns. A further sample heated in a 3 hydrogen:1 nitrogen atmosphere for about 2 weeks at 500°C and rapidly cooled gave the same negative result. Investigations using a high-temperature X-ray diffraction camera (7), also revealed no change in the crystal structure between 25° and 770°C.

Although X-ray analysis of a sample prepared at 600°C revealed no trace of V_2O_3, after use as a catalyst (i.e., after treatment with a hydrogen/nitrogen mixture for about 2 weeks) the dominant V_2O_3 peaks became apparent. Simultaneously with the appearance of V_2O_3, the rock salt (VN–VO) lattice constant increased from 4.104 to 4.119 Å, probably due to the removal of VO from the rock salt lattice. Furthermore, although one sample prepared at 1100°C showed no change on X-ray analysis after treatment in the reactor for about 3 weeks, another 1100°C sample, which had been under a hydrogen/nitrogen atmosphere for 3 months, but had also been exposed to the atmosphere for about a year, gave very distinct V_2O_3 peaks.

Magnetic Susceptibility

The temperature dependence between 20° and 700°C of two 1100°C VN samples is shown in Fig. 6 (curves 1 and 2); the magnetic susceptibility per gram χ, for both samples varied by $<2\%$ over the range investigated. Curve 3 (Fig. 6) illustrates the temperature dependence of a 1500°C sample *after* use as a catalyst in ammonia synthesis runs. The room temperature susceptibility of this sample (3.0×10^{-6}) was appreciably greater than that of the previous samples (mean: 2.2×10^{-6}). How-

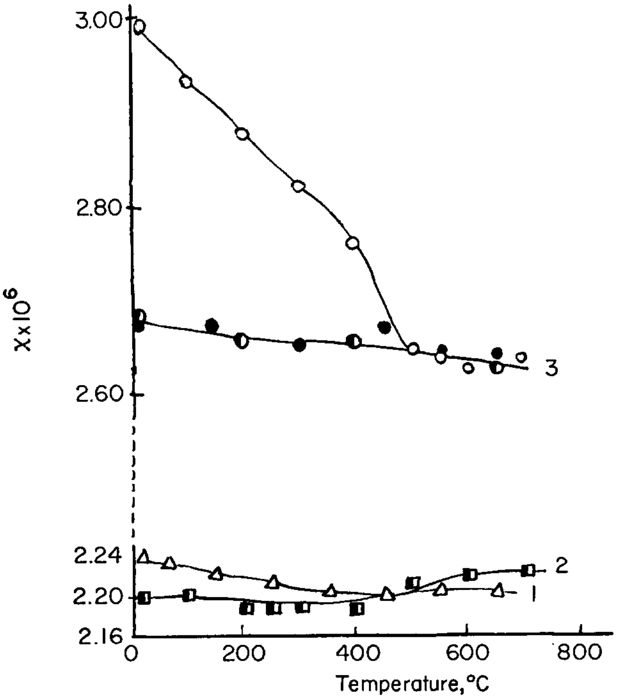


FIG. 6. Variation of magnetic susceptibility of VN with temperature: curves 1 and 2, samples before use as catalysts; curve 3, sample after use as catalyst; ○, temperature increasing; ●, temperature decreasing; △, ◧, ◑, random.

ever, on increasing the temperature, χ decreased markedly, the largest decrease occurring between 400° and 500°C; at higher temperatures χ remained constant at about 2.6×10^{-6}. On decreasing the temperature to 20°C and increasing it again to 700°C the susceptibility varied by $<2\frac{1}{2}\%$, the behavior being very similar to that of the previous samples. Thus the initial decrease, involving a change of about 12%, was irreversible.

The variation of χ with temperature for the 1100°C sample found to contain V_2O_3 as an impurity (after prolonged treatment in H_2 and N_2 and exposure to the atmosphere), is shown in Fig. 7. At 20°C, $\chi = 5.86 \times 10^{-6}$, more than twice the value of other samples; between 20 and 500°C, the behavior bears a very marked resemblance to that shown in curve 3, Fig. 6, but above this temperature χ decreased even more sharply, and the curve was entirely reversible, on heating and cooling, over the whole range.

The room temperature susceptibilities of a number of samples prepared from NH_4VO_3 in ammonia at temperatures between 500° and 1500°C, both before and after use as catalysts, were determined (Fig. 8). The value of χ reaches a minimum for samples

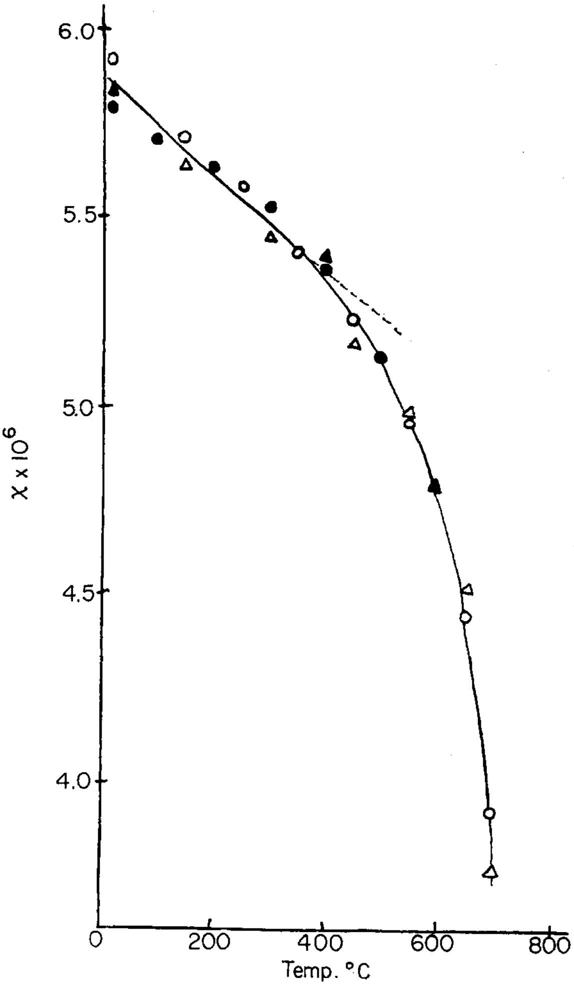


FIG. 7. Variation of magnetic susceptibility with temperature for VN containing a substantial amount V_2O_3 (after use as a catalyst); ○, △, temperature increasing; ●, ▲, temperature decreasing.

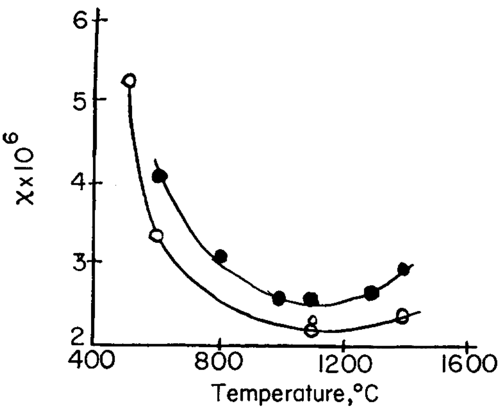


FIG. 8. Variation of room temperature susceptibilities with sample preparation temperature; ○, freshly prepared sample; ●, after use as catalyst.

prepared at 1100°C; moreover, the susceptibility of samples after use as catalysts was about 10% higher than that of the fresh samples. For samples prepared at lower temperatures this difference is partly due to the loss of nitrogen noted in Part 1, but it is likely that the increase is also due to the formation of V_2O_3 in the samples during use as catalysts; where X-ray diffraction did not confirm this, the amount of V_2O_3 was probably too small for detection by this method.

DISCUSSION

Freshly prepared VN samples showed little variation of susceptibility with temperature, whereas the susceptibility of a sample containing appreciable quantities of V_2O_3 (revealed by X-ray analysis) has a negative temperature coefficient, and furthermore showed reproducible anomalous behavior above 400°C; this behavior can therefore be attributed to the V_2O_3 impurity. The irreversibility of the analogous anomalous behavior observed with the 1500°C sample probably containing a small amount of V_2O_3 (not detected by X-ray analysis) may be due to dissolution of the V_2O_3 into the rock salt VN–VO lattice on heating above 500°C in a vacuum; this is confirmed by the fact that the room temperature susceptibility after heating above 500°C was about 10% lower than before, being lowered in this case due to the loss of V_2O_3 (cf. Fig. 8). The sample which exhibited reversible anomalous behavior probably possessed a sufficiently large quantity of V_2O_3 for the two phases to coexist at temperatures up to 700°C. This explanation finds further support from the results of Teranishi and Tarama (*8*), and Grossman *et al.* (*9*); both report distinct discontinuities in the temperature dependence of the susceptibility of V_2O_3 at 260–385°C, the exact temperature of the anomaly depending on the degree of reduction of the sample. It is likely that V_2O_3 embedded in VN may exhibit this transition at somewhat higher temperatures. Hoy has reported anomalous behavior in the temperature–electrical resistance characteristics of vanadium nitride samples (prepared, as in the present paper, from NH_4VO_3) in the region 300° to 520°C, the nature of the anomaly varying according to the history of the sample used (*10*); typical results are shown in Fig. 9. The resistance was studied in atmospheres of argon, nitrogen, ammonia, and hydrogen, and the results were found to be independent of the gas used. The anomalous behavior was attributed to the presence of small amounts of oxygen in the samples, and it would appear likely that, since the conductivity behavior of V_2O_3 above room temperature is so similar (*11, 12*), this anomaly was also due to small traces of V_2O_3.

Whereas the transition observed in the ammonia synthesis runs was very sluggish (and was in fact not observed when runs were performed rapidly) the anomalous magnetic susceptibility curves were not found to be time-dependent, indicating a rapid transition. Thus two separate phenomena are indicated, and in fact a close examination of Hoy's electrical resisticity results (*10*) shows that both transitions are indicated; anomalous behavior was always observed when runs were completed within 10 hr, but in a single instance when the time-dependence of the resistivity was investigated at various temperatures, it was found that, on increasing the temperature, whereas the resistance was invariant with time at 410° and 440°C, a marked increase occurred at 470° and 490°C, requiring more

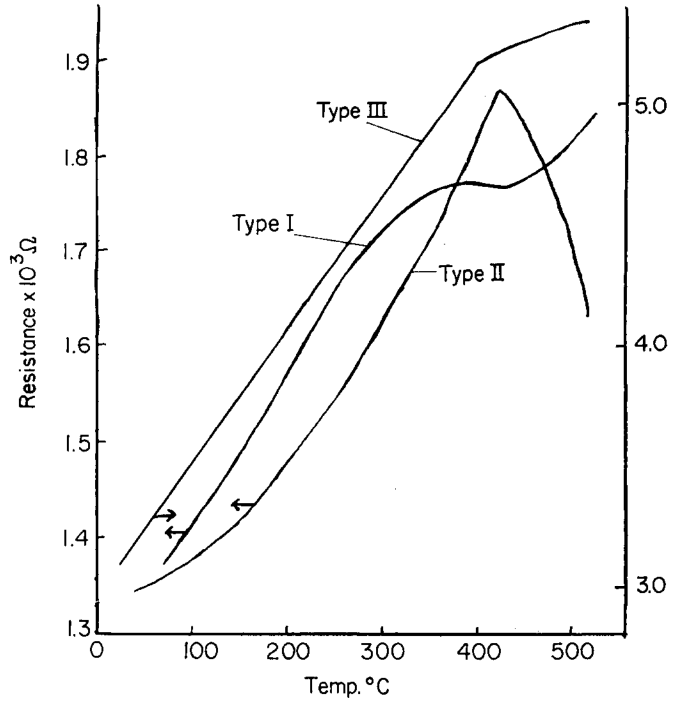
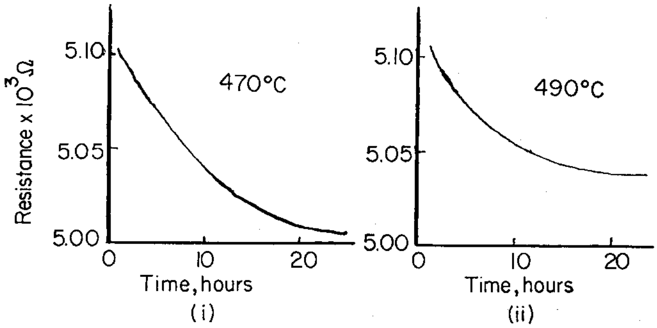


FIG. 9. Resistance of VN pellets, containing oxygen as an impurity, as a function of temperature. (Reproduced from the M.Sc. thesis of J. Hoy by kind permission of the author.)

than 25 hr to reach equilibrium (Fig. 10). These results can be seen to be very similar to the activity–time curves in Figs. 2 and 4, and the phenomenon occurred in the same temperature region. The rapid transformation has already been attributed to the presence of small traces of V_2O_3, and it remains to discuss a mechanism for the slow transition.

The high-temperature X-ray data indicate that the position of the vanadium atoms, in a fcc lattice, is unchanged during the transition. Furthermore, E. G. King (*13*) determined the heat content of VN between 400° and 1611°K, and found the curve to be perfectly smooth over the entire range. This result would seem to eliminate completely the possibility of a phase



(i)

(ii)

FIG. 10. Variation of resistance with time on increasing the temperature to (i) 470°C and (ii) 490°C. (Reproduced from the M.Sc. thesis of J. Hoy by kind permission of the author.)

change; however, E. G. King used a sample of VN prepared from carburized vanadium, and the product was probably oxygen-free. Thus, if it is to be maintained that the VN used in the present work undergoes a phase change at about 480°C, it must be due to the presence of fairly appreciable quantities (up to 4%) of oxygen in the samples prepared from NH_4VO_3. It is therefore considered likely that the phenomenon is an order–disorder transformation, in which the V atoms remain fixed while the N and O atoms are able to move into positions of order or disorder with respect to one another.

The catalytic results are readily explained on this basis. The linear portion below 450°C of the Arrhenius plot shown in Fig. 1 represents the activity of the ordered state, while the linear portion above 506°C corresponds to the completely disordered state. The transition takes place over a range of about 60°, and, furthermore, at about 477°C the activity undergoes a discontinuous increase, and, if the activity change is taken as a measure of the degree of disorder in the catalyst, this indicates a discontinuous change in the degree of order. This is in agreement with the requirements of the theory of order–disorder phenomena since, in contrast to a bcc lattice, an fcc structure is expected to undergo a discontinuous change (*14*). The occurrence of hysteresis is also explained since, on cooling, the rate of formation of the ordered state is only appreciable at temperatures below the critical temperature. Furthermore, it was possible to quench the disordered state by cooling rapidly from 570° to 388°C; only on heating to 407°C did the transformation to the ordered state begin.

A time lag in nucleation is often found in practice, and it may be that in the case under consideration the phenomenon of athermal nucleation (*17*) occurred; athermal nuclei are formed only while the temperature is changing, and it is possible that the action of increasing the temperature from 388° to 407°C caused the formation of such nuclei, thereby initiating the phase change. It would probably be erroneous to conclude that, since an increase of only 19°C was sufficient to promote the phase change, the ordering process must require a very high activation energy.

The activity of almost every VN sample investigated was far more reproducible in the disordered state, at high temperatures, than in the ordered state; this was particularly apparent in the case of the sample sintered at 1100°C (Fig. 5) and must be due to incomplete ordering of the samples in the low-temperature region. At high temperatures complete disorder was more readily attained, and the readings at these temperatures were therefore taken on a single phase.

The total activity increase through the transformation, as measured by extrapolating the two straight lines on the Arrhenius plot to the same temperature, varied from threefold for the sample prepared at 1100°C (Fig. 1) to twofold for a 1500°C sample (Fig. 3, Part 1). This variation may be due to a variation in the oxygen content of the catalysts. Samples prepared at 600° and 800°C did not reveal a slow transition over the temperature range investigated, although some anomalous behavior was observed at lower temperatures with the 800°C sample (not akin to the normal behavior; the "kink" in the Arrhenius plot at about 390°C may be due to the previously noted effect of the V_2O_3 impurity on the electrical and magnetic properties of the catalyst). The oxygen content of these samples was probably too high for the formation of a superlattice.

Hoy's results on the resistivity of VN, a decrease in the resistance as a function of time being reported at 470° and 490°C on the up-temperature curve, may be attributed to the formation of the disordered state, with an inverse change of resistivity. (A decrease in resistance on ordering may be due to better contact of the particles owing to the anomalous expansion through the critical temperature.)

Any reasons proposed for the increased activity of the disordered phase must at this stage be purely speculative. Superlattice Brillouin zones in the ordered state may alter the density of states curve, and hence the number of holes (or unpaired electrons) in the *d* bond available for nitrogen adsorption. Alternatively, the explanation may be thermodynamic, since the bonding energy is higher in the disordered than in the ordered state.

Logan and Kemball have reported anomalous behavior in the temperature dependence of the activity of vanadium nitride films for the decomposition of ammonia, at 515° and 570°C (*15*); at these temperatures a considerable, anomalous, decrease in the rate was observed. It is probable that VN prepared by nitridation of the metal at low temperatures contains N atom vacancies in the lattice, whence ordering between vacancies and N atoms may occur [by analogy with evidence for the formation of superlattices in titanium and vanadium oxides (*16*)]. This therefore offers an explanation for the observed change in activity at higher temperatures, if it is assumed that ordered and disordered states differ in activity for the ammonia decomposition reaction.

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