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The Catalytic Synthesis of Ammonia over Vanadium Nitride Containing Oxygen

I. The Reaction Mechanism

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Vanadium nitride prepared from ammonium metavanadate is a catalyst for ammonia synthesis. The presence of oxygen in the lattice plays a part in the catalysis. Products prepared at high temperature showed anomalous behavior between 460° and 500°C. The compensation effect applies to these catalysts. The slow step in the reaction is that in which nitrogen is adsorbed into an active state in what is probably V_2O_2N.

INTRODUCTION

The ammonia synthesis reaction over a stable nitride is of particular interest, since the reaction is generally believed to proceed with the adsorption of nitrogen as the rate-determining step, and recently attempts have been made to compare the chemisorption bond with bonding in the corresponding bulk compound. The decomposition of ammonia over a number of nitrides of the first series transition metals has been investigated by Lotz and Sebba (*1*) and of the "metallic" nitrides TiN, VN, and "Cr_3N_2," VN was found to be the most active; it was therefore chosen for investigation in the present work.

EXPERIMENTAL

Catalyst Preparation and Analysis

All catalyst samples were prepared by the thermal decomposition of ammonium metavanadate, as described by Roscoe (*2*). Such decomposition, in ammonia and in a nitrogen-hydrogen mixture, has been investigated between 125° and 1400°C by Epelbaum *et al.* (*3, 4*) who concluded that the optimum preparation temperature for VN was 1100°C. Above this temperature it was found that nitrogen is lost from the lattice, while at lower temperatures substantial quantities of oxygen remain in the sample. For the present investigation samples were prepared in a tube furnace in ammonia at temperatures between 500° and 1500°C, each sample being removed from the furnace after about 24 hr, mixed, and returned for a similar period. In addition, samples of V_2O_3 were prepared from NH_4VO_3 in hydrogen at 1000°C.

The samples were analyzed for nitrogen by a modified micro-Kjeldahl method (*5*); it was important to keep the time of digestion as short as possible (about 30 min) as it was found that longer periods resulted in low nitrogen values. Results are given in Table 1. Even at 1100°C the theoretical value for stoichiometric VN, i.e., 21.6 wt %

TABLE 1
ANALYSIS OF CATALYSTS

Preparation temperature (°C)	Wt % N	Lattice constant (Å)
500	7.8	(4.08)
600	13.7	4.104
800	16.1	4.127
1000	18.4	4.133
1100	19.5	4.133
1500	18.2	—

N, was not attained. Vanadium analysis (amperometrically, after oxidation with HNO_3) of a sample prepared at 1100°C gave 76.7 wt % (cf. 78.4 wt % for VN). Thus by difference, this sample contained 3.8 wt % oxygen, in fairly good agreement with the results of Hardy and Hulm (*6*), who analyzed vanadium nitride samples by the vacuum fusion method, and found 2.3 wt % O and 18.6 wt % N in a sample prepared in the same manner as above, at 1200°C; heating to a higher temperature (1350°C) was found by these authors to be quite ineffective in removing the remaining oxygen from the lattice.

X-ray analysis revealed that samples prepared at and above 600°C consisted exclusively of the face-centered-cubic structure, while the sample prepared at 500°C showed strong V_2O_3 (corundum structure) peaks, and only very faint fcc peaks. Lattice constants are given in Table 1, and are in agreement with values reported in the literature (*3*, *6*).

The degree of crystallinity of the samples, as revealed by peak intensities, decreased progressively with decreasing preparation temperature.

For use as catalysts the amorphous powders were pelleted in an hydraulic press at 200 atm pressure.

APPARATUS

In order to attain appreciable yields of ammonia the catalytic reaction was conducted at the moderately high pressure of 25 atm. Essentially, the procedure involved the passage of a mixture of nitrogen and hydrogen of known composition through a catalyst bed at a controlled rate, pressure, and temperature, and subsequent analysis for the ammonia formed. Nitrogen and hydrogen were available in cylinders, and, in the absence of a compressor, it was found convenient to feed the gases directly from the cylinders, under pressure, into a storage vessel capable of withstanding 100 atm; a rough estimate of the gas composition was obtained by filling the vessel with each gas to the desired pressure as indicated by a pressure gauge. From this vessel the gas mixture was passed through a purification train (Pd-asbestos at 300°C; KOH, SiO_2 gel, and $MgClO_4$) and then through a stainless steel reactor, fitted with a pressure gauge and a thermocouple, containing the catalyst.

Ammonia formed in the reactor was analyzed by bubbling the exit gases through a measured volume of ammonia-free water for a timed period, and then determined by spectrophotometric analysis using Nessler's reagent. The composition of the synthesis gas mixture was determined by means of a catharometer, and the over-all gas flow rate with a capillary flow meter.

A vacuum system, capable of pumping the high-pressure system down to 10^{-4} Torr, was attached to the apparatus, and before the activity determinations, each catalyst was evacuated for a few hours, at the highest temperature to be used.

A blank run was performed in which the synthesis gas mixture was passed through the reactor, with an empty catalyst cage in place, at 25 atm pressure and a flow rate of 4.5 liter (NTP)/hr; no detectable quantities of ammonia were formed at temperatures up to 550°C.

RESULTS AND DISCUSSION

Initial Rate of Ammonia Formation

A 3 hydrogen:1 nitrogen gas mixture at 25 atm, 4.5 liter (NTP)/hr, and 440°C, was passed over each of the catalysts prepared from ammonium metavanadate in ammonia, and the runs were continued until a constant concentration of ammonia was detected in the exit gases. For samples prepared at temperatures at and above 1100°C, a constant rate of ammonia production was attained within a few hours, this induction period probably being required for temperature equilibration of the catalyst. However, as shown in Fig. 1 (plotted on a semilog scale for convenience), the initial activity of samples prepared below 1100°C was very much higher than that of an 1100°C sample (dashed line), and in all cases the rate of ammonia formation decreased appreciably before attaining a constant value after about 120 hr. In the case of the 800°C sample, the temperature was increased to

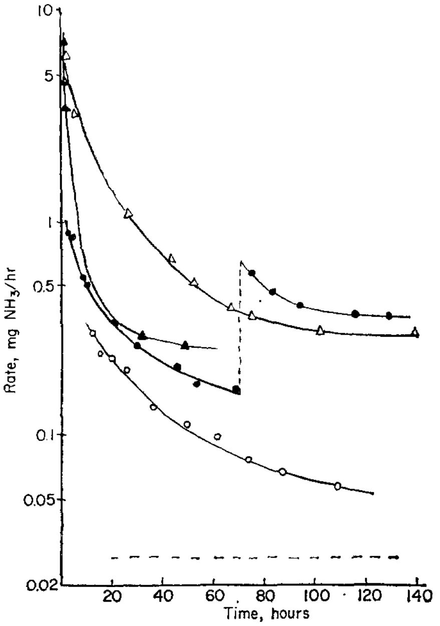

FIG. 1. Initial rate of ammonia formation over catalysts prepared at: ○, 1000°C; ●, 800°C; △, 600°C; ▲, 500°C.

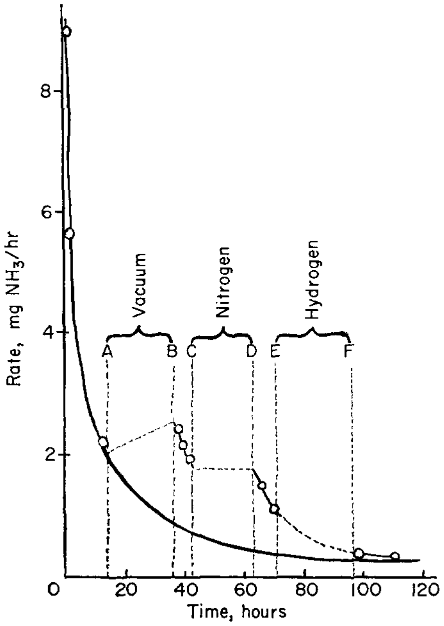

FIG. 2. Initial rate of ammonia formation: Sample prepared at 600°C.

486°C after 70 hr (before a constant rate had been attained) and the activity decreased to a constant value more rapidly at this higher temperature.

The cause of the large decrease in activity of samples prepared at low temperatures was investigated by flowing a second sample prepared at 600°C with the synthesis gas mixture, under identical conditions (Fig. 2). Activity measurements over the first 4 hr were in good agreement with the previous run over a 600°C sample. After this period the reactor was evacuated and maintained under vacuum, at 440°C, for the next 22 hr (A to B on Fig. 2), whereafter the gas mixture was reintroduced for activity measurements. At C, the reactor and storage vessel were evacuated, and pure nitrogen at 6 atm and 1.1 liter (NTP)/hr (equivalent to the pressure and flow rate of nitrogen present in the 3:1 gas mixture) was passed through the reactor for the next 19 hr. At D a 3:1 gas mixture was returned to the reactor, and at E pure hydrogen at 19 atm and flowing at 3.4 liter (NTP)/hr, was introduced into the system after all traces of nitrogen had first been removed by evacuation. At F a 3:1 gas mixture was allowed to flow over the catalyst for the final activity measurements. The results show that the decrease in the rate of ammonia production was entirely due to the presence of hydrogen; the increased activity after prolonged evacuation (A to B Fig. 2) will be discussed presently.

A further 600°C sample, in the reactor, was put into a stream of pure hydrogen at 440°C, and the following quantities of ammonia were detected in the exit gases: after 2 hr, 6.47 mg/hr; after 18 hr, 1.26 mg/hr. Thus the initial high rate of ammonia formation over samples prepared at temperatures from 500° to 1000°C was due to the reaction of hydrogen from the gas phase with nitrogen from the catalyst itself, not from the gas phase, the process requiring about 120 hr to terminate; after this period ammonia formation is attributable to the reaction of hydrogen and nitrogen both from the gas phase. This was confirmed by nitrogen analysis of catalysts after use, e.g., the N content of a 600°C sample was 2.3% lower after use, whereas the 1100°C sample was unchanged. It was found that at temperatures up to 600°C no reaction occurred between hydrogen and a sample of vanadium nitride prepared at 1100°C; this is supported by the work of Shomate and Kelley (*7*) who found that treatment of VN with hydrogen at 1100°C did not result in the loss of N from the lattice.

Hence it may be inferred that samples prepared below 1100°C contain two distinguishable types of bonded nitrogen, one which readily reacts with hydrogen to form ammonia, and another which is quite inert under the same conditions. The lower the temperature of preparation, the greater the per cent of loosely bound reactive nitrogen in the sample (see Fig. 1); for a 600°C sample the loosely bound nitrogen constitutes about one-sixth of the total amount present. It is probable that in the preparation of VN from NH_4VO_3 in the presence of ammonia the first atoms of nitrogen to react with V_2O_3 (which is readily formed at lower temperatures) enter the corundum lattice, forming V_2O_2N. The corundum structure is weakened by their presence and therefore, in the normal course of nitridation, tends to break up to form the more thermodynamically stable sodium chloride structure, a VO–VN substitutional alloy. The N atoms present in V_2O_2N are very reactive, and hence react readily with hydrogen to form ammonia; the amount of V_2O_2N present in samples prepared at 600°C was too small to detect by X-ray diffraction, but in the 500°C sample it was probably the dominant form of nitrogen. This mechanism explains why V_2O_3 is quite stable in hydrogen at 1500°C (it is not reducible to VO) and yet reacts with ammonia at 500° to 600°C; the substitution of N for O atoms in the corundum lattice weakens the structure.

It has been shown that the reaction of hydrogen from the gas phase with weakly bound nitrogen in the catalyst proceeds at a much greater rate than the reaction of hydrogen and nitrogen both from the gas phase, whence it may be concluded that the rate-determining step in the ammonia synthesis over vanadium nitride is that in which nitrogen is adsorbed into an active state. This result closely parallels that of Kozhenova and Kagan (*8*), who showed that the hydrogenation of previously adsorbed nitrogen on an iron catalyst proceeds more rapidly than the synthesis from gaseous hydrogen and nitrogen. Similarly, Goodeve and Jack (*9*) have estimated that the rate of hydrogenation of Fe_4N is about 10^4 times more rapid than the desorption to nitrogen. However, nitrogen present as VN is inert in a hydrogen atmosphere, even at 1100°C, and it must be concluded that chemisorbed N atoms, capable of reaction with hydrogen, are much more weakly bound than N atoms present in the bulk material. A very large difference in bond strengths is indicated, and the many comparisons which have recently been made of the chemisorption bond with bonding properties of the bulk nitride appear to be unfounded in this case. The argument of Frankenburg (*10*), that vanadium metal is not a catalyst for the ammonia synthesis reaction due to the strength of the metal–nitrogen bond in the bulk compound is therefore also negated by the result of the present work.

Vanadium sesquioxide was found to be active as a catalyst for the ammonia synthesis reaction, and it was expected that nitridation of the catalyst would occur. However, after treatment with the synthesis gas mixture for a week at temperatures up to 580°C, chemical analysis revealed no trace of nitrogen, in contrast to a sample similarly treated in ammonia (see Table 1). This may be explained if it is assumed that (i) the rate of formation of VN from V_2O_3 is dependent on the activity of the adsorbed nitrogen, and (ii) the slow step in the ammonia synthesis is the adsorption of nitrogen (or the desorption of nitrogen in the decomposition of ammonia). From (ii), the Temkin-Pyzhev theory leads to the following expression for the concentration of N at the surface:

$$\theta = (1/f) \ln aP_A^2/P_H^3$$

where f and a are constants and P_A and P_H are the ammonia and hydrogen partial pressures, respectively. During the synthesis reaction P_A is very small compared with P_H, whence θ must be virtually negligible. Thus, from (i), the rate of VN formation must also be negligible. However, in ammonia, which is decomposed at the surface, $P_A \gg P_H$, whence θ, and the rate of VN formation, will be appreciable.

The fall-off in the rate of reduction of nitrogen from the catalysts with time (Fig. 1) must be due to a decrease in the concentration of weakly bound N atoms at the catalyst surface, the rate of diffusion to the surface being slow. The observed increase in the rate of ammonia production after prolonged evacuation of the catalyst could then be explained if, during evacuation, diffusion to the surface had continued, resulting in an accumulation of active N atoms at the surface and an increase in the reaction rate when hydrogen was reintroduced. However, if this is true, it is not clear why no increase in ammonia production was observed after treatment in pure nitrogen, unless the increase was too small to be noticed.

Rate Constants

The influence of gas flow rate on the reaction rate over an 1100°C sample was determined by varying the over-all flow rate at constant pressure (25 atm), composition (3 H_2:1 N_2) and temperature (456°C); results are given in Table 2. Integration of the Temkin-Pyzhev equation, assuming the above conditions and low yields, yields the following expression for the rate constant:

$$k = -V \ln [1 - (x/x_e)^2]$$

where V is the space velocity, and x and x_e the exit and the equilibrium ammonia concentrations, respectively. The calculated values for k (Table 2) are reasonably constant.

TABLE 2
RATE CONSTANTS FOR AMMONIA SYNTHESIS[a]

V (hr^{-1})	$x/x_e \times 10^3$	$k \times 10^3$ (hr^{-1})
1470	1.01	1.50
947	1.35	1.72
543	1.72	1.61
257	2.38	1.46
393	1.97	1.53

[a] Wt. of catalyst = 8.1g.

This is essentially in agreement with the results of McGill and Sebba (*12*) who found that the ammonia decomposition reaction over vanadium nitride obeys the Temkin-Pyzhev kinetics, provided that the reaction was performed in the presence of quantities of hydrogen greater than 10%.

Temperature Coefficient of the Reaction Rate

After a steady state had been attained with respect to the rate of ammonia formation, as described above, the temperature dependences of the activity of the samples prepared at 600°, 800°, 1100°, and 1500°C were determined; similar determinations were also made using two samples of V_2O_3 (Fig. 3). Anomalous behavior was observed for the samples prepared at and above 1100°C, indicative of a slow phase change. The detailed nature of this behavior will be considered in the next paper in this series; it is of interest here, however, to note that the activation energy was apparently the same above and below the transition region. In Table 3, the apparent activation energies, E_a (calculated from the linear portions of the log rate vs. 1/T plots), the activity at 440°C, r' (expressed as milligrams of NH_3 formed per hour per gram of catalyst), and the log of the pre-exponential factors A in the Arrhenius equation written in the form $r' = A \exp(-E_a/RT)$, are given.

TABLE 3
DATA FOR CATALYSTS PREPARED FROM NH_4VO_3 IN NH_3

Preparation temperature (°C)	Wt of catalyst (g)	E_a (kcal/mole)	r'(440°C) [mg hr^{-1} (g cat)$^{-1}$]	log A
600	6.8	21.7	0.0415	5.17
800	7.3	26.2	0.0160	6.24
1100	8.1	32.1	0.0033	7.36
1500	9.3	36.8	0.0014	8.43

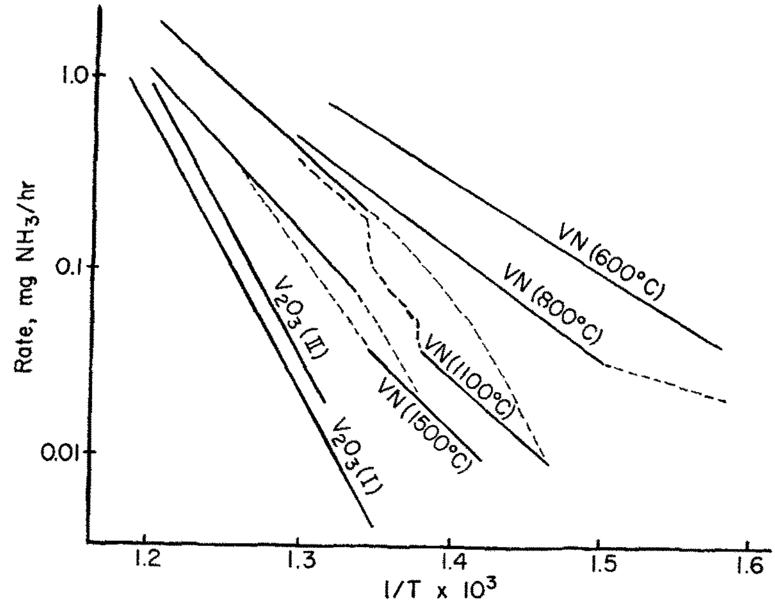

FIG. 3. Arrhenius plots for the ammonia synthesis over catalysts prepared from ammonium metavanadate; preparation temperatures of samples prepared in ammonia are given in parentheses.

An increase in catalyst preparation temperature resulted in an increase in activation energy and a decrease in activity; in Fig. 4 it can be seen that the compensation *effect is obeyed. These results may be explained* in terms of an *a priori* surface heterogeneity, since the most active sites are probably destroyed on increasing the temperature, resulting in an increase in the activation energy; furthermore, it can be shown (*11*) that on the assumption of an energetically heterogeneous surface the rate equation may be written in the form $r = g \exp(E/b) \exp(-E/RT)$, where g and b are constants; hence the activation energy E also appears in the "pre-exponential term" A, resulting in a compensation effect.

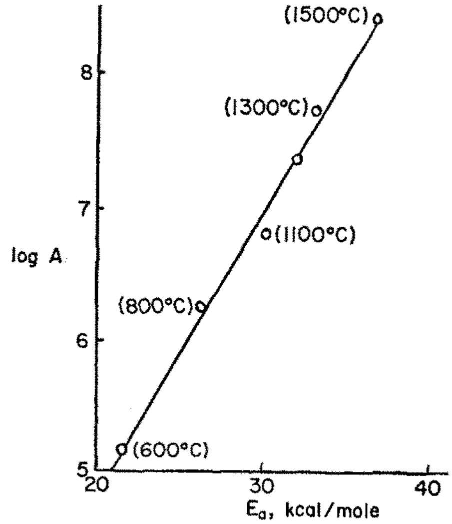

FIG. 4. The compensation effect; catalyst preparation temperatures are given in parentheses.

It may be suspected that the activity of V_2O_3 was due to the formation of a thin film of VN on the surface of the oxide, and not to the oxide itself; however, this is considered unlikely, as the apparent activation energy (mean value: 66.9 kcal/mole) for the two samples investigated was more than twice that of VN, indicating a substantially different active surface. Furthermore, if nitridation occurred at the surface, it would be expected that some diffusion of the nitrogen atoms into the bulk of the sample would occur, whereas analysis, both of surface scrapings and bulk material, after use as a catalyst, indicated no detectable nitrogen; X-ray analysis confirmed that it was unchanged. It is noteworthy that V_2O_3 is a metallic conductor at high temperatures (*13*), and therefore fulfills, in this respect, the normal requirements for ammonia synthesis catalysts.

Surface Area Determination

The BET surface area of a typical sample of VN, prepared at 1100°C and pelleted as in the synthesis runs, was found to be 0.32 m^2/g, using nitrogen adsorption at 76°K.

SUMMARY

Samples of vanadium nitride, prepared by the thermal decomposition of ammonium metavanadate in ammonia at temperatures between 500° and 1500°C, have been investigated as catalysts for the ammonia synthesis reaction at 25 atm pressure. Chemical and X-ray diffraction analyses revealed that the catalysts prepared at temperatures above 600°C consisted of a VN–VO solid solution (rock salt structure), the amount of nitrogen in the lattice increasing with increasing preparation temperature but never reaching the stoichiometric value.

Evidence was found for the existence of a weakly bound nitrogen species in catalysts prepared at temperatures below 1000°C, probably present as V_2O_2N. The rate of the reaction of this N species with hydrogen to form ammonia was much greater than the rate of the catalytic reaction between hydrogen and nitrogen from the gas phase, and it is therefore concluded that the slow step in the synthesis reaction is that in which nitrogen is adsorbed into an active state. Rate constants calculated from runs performed at various flow rates support this conclusion.

The temperature dependence of the activity of a number of the catalysts was investigated, and anomalous behavior found at about 460° to 500°C for the samples prepared at higher temperatures. The compensation effect was shown to operate with these catalysts, the apparent activation energy being lowered by decreasing the preparation temperature.

Vanadium sesquioxide was found to be catalytically active, with the evidence indicating that no bulk nitride formation occurred during the ammonia synthesis at temperatures up to 580°C.

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