The Kinetics of Ammonia Decomposition over Vanadium Nitride

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The kinetics of ammonia decomposition over a powdered vanadium nitride catalyst was studied at 700 mm Hg in the temperature range 400° to 480°C. When the hydrogen partial pressure in the gas phase exceeds about 200 mm Hg the decomposition of ammonia follows the Temkin-Pyzhev (1) kinetic equation with nitrogen desorption constituting the rate-determining step. With less hydrogen in the gas phase the amount of hydrogen has little effect on the rate of reaction while, in the absence of hydrogen in the gas, the ammonia index in the rate equation changes from about 1.0 to 0.5.

EXPERIMENTAL

Catalyst preparation. Vanadium nitride (VN) was prepared by heating A.G. ammonium vanadate in a rapid stream of dried ammonia at 1100°C according to the method of Epelbaum and Brager (2). This is claimed to produce a face-centered cubic interstitial nitride. The gray-brown product was analyzed by the Dumas method.

Sample 1. Nitrogen 20.95, 20.95, 21.06.

Sample 2. Nitrogen 20.70, 20.73, 21.22, 21.33. VN requires 21.6% Nitrogen.

Ammonia. Ammonia, specified 99.98% pure, was obtained from cylinders and dried over CaO that had previously been ignited at 1000°C.

Hydrogen. Hydrogen was obtained from cylinders. Possible traces of CO_2 were removed by passage over KOH. Oxygen was removed by passing over palladized asbestos at 480°C and the gas dried over magnesium perchlorate.

Nitrogen. High purity nitrogen containing less than 10 p.p.m. (by volume) of oxygen was supplied from cylinders. Oxygen was removed by reduction over freshly reduced copper at 480°C. CO_2 was removed by passing over KOH and the gas dried over magnesium perchlorate.

Argon. Argon, supplied from cylinders, was dried over KOH and magnesium perchlorate.

Procedure. The pelleted catalyst was contained in a glass cage in an electrically heated thermostated reaction vessel. Each gas mixture was passed for 8 hr at a fixed total gas flow rate over the catalyst, held at the reaction temperature. After this time, when a steady reaction rate had been obtained the reactor was isolated and the rate of the reaction measured, in a static system, by following the change in pressure with time. On completion of a run a new gas mixture of different composition was allowed to flow for 8 hr before doing the next run. The gas composition used in each run was determined by analysis of a sample of the gas passing over the catalyst just before the commencement of the run. The activation energy was determined from a series of runs using pure ammonia at various temperatures selected at random.

RESULTS

The catalyst has an activation energy for the decomposition of ammonia of 33 kcal mole (Fig. 1). The results of the kinetic runs are shown in the graphs and summarized in Table 1.

When using gas mixtures of NH_3 and N_2 an ammonia index of 0.5 and a nitrogen index of zero are indicated. That nitrogen had no effect on the rate equation was confirmed by substituting A for N_2 in a
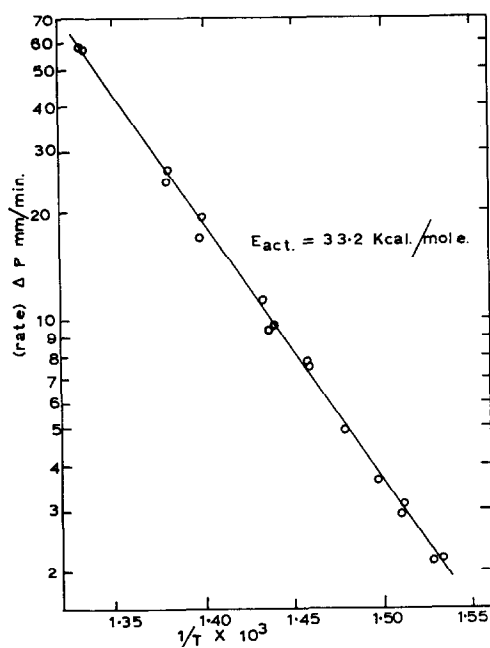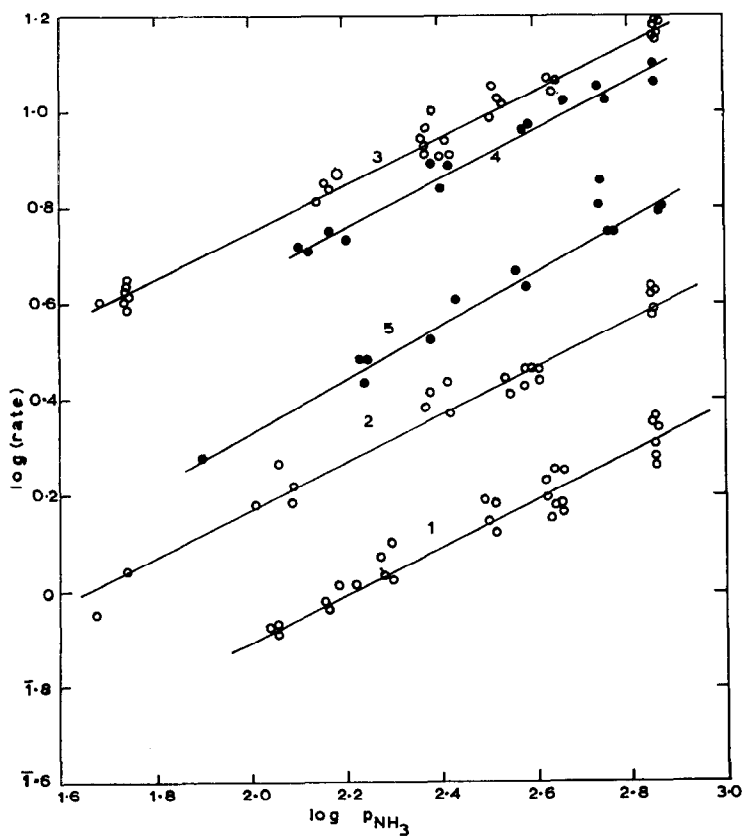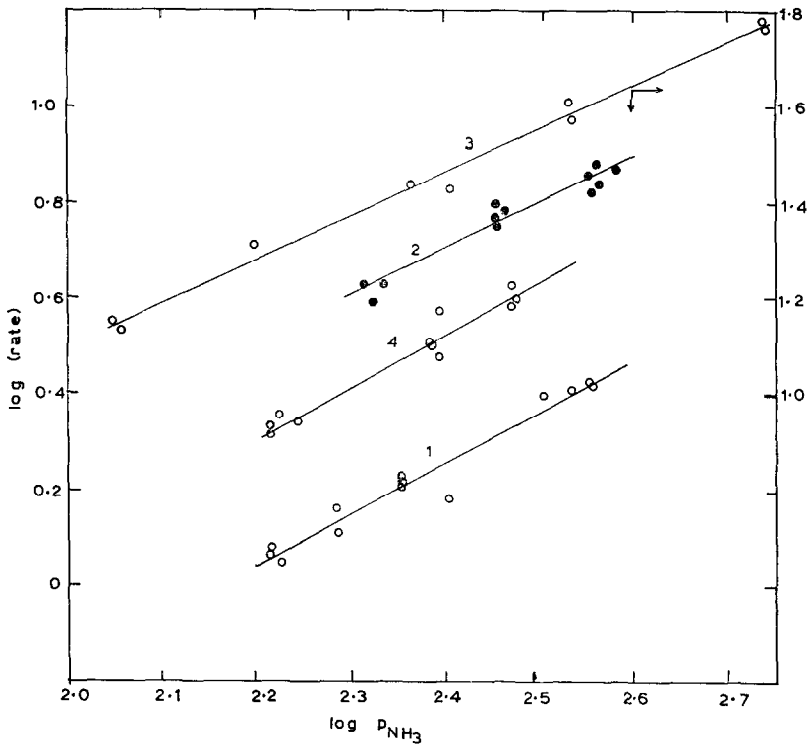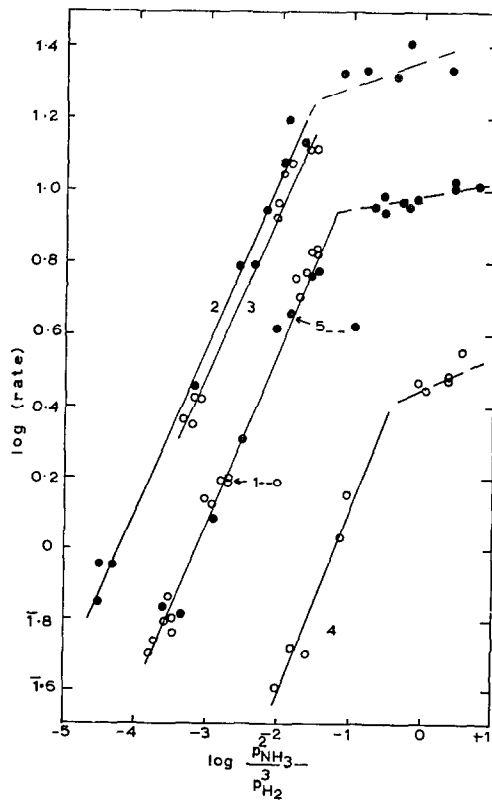
FIGURE 1.

FIGURE 2.

FIGURE 3.

FIGURE 4.

TABLE 1
SUMMARY OF KINETIC DATA

Figure	Gas mixture	Curve	Catalyst sample	Reaction temp. (°C)	NH₃ index	H₂ index	Remarks
2	NH_3-N_2	1	1	408	0.48	—	⎫
		2	1	434	0.49	—	⎪ Range investigated 10–100% ammonia
		3	1	468	0.48	—	⎬
		4	2	440	0.51	—	⎭
2	NH_3-A	5	1	434	0.52	—	Range investigated 15–100% ammonia
3	NH_3-N_2-H_2	1	1	450	1.06	—	H_2 constant at 50% H_2
		2	1	452	0.93	—	H_2 constant at 25%
		3	1	448	0.90	—	H_2 constant at 10%
		4	2	459	1.0	—	H_2 constant at 58%
4	NH_3-H_2	1	1	462	1.02	1.53	Studied only at H_2 pressures above 300 mm Hg
		2	1	468	0.94	1.41	When H_2 pressure exceeds 210 mm Hg[a]
		3	1	440	1.04	1.56	When H_2 pressure exceeds 150 mm Hg[a]
		4	1	416	1.0–1.2	1.5–1.8	When H_2 pressure exceeds 100 mm Hg[a]
		5	2	440	1.02	1.53	When H_2 pressure exceeds 180 mm Hg[a]

[a] When the H_2 pressure is below these values the H_2 index is about zero.

series of runs when an ammonia index of 0.52 was found. The rate equation becomes

$$r = kP_{NH_3}^{0.5} \qquad (1)$$

Runs on NH_3-H_2 gas mixtures showed that for H_2 pressures above 200 mm Hg the Temkin-Pyzhev (1) rate equation

$$r = k(P_{NH_3}^2/P_{H_2}^3)^\beta$$

is obeyed when, β the constant, is changed to ½. This has the effect of changing the ammonia index of 0.5 in Eq. (1) to 1.0. This change in the ammonia index in the presence of hydrogen was confirmed by runs with mixtures of NH_3 and N_2 containing constant amounts of hydrogen. In this case the rate equation becomes

$$r = k^1 P_{NH_3}/P_{H_2}^{1.5} \qquad (2)$$

For hydrogen pressures of less than 100–200 mm Hg deviation from the Temkin-Pyzhev equation occurs and a further decrease in the amount of hydrogen has little effect on the rate of the reaction. A series of runs with a constant amount of 10% H_2 showed that the ammonia index in this lower hydrogen pressure region is also about 1.0. The rate of the reaction in this region is best represented by the equation

$$r = k^{11} P_{NH_3}/A^{1.5} \qquad (3)$$

where A is the hydrogen pressure in the region where deviation from the Temkin-Pyzhev equation starts occurring.

DISCUSSION

In the absence of hydrogen, or at low hydrogen pressures, the reaction does not follow the Temkin-Pyzhev rate equation. It may be that a different mechanism to that of Temkin-Pyzhev is operative here. However, at higher H_2 pressures, the Temkin-Pyzhev kinetics are followed. In this case, one could expect to form some sort of surface nitride by chemisorption of nitrogen. This presents some difficulty as the surface is already a nitride. It is necessary to consider the possibility of a partial hydrogenation of the surface of the nitride powder under these conditions. For catalyst sample 1 the value of the hydrogen pressure [A in Eq. (3)] at which deviation from the Temkin-Pyzhev equation occurred, increased linearly with increase in the reaction temperature. Hydrogenation of VN is a highly endothermic reaction (3) and the fact that the Temkin-Pyzhev kinetics are followed at higher tempera-

tures only in the presence of more hydro-gen, makes partial denitriding of the sur-face as an explanation for the reaction, when it follows the Temkin-Pyzhev equa-tion, unlikely.

The formation of a second catalyst (V or V₃N together with VN) to account for the change in the kinetic equation in the presence of hydrogen appears unlikely for the following reasons:

1. Reduction of VN is endothermic, and, therefore, it would be expected that there would be more reduction at higher tem-peratures. But it is found experimentally that raising the temperature is not enough to change the kinetics. The H_2 pressure must also be raised in order to change the H_2 index from 0 to -1.5.

2. Logan and Kemball (5) have shown that vanadium is about four times as active for the decomposition reaction as the nitrided vanadium film. Should surface reduction of the nitride occur when the hydrogen concentration exceeds a certain value, the Temkin plots should show a discontinuity as free vanadium in the sur-face should lead to an increase in the rate of the reaction. Should surface reduction of the nitride occur gradually with increased amounts of hydrogen in the gas, the Tem-kin graphs should show curvature with relatively higher rates of reaction for high concentrations of hydrogen in the gas phase.

3. VN (1:1) can be prepared by passing a 3–1 mixture of H_2 and N_2 over am-monium vanadate or vanadium powder (6). It is unlikely the nitride will be par-tially reduced to V under the reaction conditions since the H_2 concentration was in most cases below this value.

Chemisorbed nitrogen must be more loosely held on the surface than is the bulk nitrogen, but it is difficult to guess on which sites it is adsorbed. The value of A [Eq. (3)] for catalyst sample 2 did not coincide with that for sample 1 but it is difficult to decide at just what H_2 pressure deviation from the equation starts occurring. Chang-foot and Sebba (4) suggested that the mechanism of NH_3 decomposition on phos-phides, or for that matter, on nitrides, need

not be the same as on metals, though chem-isorption of nitrogen on metals may be supposed to produce something like a sur-face nitride. If there is already a phos-phide, a surface nitride could not be pro-duced without the elimination of phosphine. A kinetic study over a phosphide catalyst may help to decide this point of surface hydrogenation.

The deviation of the rate of the reaction from the Temkin-Pyzhev equation at lower hydrogen pressures cannot be due to dif-fusion control as straight line plots were obtained for NH_3–N_2 mixtures over an even larger range of gas compositions. The Temkin-Pyzhev rate equation is not ex-pected to hold for values of the surface coverage approaching zero.

When the composition of the gas mixture passing over the catalyst was changed, the rate of reaction of this new gas mixture changed slowly with time, i.e. a run at-tempted 2 hr after a gas mixture of changed composition started flowing over the cata-lyst, resulted in an apparent different rate of reaction, to a run conducted 3 hr after the change. Only after a period of up to 8 hr (depending on the extent of the change) was a constant rate of reaction observed. This suggests the existence, on the surface of the catalyst, of a slow reaction deter-mining the equilibrium between the (un-known) surface species.

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