BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 344—348 (1969)

Decomposition of Ammonia and Reactivity of Nitrogen Absorbed on Molybdenum

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(Received June 16, 1968)

Adsorption measurements during the course of ammonia decomposition over molybdenum catalyst have been carried out in a closed circulating system. It was found that most of the nitrogen produced was taken up by molybdenum, and the initial rate of the reaction was independent of the ammonia pressure in a certain region. During the decomposition the nitrogen uptake was several times as much as the amount required to saturate the catalyst surface, which indicates the formation of nitride layers. The catalytic activity of molybdenum trioxide for ammonia decomposition was also observed, and the formation of nitride layers was again suggested. The nitrogen sorbed on molybdenum was removed as ammonia by admitting hydrogen and was displaced by oxygen added afterwards.

Extensive studies[1-4] have been carried out on the ammonia synthesis or decomposition reaction over molybdenum, and the decomposition was found to be zero-order. It is generally admitted that the reaction follows zero-order kinetics when the catalyst surface is fully covered by the reactant or the reaction inermediate. In the case of ammonia decomposition over molybdenum, the zeroth order kinetics might be due to the saturated adsorption of nitrogen on the catalyst surface. The formation of nitride layers was suggested during the decomposition reaction of ammonia on tungsten, which is of zero-order kinetics.[5] Further information on the surface species would be obtained by measuring the adsorption during the ammonia decomposition reaction over molybdenum.

Nitrogen is an inactive element as is well known, and the formation of reactive nitrogen is a subject of interest. The reactant adsorbed must be more reactive than it is in the gas phase, and thus the nitrogen adsorbed on the molybdenum would be reactive.

In this study, the authors also investigated the reactivity of nitrogen sorbed on molybdenum with hydrogen and oxygen, and obtained some information on this system.

Experimental

The apparatus employed is a closed circulating system and the experimental procedures are similar to those described in a previous paper.[6] The amounts of gases sorbed on the catalyst surface were estimated from the amounts of reactants introduced, and the pressure and composition of the circulating gas. The composition of the circulating gas mixture comprised of ammonia, nitrogen and hydrogen was determined by gas chromatography after removing ammonia by means of a trap. The amount of ammonia in the gas phase was estimated from a knowledge of the volume of the system and the decrease in the total pressure by trapping.

Before hydrogen was introduced, the gases were removed by a few minutes' evacuation of the system, assuming that the nitrogen uptake on the surface can hardly be lost by pumping.

The reaction between hydrogen and sorbed nitrogen was carried out in the circulating system with trap cooled in liquid nitrogen. The amount of ammonia thus formed and collected in the trap was estimated from the increase in the total pressure on removal of the liquid nitrogen and a knowledge of the volume of the system.

The ammonia was obtained by distillation from ammonium hydroxide at room temperature and was purified by repeated fractional distillation from dry-ice to liquid nitrogen traps.

The molybdenum-A catalyst was prepared by treating and stabilizing reagent grade commercial molybdenum, with ammonia several times, the decomposition of ammonia taking place. The commercial molybdenum was reduced at 600°C with hydrogen for 50 hr to prepare the molybdenum-B catalyst. No water formed when

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[1] C. H. Kunsman, *J. Am. Chem. Soc.*, **50**, 2100 (1928).

[2] S. Kiperman and M. I. Temkin, *Acta Physicohim. U. S. S. R.*, **21**, 267 (1946).

[3] M. R. Hillis, C. Kemball and M. W. Roberts, *Trans. Faraday Soc.*, **62**, 3570 (1966).

[4] W. G. Frankenburg, "Catalysis III," ed. by Emmett, Reinhold, New York (1955), p. 185.

[5] K. Tamaru, *Trans. Faraday Soc.*, **57**, 1410 (1961).

[6] S. Tsuchiya and T. Shiba, *J. Catalysis*, **4**, 116 (1965).

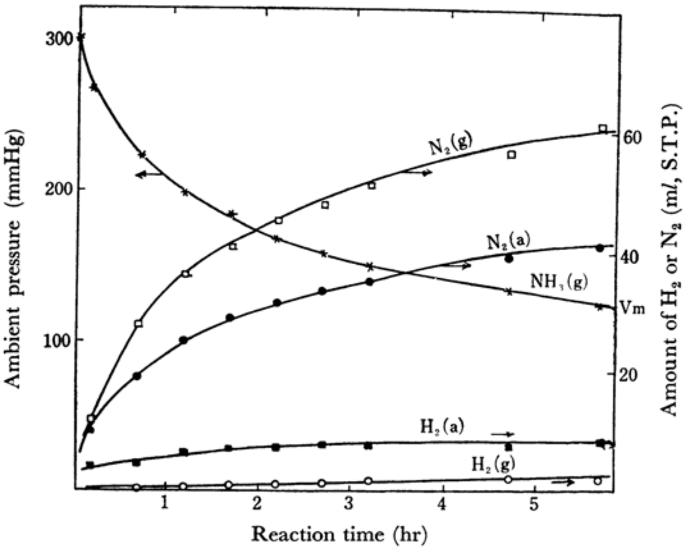

Fig. 1. Decomposition of ammonia over moylbdenum-A at 390°C. *: NH_3 in the gas phase, ○: N_2 in the gas phase, ●: N_2 uptake by the catalyst, □: H_2 in the gas phase, ■: H_2 uptake by the catalyst.

both molybdenum-A and -B were reduced at 500°C with hydrogen. The molybdenum trioxide catalyst was prepared by decomposing ammonium molybdate at 400°C. Before each run, the catalysts were evacuated to 10^{-4} mmHg for four hours at 580°C, and the molybdenum-B catalyst was beforehand treated with hydrogen at 580°C to remove the sorbed nitrogen, the amount of ammonia formed by the treatment being checked. In this way the experimental results were satisfactorily reproducible.

Results

Typical results of ammonia decomposition reaction over molybdenum are shown in Figs. 1 and 2, where the catalysts used were different. (Fig. 1: cat. A 160 g, Fig. 2: cat. B 39.6 g) As the decomposition proceeded, the partial pressure of ammonia decreased with time, and the pressure of hydrogen and nitrogen increased, while the uptake of nitrogen increased, and the amount of hydrogen taken up was very small as shown in Fig. 1. In the case shown in Fig. 2, no uptake of hydrogen was observed. At higher temperatures above 500°C, no uptake of hydrogen took place, even when molybdenum-A was used as the catalyst, and at 560°C the atomic ratio of molybdenum to sorbed nitrogen increased to approximately 0.5. The sample was identified as Mo_2N by X-ray diffraction.

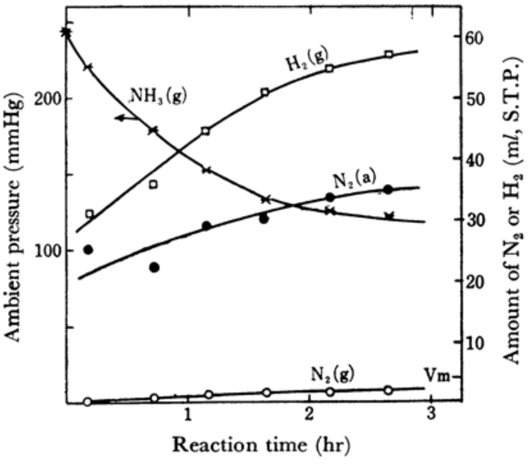

Fig. 2. Decomposition of ammonia over molybdenum-B at 404°C. The symbols used are the same as Fig. 1.

The results for decomposition of various amounts of ammonia are shown in Fig. 3, where the initial rate of increase of the hydrogen pressure due to

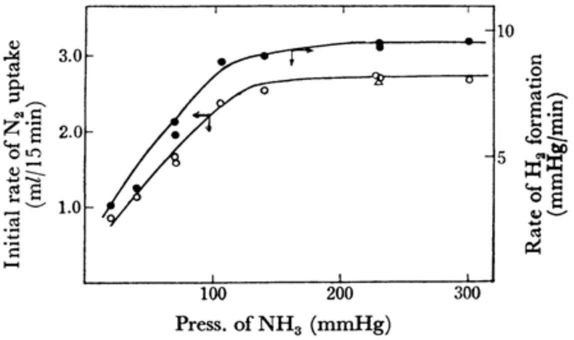

Fig. 3. The plots of the rate of ammonia decomposition (○) and the amounts of nitrogen uptake (●) against the initial partial pressure of ammonia at 454°C (Mo-A).

the ammonia decomposition and the amounts of nitrogen uptake over first fifteen minutes are plotted against the ambient pressure of ammonia. Both the initial rate of the formation of hydrogen and the rate of nitrogen uptake at the initial stage of the reaction were almost independent of the pressure of ammonia above 140 mmHg; rate dependence upon the pressure of ammonia, however, occurs below 140 mmHg.

The apparent activation energies of the ammonia decomposition over the different catalysts, together with those of other workers relevant to the discussion, are given in Table 1, being estimated from the Arrhenius plots (shown in Fig. 4) of the amounts of gas initially evolved. These values are in good agreement with one another.

Table 1. Activation energies for the decomposition of ammonia over molybdenum catalyst

Catalyst	Temperature (°C) range	Activation energy (kcal/mol)
Mo-A	390 — 610	42.6
Mo-B	400 — 440	40.0
MoO_3	400 — 460	43.4
Mo powder[2)]	447 — 550	42.5
Mo wire[1)]	725 — 850	42.7

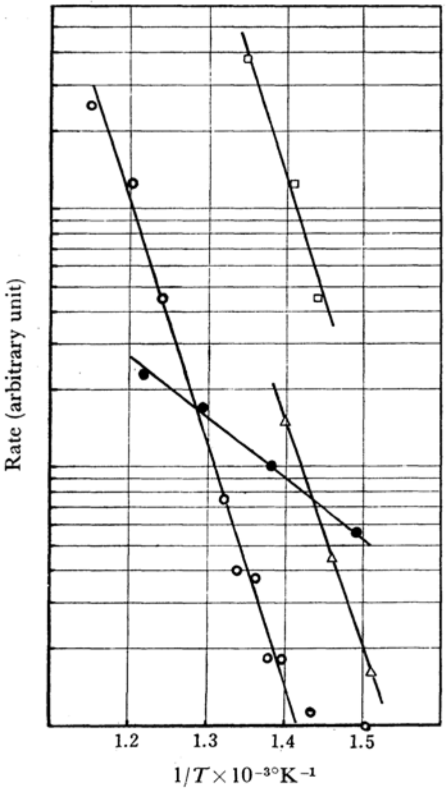

Fig. 4. Arrhenius plots for the ammonia decomposition over different catalyst (○ Mo-A, △ Mo-B, □ Mo oxide) and the reaction between nitrogen sorbed and hydrogen (●).

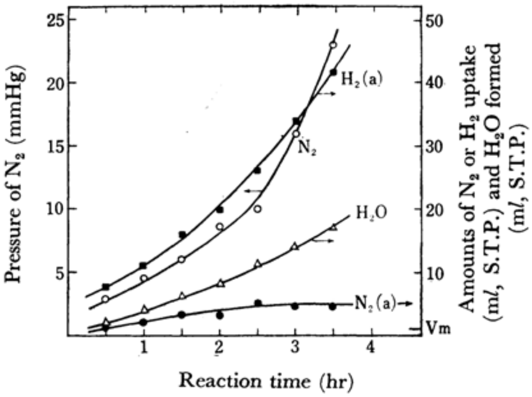

Fig. 5. Decomposition of ammonia over molybdenum trioxide (3.45 g) at 420°C.
△: water vapor formed, the other symbols used are the same as Fig. 1.

When molybdenum trioxide was used as the catalyst, the ammonia was also decomposed, considerable amount of hydrogen and nitrogen was taken up and the formation of water vapor and nitrogen gas was observed, while no hydrogen was detected in the gas phase, as shown in Fig. 5. The hydrogen taken up may exist in the form of H_2O.

The reaction between the hydrogen and nitrogen held on molybdenum was also carried out with the nitrogen-sorbed surface being prepared by decomposition of ammonia and the product observed was identified as only ammonia from its vapor pressure measurement.

The hydrogen pressure dependence of the rate of the hydrogenation of sorbed nitrogen, represented by the cumulative amount of ammonia formed over the first one-hour period, was proportional to $P_{H_2}{}^{1.5}$ as shown in Fig. 6, where P_{H_2} is the pressure of hydrogen, ammonia being formed linearly with time. The ambient pressure of the hydrogen was represented by the average value over the one-hour period.

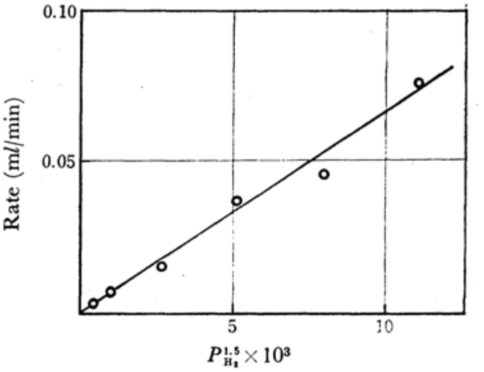

Fig. 6. Dependence of the reaction rate on hydrogen pressure (510°C), the amount of nitrogen uptake being 40 ml (Mo-B).

The rate of the reaction depends on the amount of the nitrogen presorbed on molybdenum as shown in Fig. 7. The rate is proportional to the amount of nitrogen presorbed until the amount reaches eleven times the monolayer value of 4.5 m*l* for the surface.

The apparent activation energy for the hydrogenation was estimated from the Arrhenius plot of the amounts of ammonia formed at fixed conditions of hydrogen pressure (400 mmHg) and nitrogen sorbed (40 m*l*), to be 12 kcal/mol as shown in Fig. 4.

The influence of the oxygen addition to the nitrogen uptake is shown in Fig. 8, and the nitrogen taken up was displaced by successive additions of oxygen where the time intervals between each run were about one-hour. In this case the total displacing ratio of nitrogen to oxygen was approximately ten.

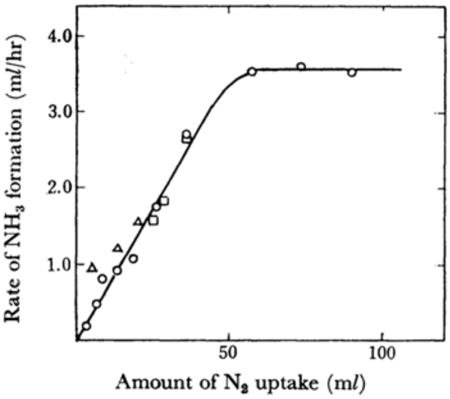

Fig. 7. The dependence of the rate of the reaction upon the amounts of nitrogen uptake at 510°C, the ambient pressure of hydrogen being 400 mmHg (Mo-B).

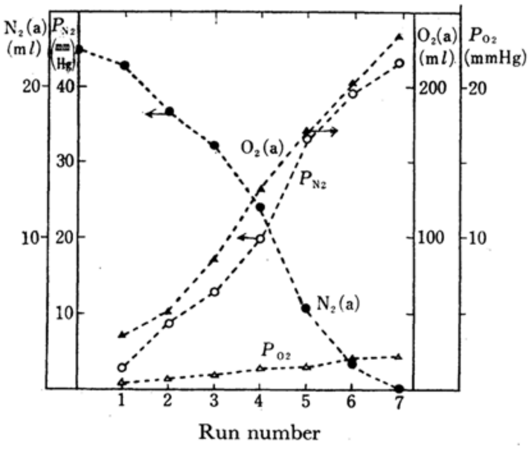

Fig. 8. The effect of oxygen addition to the nitrogen uptake on molybdenum at 400°C. ○: ambient pressure of nitrogen, ●: amounts of nitrogen uptake N_2(a), △: ambient pressure of oxygen, and ▲: amounts of oxygen uptake O_2(a) (Mo-B).

The BET method with nitrogen adsorption revealed the surface area of molybdenum-A to be 0.8 m²/g, that of molybdenum-B 0.5 m²/g, and that of molybdenum trioxide, 1.2 m²/g.

Discussion

1. Decomposition

As shown in Figs. 1 and 2, during the reaction the amounts of nitrogen uptake are greater than V_m in the BET equation, 31.4 m*l*/160 g and 4.56 m*l*/39.6 g, respectively. The results suggest that "surface nitride layers" ate formed of several layers thickness during the ammonia decomposition reaction; the ratio of molybdenum to nitrogen uptake and the result of X-ray diffraction of the sample over which the ammonia was decomposed at higher temperature also support this suggestion.

The decomposition of ammonia over molybdenum may accordingly be shown as

$$NH_3 + 2Mo \rightarrow Mo_2N + 3/2H_2$$

As shown in Fig. 3, the rate of reaction of ammonia with molybdenum is almost independent of the ambient pressure of ammonia above 140 mmHg and seems to be controlled by the rate of diffusion of adsorbed nitrogen into the bulk molybdenum.

The reaction of ammonia with molybdenum trioxide resulted in the decomposition of ammonia to form nitrogen and water vapour, considerable amount of nitrogen being taken up, and the rate of evolution of nitrogen increased with time as shown in Fig. 5. The results may be explained in the following way: molybdenum trioxide is first reduced by ammonia being accompanied by the formation of the nitride; the nitride surface thus formed is active for the decomposition of ammonia and the number of active sites increases with time, while the hydrogen formed may be oxidized immediately to water by molybdenum trioxide.

The agreement in the value of activation energies of the decomposition carried out on the different kinds of catalyst suggests that the active sites on the surfaces are of the same kind and that they exist on a molybdenum nitride surface.

2. The Hydrogenation

The rate of hydrogenation of sorbed nitrogen can be expressed by Eq. (1), as evidenced by the results shown in Figs. 6 and 7.

$$r = k P_{H_2}^{1.5} X_{N_2}$$

where X_{N_2} is the amount of nitrogen taken up, provided that the volume of X_{N_2} is less than 50 m*l*/39.6 g. This dependence of the rate on the amount of nitrogen sorbed is to be noted. Since the monolayer of nitrogen on the surface of the catalyst is 4.6 m*l*, the amount of nitrogen up to 50 m*l* substantially exceeds the V_m value. The fact means that the nitrogen sorbed into the bulk does promote the rate of hydrogenation of surface nitrogen.

The heat of adsorption of nitrogen on a metal would reasonably be expected to be higher than on a metal nitride, and the stability of the adsorbed nitrogen would be decreased due to the nitride layers. The saturation of the promotion shown in Fig. 7 suggests that the bulk nitride phase is established by sorbed nitrogen.

The interpretation of the reaction order in hydrogen must await further investigation.

The high displacing ratio (such as ten) of nitrogen desorbed to oxygen sorbed must be due to oxygen having a higher affinity than nitrogen for molybdenum, and the formation of bulk oxide is suggested.

The interconversions between metal, nitride and oxide are schematically expressed as follows:

$$\begin{tikzcd}
MoO_3 \arrow[r, "NH_3"] \arrow[rr, bend right, "H_2"'] & Mo_2N \arrow[r, shift left, "H_2"] & Mo \arrow[l, shift left, "NH_3{,}\ N_2"]
\end{tikzcd}$$

The authors are grateful to Professor M. Taniguchi for his X-ray analysis.