Mechanism of Ammonia Synthesis over Molybdenum Nitride

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The mechanism of ammonia synthesis has been studied extensively with iron catalysts by many workers, but less frequently with other catalysts of different elements. It has been accepted for the iron catalyst that the elementary step of dissociation of nitrogen molecule determines the rate of the reaction.1) This might be different for the other catalysts. It has been suggested, for those metals which are known to form stable nitrides, that the step of hydrogenation of the dissociated nitrogen determines the rate of the reaction, the step of the dissociation being fast enough.2) In accordance with this suggestion, Kemball *et al.*3) have concluded that the rate of ammonia synthesis over molybdenum nitride is determined by the hydrogenation of adsorbed nitrogen. Since the ready formation of nitride is known with molybdenum, this conclusion appears to be reasonable. However if this conclusion is true, a normal isotope effect by deuterium is expected for the rate of ammonia synthesis over the molybdenum nitride, although a reverse isotope effect was observed for the iron catalyst.4) Thus the deuterium isotope effect in ammonia synthesis over molybdenum nitride was investigated. The catalyst was prepared by reducing molybdenum trioxide (5.09 g) with flowing hydrogen at 492°C followed by nitriding with nitrogen at 502°C. The catalyst thus obtained was identified by X-ray analysis to be Mo_2N. The synthesis runs were carried out in a closed circulating system with a liquid nitrogen trap. The reaction rate was measured by the decrease in total pressure.

It was found that the rate depended on the flow rate and that deuterium reacted faster than hydrogen. A kinetic equation which fits the rate data at 330°C irrespective of the isotopic species of hydrogen is obtained

$$r = 2.5\times 10^{-3}\, P/(1+Ky\sqrt{P})^2,\ (l_{NH_3}/\mathrm{hr})$$

where P is the total pressure, y the concentration of ammonia in the effluent gas from the reactor and K a constant, the value of which is different for hydrogen and deuterium, that is, $K_H=1900$, $K_D=600$.

This result is similar to that on the iron catalyst,4) and a similar interpretation can be applied, that is, the constant K can be interpreted as the equilibrium constant of a dissociative adsorption of ammonia.

$$NH_3 \rightarrow N(a) + 1.5H_2$$

The value of the ratio K_H/K_D ($=1900/600=3.2$) is close to the theoretical one (3.82) which is given as the inverse ratio of the equilibrium constants of ammonia synthesis with hydrogen and deuterium. Thus the rate determining step of the synthesis over molybdenum nitride seems to be the dissociation of nitrogen molecule as was the case for the iron catalyst.

The last conclusion was further examined by the isotopic exchange in nitrogen during the synthesis reaction. The initial isotopic composition of the reactant nitrogen was as follows.

$$^{30}N_2,\ 28.9\%;\ ^{29}N_2,\ 26.6\%;\ ^{28}N_2,\ 44.5\%$$

Seventeen samplings were made during 122 hr of the synthesis over the molybdenum nitride at 330°C by which 72.6 m*l* (N.T.P.) of the reactant gas was consumed. During this synthesis the concentration of $^{29}N_2$ remained at $26.6\pm0.2\%$. This result clearly shows the absence of isotopic mixing in nitrogen during the synthesis and confirms the non-equilibration of nitrogen dissociation during the synthesis reaction.

It may be concluded that the rate of the ammonia synthesis over molybdenum nitride is not determined by the step of hydrogenation of adsorbed nitrogen atom, but by that of dissociation of nitrogen. The rate equation obtained, the isotope effect observed and the non-equilibration of nitrogen dissociation during the synthesis can be understood only from this view.

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1) K. Tanaka, *J. Res. Inst. Catalysis Hokkaido Univ.*, **13**, 119 (1965).

2) W. G. Frankenburg, "Catalysis," Vol III, ed, by P. H. Emmett, Reinhold, N. Y. (1955), p. 190.

3) M. R. Hill, G. Kemball and M. W. Roberts, *Trans. Faraday Soc.*, **63**, 3570 (1967).

4) A. Ozaki, M. Boudart and H. S. Taylor, *Proc. Roy. Soc.*, **A258**, 47 (1960).