Reactivity of Chemisorbed Nitrogen on an Ammonia Synthesis Catalyst

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The ammonia synthesis on an ammonia synthesis catalyst has been treated by means of a new approach, studying the nitrogen chemisorption and the reaction between the chemisorbed nitrogen and hydrogen separately under the reaction conditions. The experimental apparatus and procedures were approximately the same as those previously reported.[1] The catalyst (198 g. with aluminum oxide 5% and potassium oxide 1% before the reduction) was reduced with hydrogen at 500°C for about three thousand hours in a closed circulating system with a liquid nitrogen trap.

The rate of hydrogenation of the chemisorbed nitrogen to form ammonia was proportional to the partial pressure of hydrogen at approximately the same amount of nitrogen chemisorbed, as is shown in Fig. 1, the ammonia produced being always trapped out of the circulating system. The adsorption of hydrogen during the reaction approximately reaches the saturation point at higher pressure, as has been reported previously.[1] Consequently, the rate of the reaction is apparently correlated not with the amount of hydrogen chemisorbed, but with the pressure of hydrogen.

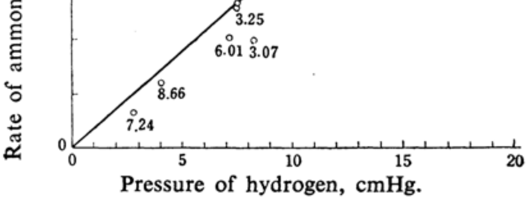

Fig. 1. Dependence of the reaction rate upon hydrogen pressure at 250°C. (N(a) = 33∼37 ml. (stp)) The numbers designate the pressure of nitrogen in cmHg.

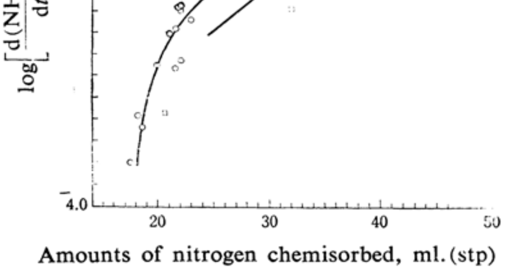

Fig. 2. The rate of hydrogenation of chemisorbed nitrogen to form ammonia as a function of nitrogen adsorption.

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[1] K. Tamaru, Proc. 2nd Intern. Congr. on Catalysis, 1960, p. 325. Technip, Paris, 1961.

The reaction rate was similarly studied in connection with the amount of nitrogen chemisorbed, as Fig. 2 shows. The rate of the reaction was nearly independent of the circulation rate of the reacting gas under the experimental conditions employed.

As Figs. 1 and 2 show, the rate of ammonia formation from the chemisorbed nitrogen and hydrogen, when a negligible amount of ammonia is present, conforms to the following equation except for smaller amounts of nitrogen chemisorbed : $d(NH_3)/dt = CP_{H_2}\exp(\gamma N(a))$ where P_{H_2} is the pressure of hydrogen in the ambient gas, $N(a)$ is the amount of nitrogen chemisorbed, and C and γ are constant. This equation suggests that the Eley-Rideal mechanism is involved.

It is also interesting to note that the reaction of the chemisorbed nitrogen with deuterium proceeds much faster than with hydrogen, as Fig. 2. The author previously found no isotopic effect of hydrogen in the simultaneous adsorption of nitrogen and hydrogen on the catalyst surface.(2) The isotopic effect in the overall reaction, which has been observed by Ozaki, Boudart and Taylor,(3) should, accordingly, be attributed to the effect in the reaction between chemisorbed nitrogen and hydrogen.

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2) K. Tamaru, *Trans. Faraday Soc.*, **59**, 979 (1963).

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