Remarks on the Mechanism of Ammonia Synthesis

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The importance of adsorption measurements during surface catalysis has recently been emphasized[1] and the adsorption measurements during ammonia synthesis on a doubly promoted iron catalyst has been carried out in a closed circulating system. The apparatus was almost the same with that schematically illustrated in a previous paper[1]. The reaction vessel is 12 cm. in length and 3.5 cm. in internal diameter. The circulation pump has a circulation rate between 4.5 and 8.0 l. (stp) per hour depending upon the pressure,

1) K. Tamaru, This Bulletin, **31**, 666 (1958); *Trans. Faraday Soc.*, **55**, 824, 1191 (1959); *Nature*, **183**, 319 (1959).

reaction temperature and composition of the reaction mixture. The reaction usually proceeded in such a way that the ammonia produced was collected in a trap cooled with liquid oxygen. The composition of the circulating mixture of nitrogen and hydrogen was determined with a thermal conductivity cell connected to the circulating system. The amount of ammonia trapped was determined by releasing it into a space between two stopcocks at room temperature. The amounts of the gases adsorbed on the catalyst surface were estimated from the amount of reactants introduced, the pressure and the composition of the circulating gas, and amount of ammonia trapped. Due allowance was made for the analytical samples removed from the apparatus. The promoted iron catalyst employed was obtained from the Government Industrial Research Institute, Tokyo, and contains 5% Al_2O_3 and 1% K_2O. The catalyst (198 g.) was powdered to smaller than 20 mesh and was reduced at 500°C for about 1000 hr. in a hydrogen flow of about 36 l. per hour at about atmospheric pressure, water vapor being removed by means of dry ice or liquid oxygen traps in the reaction system. Before each run the catalyst was evacuated for a few hours, treated with circulating hydrogen for 15 hr. in the system, with the traps maintained at liquid oxygen temperature, and then degassed for one hour. All these operations were carried out at 500°C.

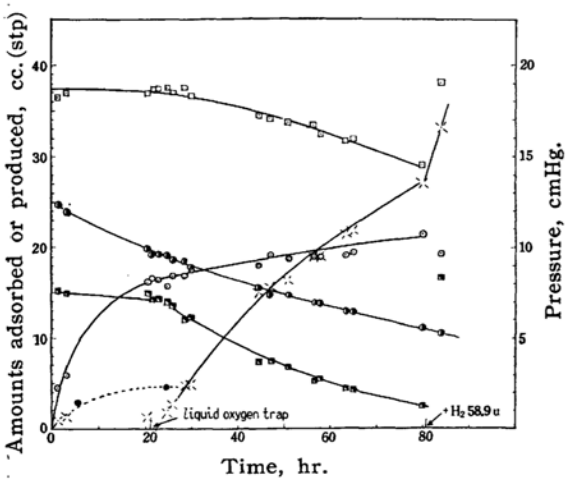

Fig. 1. Adsorption measurements during ammonia synthesis at 180°C. Amounts introduced: Hydrogen, 80.4 cc., Nitrogen, 71.8 cc. (stp).
▣: Hydrogen adsorbed (cc.).
⊙: Nitrogen adsorbed (cc.).
×: Ammonia produced (cc.).
◥: Ambient hydrogen pressure (cm.).
◑: Ambient nitrogen pressure (cm.).
●: Nitrogen adsorption in the absence of hydrogen at P_{N_2}=15.13 cmHg.

TABLE I

Flow rate l.(stp)/hr.	Relative reaction rate
11.23	1.00
5.58	0.95
10.18	1.00
4.98	1.06
12.27	1.00
5.56	0.89
7.70	1.00
3.37	0.98
7.39	1.00
2.98	0.95

Typical results for the experiments at 180°C are shown in Fig. 1 which illustrates experiments in which the ammonia trap was not cooled during the first 21 hr. The reaction rate was measured at a variety of circulation rates including alternately slow and fast rates at 250°C, and the results are shown in Table I, where the total pressure of the circulating reactant was between 22.61 and 11.36 cmHg and the nitrogen content was 28~38%. It is shown in the table that the reaction rate is not very sensitive to the circulation rate in the region in which adsorption was studied. It would appear that in the present studies the circulation rate is so high compared to the reaction rate that the partial pressure of the ammonia produced in the reaction vessel is very small.

According to Scholten and Zwietering[2], the rate of chemisorption of nitrogen on a singly promoted iron catalyst is proportional to the pressure. Hence, if allowance is made for the difference in nitrogen pressure, the results of Fig. 1 show that the rate of adsorption of nitrogen *in the absence of hydrogen* almost corresponds to the rate of ammonia synthesis reported by Emmett and coworkers[3]. This is one reason why they consider nitrogen adsorption to be the rate-determining step in the synthesis. However, as is brought out in Fig. 1, hydrogen causes a marked acceleration in the rate of adsorption of nitrogen. This conclusion is in accordance with the

2) J. J. F. Scholten and P. Zwietering, *Trans. Faraday Soc.*, **53**, 1363 (1957).
3) P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.*, **56**, 35 (1934); S. Brunauer, K. S. Love and R. G. Keenan, ibid., **64**, 751 (1942).

observations of Joris & Taylor, and Kummer & Emmett[4], that isotopic exchange of nitrogen is accelerated by hydrogen.

As shown in Fig. 1, the removal of ammonia from an equilibrated mixture of nitrogen, hydrogen and ammonia has little effect on the adsorption of either hydrogen or nitrogen. Suppose, for example, that all the nitrogen on the catalyst surface takes part in the reaction, then, if all the ammonia in the equilibrated mixture is removed, the adsorbed nitrogen should be rapidly consumed to form ammonia if nitrogen chemisorption is slow compared to all the other surface reaction, including hydrogen adsorption and that ammonia in the reacting gas is negligible. In actual experiments it may be unrealistic to neglect the ammonia pressure completely, but it is to be expected that if all the gaseous ammonia is trapped out the amount of adsorbed nitrogen should fall by an amount corresponding to the distance from equilibrium. But no sign of this tendency could be detected. Consequently, it seems unlikely, as far as one limits his own discussion to the behavior on the whole surface, that the nitrogen chemisorption only is rate determining, though commonly so accepted at present time[5].

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4) G. G. Joris and H. S. Taylor, *J. Chem. Phys.*, 7, 893 (1939); J. T. Kummer and P. H. Emmett, ibid., 19, 289 (1951).

5) C. Bokhoven, C. van Heerden, R. Westrik and P. Zwietering, "Catalysis", edited by Emmett, Vol. III, Reinhold Publishing Corp., New York (1955), p. 265.