CHEMISTRY LETTERS, pp. 555-558, 1987.

Synthesis of Ammonia with RF Discharge.
Adsorption of Products on Zeolite

Haruo UYAMA, Takeshi UCHIKURA, Hideaki NIIJIMA, and Osamu MATSUMOTO*
Department of Chemistry, College of Science and Engineering,
Aoyama Gakuin University, Chitosedai, Setagaya-ku, Tokyo 157

The adsorption of nitrogen-hydrogen molecules formed in the RF discharge on zeolite was studied. The ammonia molecules adsorbed on zeolite as ammonium ions were detected by IR spectroscopy and TPD. The present results obtained show that the ammonia synthesis is facilitated by the surface reactions of the NH_x (x=1,2) radicals adsorbed on zeolite with hydrogen atoms.

In the recent few years, a number of papers on the plasma synthesis of ammonia at low pressure have been published. The typical synthesis procedures are classified in two categories. The first one is the ammonia synthesis by the reaction of nitrogen and hydrogen in a glow discharge at few hundred Pa. In this case, NH_x (x=1,2) radicals formed in the discharge recombined with hydrogen atoms on the surface of a cold trap.1,2) The second one is the reaction of nitrogen and hydrogen in an electron cyclotron resonance (ECR) plasma at 10^{-2} Pa. In this case, the surface reaction of excited N_2 on the wall of the generator is considered as the rate determining step.3) Hydrazine was directly synthesized on various metal oxide catalysts with active nitrogen generated by silent discharge.4,5) NH_x radicals formed in the discharge on the metal surface6) and catalysts7) were detected by XPS. The adsorption of ammonia on zeolite was studied by means of IR spectroscopy8) and a temperature programmed desorption (TPD) technique.9)

As the ammonia synthesis in an radio-frequency (RF) discharge has not been studied, we have investigated the formation of ammonia from nitrogen-hydrogen plasma generated by the RF discharge. Because the zeolite can adsorb ammonia effectively even at room temperature,8) it is used as an adsorbent of ammonia. In this letter, we describe the results obtained for the effect of the adsorption of NH_x radicals formed in the RF (13.56 MHz) discharge at few hundred Pa on zeolite upon the yield of ammonia produced as the preliminary study of the ammonia synthesis by means of plasmas.

Nitrogen-hydrogen (4:1) plasma was generated by the RF discharge in the same way as described in the nitriding of metals in the RF discharge.10) The total gas flow rate, the pressure, and the RF power were maintained at 1.2 dm^3 h^{-1}, 650 Pa, and 200 W, respectively. The discharge was carried out for 3 h in every case. Pellets of zeolite 13X (ordinary 0.1 g) were set in U-tube connected to the end of quartz discharge tube to adsorb radicals formed in the plasma as shown in Fig. 1.

Two types of zeolites were used, one of which was hydrated zeolite as received and the other the dehydrated zeolite obtained after heating at 620 K for 1 h in vacuum. The zeolite was maintained at 300 K, 273 K, or 203 K during the adsorption. Adsorption species on zeolites were analyzed by the IR spectroscopy and the Kjeldahl method. The TPD technique combined with mass spectroscopy was applied to identify the desorbed species from the zeolite. The species formed in the plasma were identified by emission spectroscopy as well as mass spectroscopy.

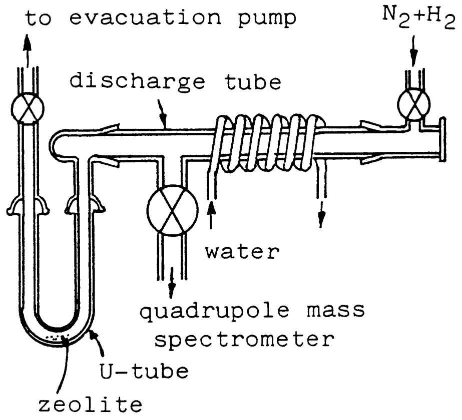

Fig. 1. Experimental apparatus.

The typical IR spectra of zeolite samples which adsorbed radicals at 300 K are shown in Fig. 2. In addition to the absorption bands of zeolite itself in either hydrated or dehydrated state, a band at 1400 cm^{-1} was observed. It was assigned as the absorption due to an NH_4^+ ion. When the adsorption was carried out with zeolite cooled, the absorption intensity was found to increase.

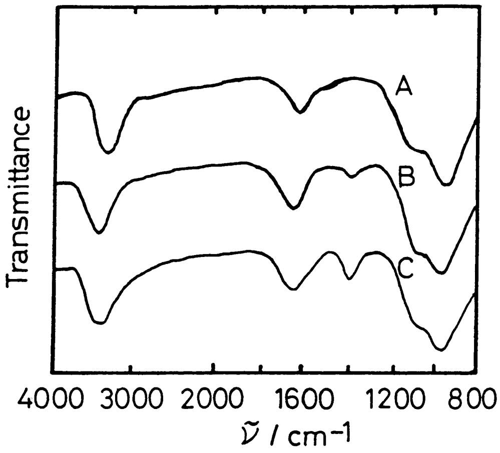

Fig. 2. IR spectra of zeolites which adsorbed nitrogen-hydrogen radicals at 300 K.
A:Zeolite 13X only, B:Adsorbed radicals (hydrated zeolite), C:Adsorbed radicals (dehydrated zeolite).

Typical TPD curves of desorbed gas from the zeolites are shown in Fig. 3. The TPD curve of the hydrated zeolite showed only peak of m/e=18. In the curves of the hydrated zeolite which adsorbed radicals, the peak intensity of m/e=18 was stronger than those of m/e=16 and 17. In the case of dehydrated zeolite, the peak intensities of m/e=17 and 18 were approximately identical and stronger than that of m/e=16. The peaks of m/e=16, 17, and 18 correspond to NH_2^+, NH_3^+, and H_2O^+. A larger amount of water was desorbed from the hydrated zeolite. A larger amount of ammonia is adsorbed on the dehydrated zeolite than on the hydrated zeolite. It was also found that the peak height of ammonia increased by cooling zeolite.

Because both the IR absorption band intensity at 1400 cm^{-1} and the TPD peak intensity due to NH_3^+ become stronger upon cooling zeolite, it is obvious that the amount of ammonia adsorbed on zeolite increases upon cooling zeolite. The yield of

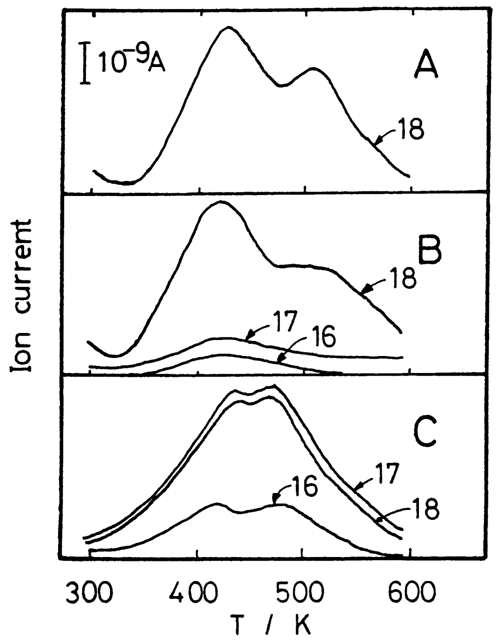

Fig. 3. TPD curves of zeolite. A:Hydrated zeolite only, B:Hydrated zeolite which adsorbed radicals at 300 K, C:Dehydrated zeolite which adsorbed radicals at 300 K, Numericals represent m/e.

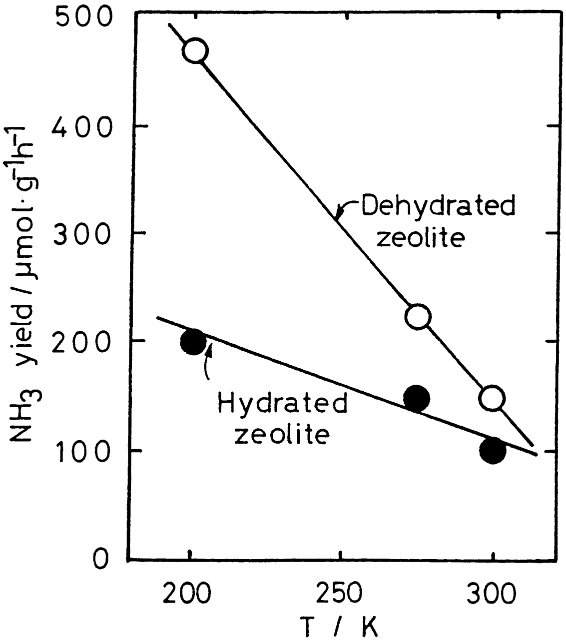

Fig. 4. Ammonia yield in the discharge of nitrogen-hydrogen mixture vs. zeolite temperature.

ammonia (including ammonium ion) determined by the Kjeldahl method is plotted against the adsorption temperature of zeolite as shown in Fig. 4. A considerable amount of ammonia was trapped on zeolite even at room temperature. The ammonia yield increased with decreasing temperature. The yield at zeolite temperature of 200 K was several times larger than that obtained when a cold trap was simply used at same temperature.$^{1)}$ The yields obtained by the discharge of pure nitrogen and for a flow of nitrogen-hydrogen mixture without discharge were also determined. The yields were 12-16 µmol g^{-1} h^{-1} for the discharge of pure nitrogen and less than 10 µmol g^{-1} h^{-1} for the flow of nitrogen-hydrogen mixture without discharge, respectively. The yields were approximately constant at every zeolite temperature.

The emission spectroscopic and mass spectroscopic measurements were carried out to identify the species in the plasma. The emission spectra from the pure nitrogen and nitrogen-hydrogen plasmas were observed with a monochromator in the wave length region between 700 and 200 nm. The first, second and fourth positive systems of N_2 and the first negative system of N_2^+ were observed in the nitrogen plasma. When hydrogen gas was added to nitrogen, the NH ($A^3\Pi - X^3\Sigma^-$) emission as well as some hydrogen atomic emission of Balmer series were observed in addition to the band systems observed in the pure nitrogen plasma. The species in the plasmas were also determined by mass spectroscopy. The ions, H^+, H_2^+, N^+, and N_2^+ were identified in the nitrogen plasma. The ions, H^+, H_2^+, N^+, N_2^+, and NH_x^+ (x=1-3) were identified in the nitrogen-hydrogen plasma.

From the results obtained in this study, it is concluded that the ammonia synthesis is facilitated by the surface reactions of the NH_x (x=1,2) radicals adsorbed on zeolite with hydrogen atoms. Ammonia was adsorbed on zeolite even at room temperature. A larger amount of the NH_x radicals were trapped on the zeolite surface than that trapped on a simple cold trap kept at the same temperature, probably because the surface area of zeolite is much larger than that of a simple cold trap.

References
1) G.Y. Botchway and M. Venugopalan, Z. Phys. Chem. Neue Folge, 120, 103 (1980).
2) K.S. Yin and M. Venugopalan, Plasma Chem. Plasma Process., 3, 343 (1983).
3) O. Nomura, H. Oyama, and Y. Sakamoto, Sci. Paper IPCR, 75, 124 (1981).
4) K. Miyahara, Chem. Lett., 1983, 1871.
5) K. Miyahara, Chem. Lett., 1984, 849.
6) O. Matsumoto, M. Konuma, and Y. Kanzaki, J. Less-Common Met., 84, 157 (1982).
7) K. Sugiyama, K. Akazawa, M. Oshima, H. Miura, T. Matsuda, and O. Nomura, Plasma Chem. Plasma Process., 6, 179 (1986).
8) D. Kunuth and K. Möller, Z. Phys. Chem. Leipzig, 259, 385 (1982).
9) Y. Morikawa, T. Takagi, Y. Moro-oka, and T. Ikawa, J. Chem. Soc., Chem. Commun., 1983, 845.
10) M. Konuma and O. Matsumoto, J. Less-Common Met., 52, 145 (1977).

(Received November 11, 1986)