is a definite need for further study of transfer coefficients at these low Reynolds numbers.

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The Effect of Alkaline Promoter on Decomposition of Ammonia over the Doubly Promoted Iron Catalyst

Several kinetic expressions have been proposed for ammonia decomposition over the doubly promoted fused iron catalysts whereby an important role of the potassium oxide in the mechanism of decomposition was suggested (*1*, *2*). Recently, the present authors have shown (*3*, *4*) that the rate-determining step of ammonia decomposition over a well-reduced doubly promoted fused synthetic ammonia iron catalyst (4.72% Al_2O_3, 0.31% K_2O, 0.05% SiO_2 as promoters) changes with rising reaction temperature, as deduced from the pressure dependencies of ammonia and hydrogen upon the rate. The rate V was thus found to be expressed as $V = k_1(P_{NH_3}/P_{H_2}^{1.5})^{\alpha}$ around 420°C or as $V = k_2(P_{NH_3}/P_{H_2}^{0.5})^{\beta}$ above 479°C, where k_1, k_2, α, and β are constants. These results showed that the rate-determining step is the desorption of the adsorbed nitrogen at lower temperature but the dehydrogenation of the adsorbed amino group $NH_2(a)$ at higher temperature.

This communication deals with the effect of potassium oxide on the reaction mechanism.

The catalyst containing a lower content of potassium oxide than that used in the previous experiments (*3*, *4*) was prepared from a different portion of the same preparation as the catalyst used previously (*3*, *4*), by immersing the unreduced catalyst of 12- to 14-mesh size in distilled water for 72 hr and thus removing a part of potassium oxide from the catalyst. Then it was dried in an oven kept at about 130°C. The content of potassium oxide in the catalyst was determined from potassium oxide dissolved in water. Alumina and silica were assumed not to be lost from the original catalyst. The catalyst thus obtained contained 4.72% alumina, 0.25% potassium oxide, and 0.05% silica as promoters, and it was reduced at 450°C for 45 hr in a stream of hydrogen at a flow rate of 500 cc/min. The apparent volume of the catalyst used was 3.5 cc. The apparatus, procedures, and the purification of gases used were the same as those reported previously (*4*). The kinetic study was made by the pressure dependencies of ammonia and hydrogen upon the rate at 378°C in a flow system using a differential reactor and

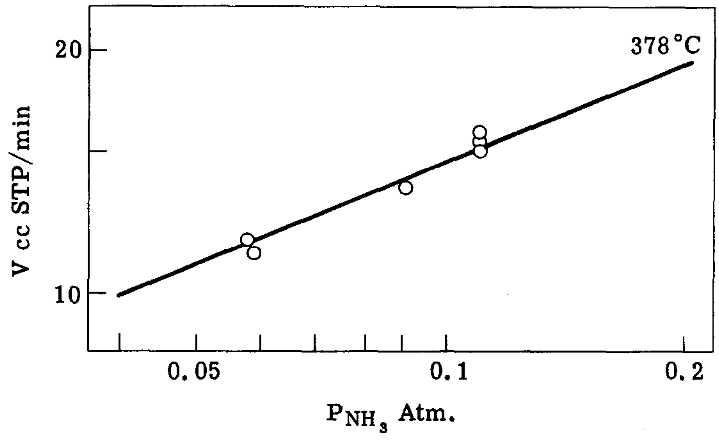

FIG. 1. Rate of ammonia decomposition vs. partial pressure of ammonia P_{NH_3} at the inlet of the catalyst bed. Total inflow, 913 cc STP/min; hydrogen inflow, 420 cc STP/min. Helium was used as diluent.

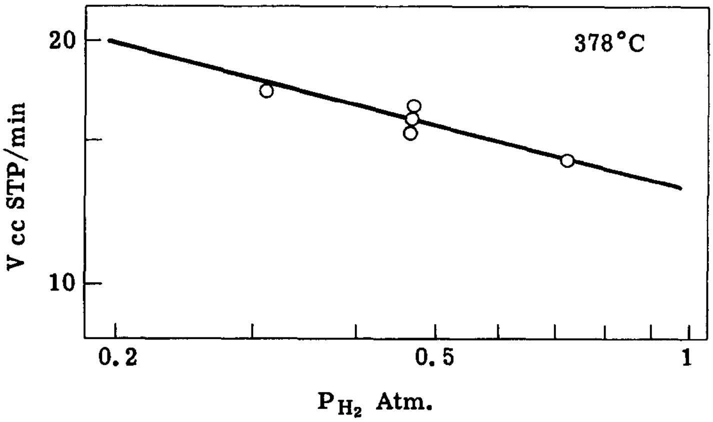

FIG. 2. Rate of ammonia decomposition vs. partial pressure of hydrogen P_{H_2} at the inlet of the catalyst bed. Total inflow 913 cc STP/min; ammonia inflow, 103.3 cc STP/min. Helium was used as diluent.

1 atm total pressure. In order to determine the dependence of the rate upon the partial pressure of ammonia, experiments were performed in which the temperature, the hydrogen flow, and the total flow were held constant and ammonia flow was varied. Helium was used as diluent. In a similar manner, the dependence upon the hydrogen was studied. The rates thus obtained are shown in Figs. 1 and 2 as a function of partial pressure of ammonia and hydrogen at the inlet of the catalyst bed. Evidently the rate V can be approximately expressed as $V = k(P_{NH_3}/P_{H_2}{}^{0.5})^{0.44}$. According to Temkin-Pyzhev theory (*5*) the ratio of the exponents of hydrogen to ammonia should be -1.5, as observed in the previous experiments (*3*, *4*) around 420°C. However, the rate equation obtained in the present experiment is quite similar to that obtained previously above 479°C.

We, therefore, conclude that the rate-determining step of the decomposition changes with the content of the potassium oxide promoter. Furthermore, on the basis of results previously obtained on another catalyst with a high content of potassium oxide at higher temperature, we concluded that the slow step is probably the dehydrogenation of the adsorbed amino group, $NH_2(a)$.

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The Effect of Ionizing Radiation on the Chemical Activity of Alumina*

Kohn and Taylor (*1*) demonstrated that ionizing radiation enhances the activity of gamma-Al_2O_3 as a catalyst for H_2–D_2 exchange. More recent experiments have been conducted with both exchange reaction (*2*) and chemisorption (*3*, *4*) to learn more about the nature of the effect of radiation on alumina. In these previous studies the behavior of the alumina after irradiation was compared to preirradiated samples. To complement these results, a different approach, used in this work, utilized measurements of catalytic activity made during irradiation.

A 5-g sample of adsorption alumina (Fisher Scientific) was irradiated in a 5 megawatt swimming-pool type nuclear reactor. The quartz reaction vessel, sealed in a water-tight canister, was positioned 18 to 30 inches from the reactor core face, where the gamma dose rate drops from 10^7 to 10^6 rad/hr. At these distances the contribution by fast neutrons is less than 1% of the total dose.

Since catalyst activity was gradually poisoned by hydrogen, before each run the catalyst was heated overnight at 500°C in hydrogen or helium. Although poisoning did occur during a run, use of 20% H_2 in helium at 25 psia for the process carrier gas permitted activity measurements in the 50° to 150°C region. To conserve the expensive

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