A New Catalyst System for Ammonia Synthesis

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The well-known doubly-promoted iron catalyst (Fe–Al_2O_3–K_2O) has been industrially adopted for ammonia synthesis since the discovery by Mittasch *et al.* in 1910.[1,2] We have studied the role of potash promoter in this catalyst.[3–6] The reaction has been elucidated in terms of adsorbed species as estimated by kinetics and isotope effect and isotopic exchange in nitrogen. The results led to the conclusion that the potash promoter gives rise to a drastic change in the main adsorbed species over iron during the course of ammonia synthesis, from nitrogen atom over pure iron or alumina promoted iron to imino group over the doubly promoted iron, thus enhancing the rate of ammonia synthesis.[3,4] Another effect of the potash promoter is enhancement of the rate of isotopic mixing in nitrogen over iron in the presence of hydrogen.[5,6] These effects of the potash promoter have been interpreted on the basis of its electron-donating nature. If the observed effects by potash are produced by an electron donation to iron, metallic potassium would be more effective owing to its much lower ionization potential. This prediction has been tested and extended to other transition metals.

Catalysts were prepared by impregnating coconut carbon with transition metal chlorides from aqueous solutions, followed by reduction in hydrogen stream at 400°C and by adsorption of potassium vapor at about 400°C. The content of transition metal was 2.5 or 5% wt. of the carbon support. The rate of ammonia synthesis was determined in a closed circulating system equipped with a liquid nitrogen trap using a stoichiometric mixture of hydrogen and nitrogen under 600 mmHg. The reaction temperature ranged from 100 to 400°C.

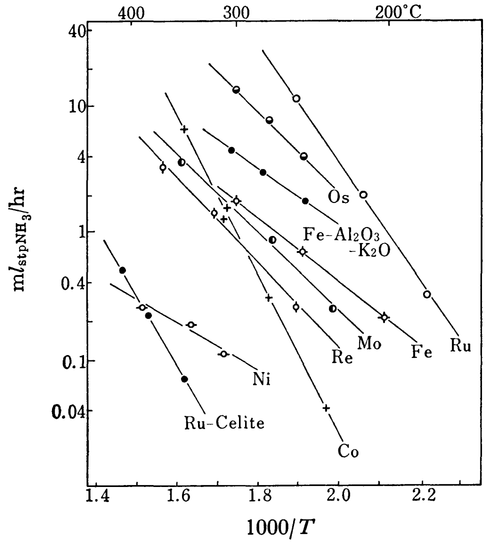

Fig. 1. Arrhenius plots of synthesis rates at a flow rate of 4.5 *l*/hr under 600 mmHg over catalysts of 2.5 g each except Fe–Al_2O_3–K_2O (0.77 g) and Ru–Celite (1.5 g). Os catalyst was prepared from OsO_4.

The results are summarized in Fig. 1 where Arrhenius plots of the rate of ammonia synthesis are shown for several transiton metals, together with previous data on ruthenium celite[7] and the doubly promoted iron.[8] None of these metals, when supported on the coconut carbon without potassium added, showed any activity even at 400°C for the ammonia synthesis, whereas pure iron or ruthenium on Celite can produce ammonia at a measurable rate.[3,7] On the other hand, potassium metal adsorbed on the coconut carbon not impregnated with a transition metal also showed no activity at 400°C, while potassium metal adsorbed on reduced iron remarkably enhanced the rate of ammonia formation. It is thus concluded that potassium metal added enhances the rate of ammonia synthesis on the transition metal.

Figure 1 shows that Ru and Os rank high among the transition metals tested. Fe, Co, Re, and Mo are moderately active, and Ni is much less active. Very little or no activity was detected on Ti, Mn, Rh, and Pd even with adsorbed potassium. The results show that the active catalysts are formed by the metals known to catalyze ammonia synthesis without a promoter such as potassium.[2] In this respect, the effect of potassium is not so specific for the kind of transition metal. But Ru–C–K catalyst has outstanding activity and is able to form ammonia with a rate of 0.037 *ml*·STP NH_3/hr 2.5 g at 146°C and 600 mmHg. This catalyst seems promising for low temperature synthesis of ammonia.

In view of rather low specificity in the effect of potassium, the basic pathway of ammonia formation would be unchanged by the addition of potassium, although the rate determining step might change. The remarkable effect of potassium can be understood if a nitrogen molecule is activated to an anionic intermediate by incorporation of a free electron in a transition metal, simply because an electron transfer from alkali to the transition metal takes place on addition of alkali metal. In agreement with this, sodium, which has a higher ionization potential than potassium, gives a much lower activity than potassium.

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