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AMMONIA SYNTHESIS OVER RHODIUM, IRIDIUM AND PLATINUM PROMOTED BY POTASSIUM

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Rhodium and Iridium on active carbon were found to be highly effective for ammonia synthesis when activated by potassium. Palladium appeared to be hardly activated, while platinum can be activated, by the addition of potassium. A characteristic activity pattern was found for the new catalyst system.

It has been reported that the rate of ammonia synthesis over transition metals is remarkably promoted by addition of alkali metal, particularly when the metals are supported by active carbon (AC)1,2) or alumina.3) It has been discussed that the promoter action is provided by a charge transfer from alkali metal to transition metal which brings about a high electron density in the transition metal, a favorable state for the activation of nitrogen.2,3)

Such transition metals as Ru, Os, Fe, Re, Mo, Co and Ni were already reported to be promoted by addition of alkali metal.1) It is to be noted that the above metals themselves are known to be active elements.4) Rh, Ir, Pd and Pt are known to have no ability for nitrogen chemisorption5) and very little or no activity for ammonia synthesis.6) Pt has been reported to catalyze ammonia synthesis at very high temperature and pressure.7) Rh, Ir and Pd are known to catalyze ammonia decomposition at high temperature,8) while never reported to catalyze ammonia synthesis.

It is interesting to examine how these noble metals are promoted by addition of alkali metal. Ru was previously reported to be the most active element when activated with alkali metal, while Rh which is adjacent to Ru on the periodic table was reported to have little activity in the previous paper.1) The authors repeated careful experiments to examine the reason for the lack of activity over Rh system. Meanwhile it was found that the previous report of no activity for Rh is

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erroneous. Ir, Pd and Pt were also examined.

The catalysts used in this work are 2.5 g of 5 wt% Rh, Ir, Pd and Pt supported on AC. The catalysts were reduced in hydrogen stream at 120°C for 6 hr and 400°C for 18 hr. They were confirmed not to catalyze ammonia synthesis at 450°C without potassium. About 15 mg of potassium was added to these catalysts, followed by standing in streaming helium at 400°C for 6 hr. The synthesis runs were carried out at 200-460°C with 600 Torr of N_2+3H_2 and 4.5 l/hr of flow rate.

Rh, Ir and Pt systems were found to be effective for ammonia synthesis, and to have stable activity. Both Rh and Ir systems have activities as high as Fe system. The apparent activation energies of Rh, Ir and Pt systems are 9, 13 and 18 kcal/mol respectively. No ammonia was detected in the run at 450°C for 26 hr over Pd-AC-K, which only absorbed hydrogen. The activities at 250°C over the transition metal-AC-K systems are plotted against $-\Delta H_0^0$ and shown in Fig. 1 together with the data of other metal systems previously reported.[1)] The value of Pt system is obtained by an extraporation from the data at 372-470°C. $-\Delta H_0^0$ in Fig. 1 is the heat of formation of highest metal oxide per metal atom that has been proposed as a general parameter for the heat of chemisorption of gases.[9)]

It is shown that the activity of new catalyst system exhibits a so-called volcano-pattern, although Co and Ni systems somewhat deviate. No activity of Pd system is reasonable on this pattern because of its low value of $-\Delta H_0^0$ (21 kcal/Pd atom).[10)] It has been assessed that the most active elements for the ammonia synthesis are Fe and Os, with Ru being less active.[4)] In this respect it is remarkable that Ru can be the most active element and Rh, Ir and Pt can be activated for the ammonia synthesis when they are promoted by metallic potassium. It is interesting to compare the activity pattern of new catalyst system to that of metal film for ammonia decomposition,[11)] which is shown in Fig. 2.[12)] It is to be noted that both figures are quite similar. Ru is the most active and both Co and Ni are irregularly less active.

It can be pointed out on the basis of above results that the effective site for ammonia synthesis over the new catalyst system lies on the transition metal surface, and not on AC nor alkali metal and that the basic mechanism is unchanged by the addition of alkali metal. However, the surface condition must be changed by the addition of alkali metal, because those metals such as Ru, Rh, Ir and Pt which are known to be unable by themselves to activate nitrogen molecule are extremely promoted by the addition of potassium. The surface of alkali metal-

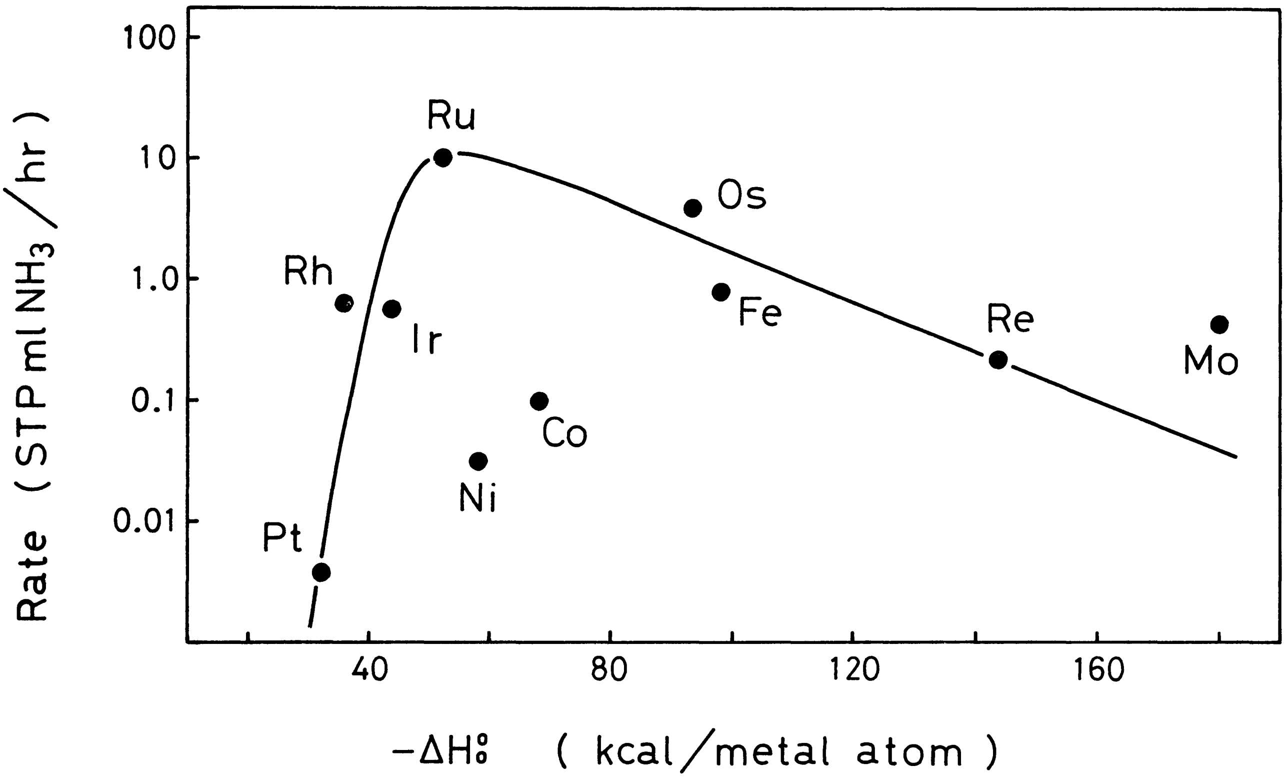

Fig. 1 Rate of ammonia synthesis over 2.5 g of 5 wt% transition metal-AC-K at 250°C, under 600 Torr and 4.5 l/hr of flow rate as a function of $-\Delta H_0^0$.

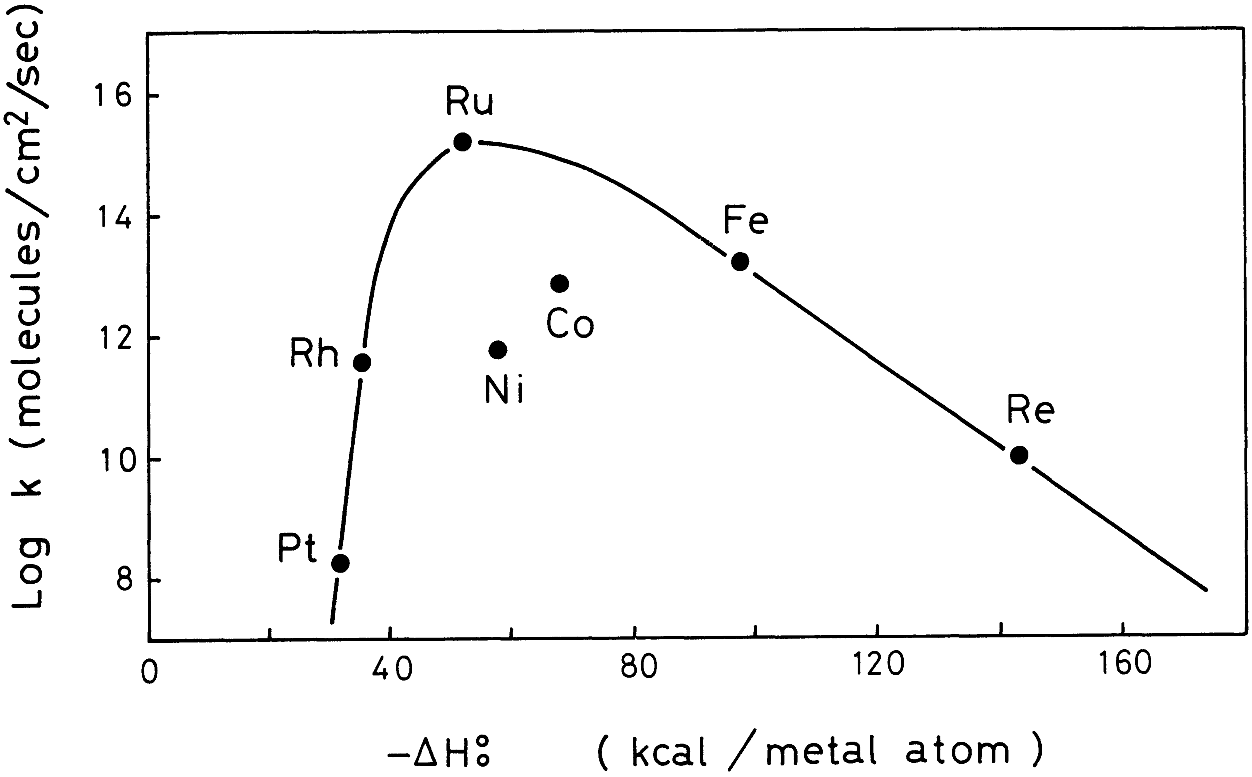

Fig. 2 The rate constant of ammonia decomposition on metal films at 400°C as a function of $-\Delta H_0^0$.

promoted transition metal should possess a high electron density and thus a stronger affinity for nitrogen.

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