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COOPERATIVE INCORPORATION OF POTASSIUM AND NITROGEN INTO METALLIC RUTHENIUM

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Nitrogen uptake by metallic ruthenium is enhanced by the presence of potassium vapor, simultaneously increasing the stable incorporation of potassium, demonstrating a "binder action" of nitrogen. The molar ratio of nitrogen uptake to the stable potassium suggests a chemical formula $(KN_2Ru)_n$, as supported by formation of hydrazine on hydrolysis.

It has been shown that ruthenium is remarkably promoted by addition of metallic potassium as a catalyst for the ammonia synthesis as well as the isotopic equilibration of nitrogen[1,2]. The Ru-K catalyst has been found to give stable activity in repeated runs at elevated temperatures[2], suggesting a strong interaction between the two components. It has been supposed that ruthenium reacts with potassium to give a sort of compound[1], as is the case with Au-Cs system[3]. A search was made to obtain an evidence for the interaction by measuring the change in electric resistance of ruthenium film on addition of cesium. Although no indication of compound formation was obtained, it was found that the resistance changed irreversibly to a lower value when nitrogen was introduced on the ruthenium film covered with cesium, suggesting an incorporation of nitrogen. In this way the present study of nitrogen incorporation has been initiated.

The ruthenium metal in a form of powder(BET area 0.9 m^2/g) was obtained from Tanaka Noble Metals and reported to be of 99.9% purity. The ruthenium powder(0.5-1.0g) was pretreated with circulating hydrogen at 470°C for 24 hr to remove sorbed oxygen followed by evacuation at 400°C for 2 hr. The metallic potassium(about 0.1g) was placed on top of a bed of the ruthenium powder at room temperature in atmosphere of helium and was melted to be distributed among the bed. After evacuation for 2 hr, nitrogen (210 torr) was introduced at room temperature and the temperature was raised in circulating nitrogen. The time course of nitrogen uptake was followed by pressure change at fixed temperature. The nitrogen was freed from oxygen by passing it into a column of reduced copper at 200°C.

The time courses of nitrogen uptake at temperatures are illustrated in Fig.1. A slow uptake is observed even at 250°C and the rate of uptake increases with increase in temperature. At each temperature the faster initial uptake is followed by much slower uptake which does not stop even after 40 or 50 hr. The amount of uptake thus attained is in a range of 0.1-0.15 mmol/gRu. Since the number of surface ruthenium atoms can be estimated to be 0.016 mmol/gRu from the BET area using a cross sectional area of ruthenium atom: 9.4 $\mathring{A}^2$ [4], the uptake reaches 6-9 times the number of surface ruthenium atoms, suggesting an absorption or a corrosive chemisorption of nitrogen. In fact when the nitrogen pressure was stepwise decreased to 3 torr, no detectable desorption was observed at 350°C for 38 hr, indicating irreversibility of the uptake.

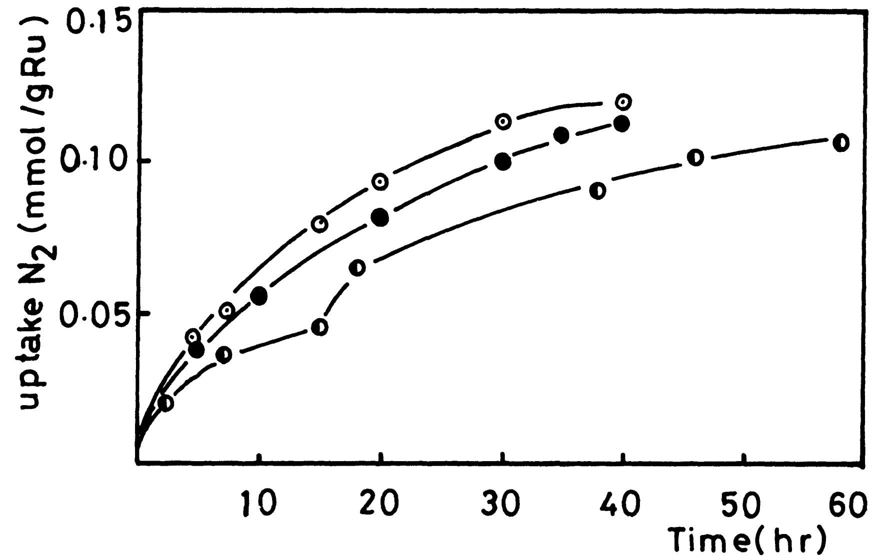

Fig. 1. Time course of nitrogen uptake
-⊙- 450°C -●- 350°C
-◐- 250°C and 300°C from 15 hr on

On the other hand the amount of potassium held by the ruthenium powder was determined by acid titration of water extract. The potassium content right after the nitrogen uptake was found to be as large as 0.6 mmol/g. Since the potassium content might involve desorbable one, the effect of evacuation on the potassium content was examined at 350°C after the uptake at 350°C for 40 hr and is illustrated in Fig.2. The potassium content decreases with increase in the evacuation time, while it approaches a stable value of about 0.15 mmol/g after 2 hr. In order to examine the effect of nitrogen, the potassium addition was carried out in helium instead of nitrogen at 350°C. Firstly the potassium content in this sample(0.18 mmol/g) was much less than 0.6 mmol/g for the sample prepared in nitrogen. Secondly the potassium content decreased to a negligible value(0.006-8 mmol/g) after evacuation at 350°C for 2 hr as shown in Fig.2. It is clear that nitrogen enhances the incorporation of potassium and strikingly increases the stability of incorporated potassium, suggesting a "binder action" of nitrogen.

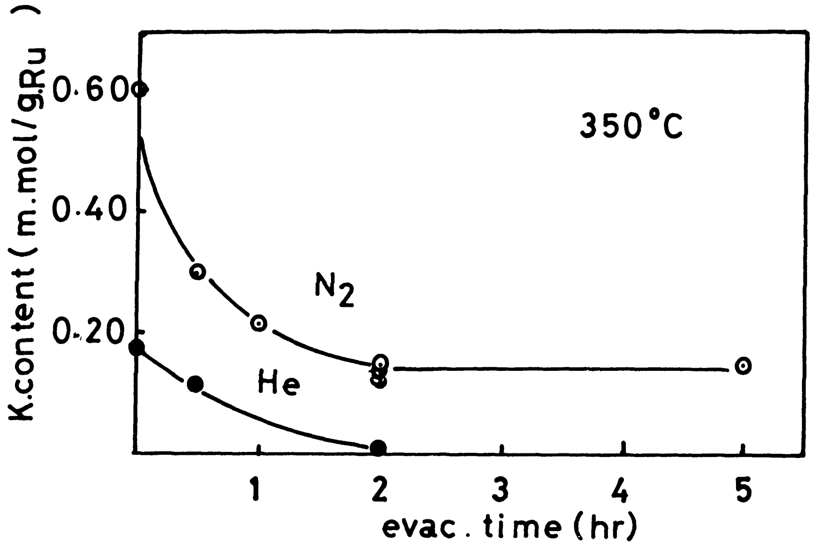

Fig. 2. Variation of potassium content with evacuation time at 350°C

Since the nitrogen uptake can be regarded to be irreversible, it may be assumed that the nitrogen content stays at the initial value during evacuation, while the potassium content decreases to the stable value which represents the part of potassium strongly held. Thus the potassium contents were determined after evacuation for 2 hr at 350°C irrespective of the temperature of potassium addition and regarded as the stable potassium content. Although the stable value not only depended on the temperature of potassium addition, but also changed a little run by run even at a fixed temperature of potassium addition, it would be of interest to examine the nitrogen uptake relative to potassium content. The ratios, N_2/K (mol/mol), are represented as a function of the stable potassium content in Fig.3. It is disclosed that the ratios are near unity in conformity with the idea of nitrogen binder, suggesting a chemical formula of $(KN_2Ru)_n$. The observed slow uptake is reasonable as a gas-solid reaction process to form such a compound.

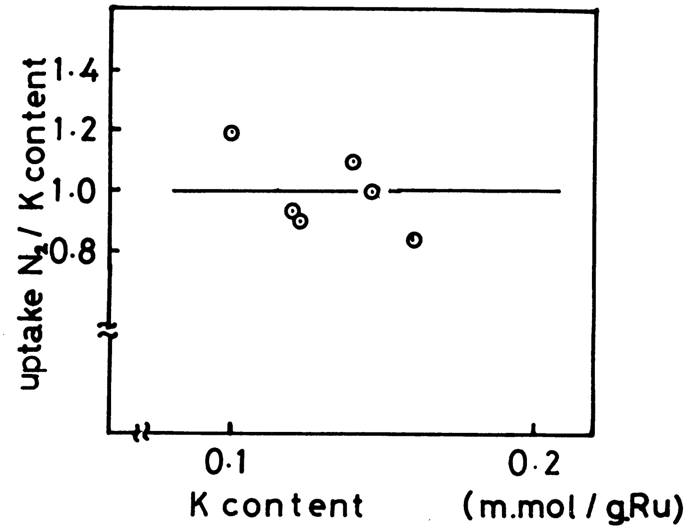

Fig. 3. Molar ratio of nitrogen uptake to stable potassium as a function of stable potassium content

Since the potassium content changes with evacuation as shown in Fig. 2., the catalytic activity of the Ru-K sample may also change with evacuation. The activity for the isotopic equilibration of nitrogen was determined after the potassium addition at 350°C for 40 hr in nitrogen or helium followed by evacuation for different periods at 350°C. The procedure of activity determination was the same as described in a previous paper[5]. As shown in Fig.4, the rate of isotopic equilibration,R, at 350°C passes a maximum and approaches a stable value on the sample prepared in nitrogen, while the rate on the sample prepared in helium is not only smaller in the initial value, but also decreased rather rapidly by the evacuation, demonstrating that the coorperatively incorporated potassium is required to give the high activity. It is suggested that the weakly held potassium also gives rise to an enhanced activity.

From the foregoing evidences it is clear that the highly active ruthenium catalyst is formed by the cooperative incorporation of nitrogen and potassium to give a compound, possibly $(KN_2Ru)_n$. Although the above evidences were obtained with the powder of ruthenium, similar slow uptake of nitrogen has been observed also on Ru-K/Al_2O_3[6] where potassium reacts with alumina so that the stoichiometric correlation between potassium and nitrogen is obscure. Moreover an intense IR band of "chemisorbed dinitrogen" has been

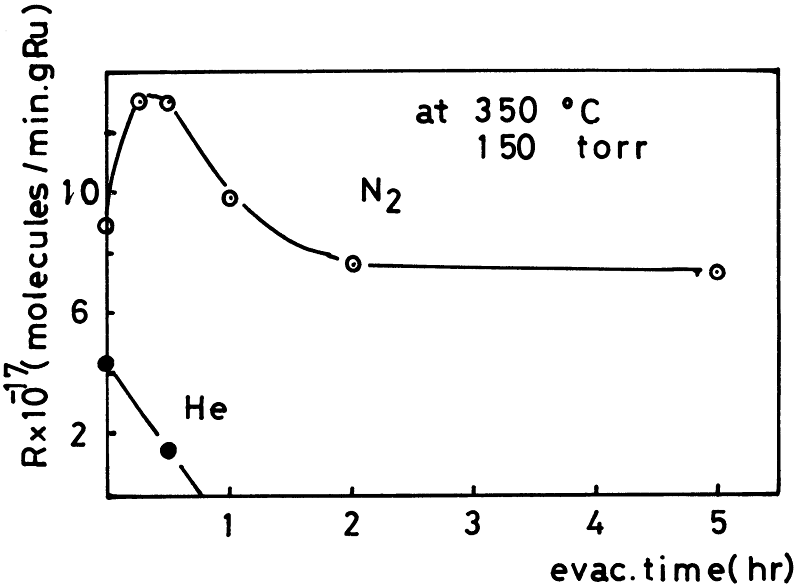

Fig. 4. Variation of catalytic activity for isotopic equilibration with evacuation time at 350°C

found at 2020 cm^{-1} on Ru-K/Al_2O_3[7]. The appearance of the band on nitrogen chemisorption is as slow as the above slow uptake. Thus it is very likely that the 2020 cm^{-1} band is ascribed to the dinitrogen species formed in the bulk. In fact when the ruthenium sample containing the incorporated nitrogen and the stable potassium was decomposed in water at room temperature in atmosphere of argon, about 10% of nitrogen uptake was recovered as hydrazine from the water extract by vacuum distillation, where hydrazine was determined by UV absorption according to the known method[8]. Moreover the dried residue of water extract was found to contain ruthenium as confirmed by emission spectrograph, suggesting a water-soluble ruthenium complex. Indeed, the residue was pinky in appearance and seemed to be mixture of a red crystalline compound with potassium hydroxide. Its IR spectrum taken with KBr gave intense bands at 2160 and 2200 cm^{-1}. Similar bands have been accepted as an indication of the presence of an N_2 molecule linearly coordinated to a metal atom[9]. In this way it is very likely that nitrogen is incorporated in a form of dinitrogen complex which is partly converted to hydrazine on hydrolysis. Interestingly a heteronuclear dinitrogen complex $KN_2Co[P(CH_3)_3]_3$ was reported very recently[10].

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