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Potassium–Dinitrogen–Ruthenium Complex as an Active Catalyst for Nitrogen Fixation

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Potassium uptake by metallic ruthenium is enhanced and stabilized by the presence of nitrogen, accompanying a significant nitrogen uptake. The stabilized part of potassium uptake which can not be removed by evacuation at 350°C is in a stoichiometric relation to the nitrogen uptake, suggesting that the uptake is caused by formation of a ternary compound $(KN_2Ru)_n$. Electric resistance of ruthenium film seems to be decreased slightly by formation of the ternary compound. The potassium adsorbed on this compound gives rise to an enhanced activity for the isotopic equilibration of dinitrogen. The dinitrogen nature of the ternary compound is supported by formation of hydrazine in addition to ammonia and a dinitrogen complex of ruthenium upon hydrolysis as well as ethanolysis.

It has been shown that ruthenium, supported or unsupported, is promoted by addition of metallic potassium for the activation of dinitrogen such as ammonia synthesis (*1*) or isotopic equilibration of dinitrogen (*2*), and that the supported Ru–K catalysts absorb considerable amounts of nitrogen during the reaction (*3, 4*). It has been suggested that there are at least three types of sorbed nitrogen species, i.e., (1) adsorbed nitrogen, atomic or molecular on the ruthenium surface, (2) bound nitrogen on potassium, (3) corrosively chemisorbed nitrogen in the bulk of ruthenium (*4*). On the other hand, it has been found that the catalytic activity of Ru–K is quite stable for a long period, suggesting a strong interaction between Ru and K. Since cesium and gold readily react to form a compound CsAu, as demonstrated by a remarkable increase in electric resistance (*5, 6*), ruthenium, having a similar magnitude of electronegativity as that of gold, might form a compound CsRu or KRu at least in the surface layer. Thus the interaction between Ru and Cs has been examined by measuring changes in electric resistance on addition of cesium vapor to ruthenium film. Although we could not find evidence for CsRu compound formation, we have incidentally found an indication for an incorporation of nitrogen into the Ru–Cs system. The present paper deals with the incorporation of nitrogen into the Ru–K system as well as the stability and reactivity of incorporated nitrogen.

EXPERIMENTAL SECTION

Material

Ruthenium powder (99.99%, 150 mesh) was obtained from Tanaka Precious Metal, Ltd. The specific surface area was determined to be 0.9 m^2/g by adsorption of krypton. The ruthenium powder was pre-

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treated with hydrogen at 470°C for 24 hr prior to use. Nitrogen gas was freed from oxygen by passing through a copper–kieselguhr column at 200°C. Metallic cesium was prepared from cesium chloride by reducing it with metallic magnesium at about 800°C and purified by vacuum distillation. Metallic potassium obtained from a commercial source was melted and packed into glass capillaries. The amount of potassium sample could be roughly estimated by measuring the length of capillary so that the desired amount of potassium could be placed in the apparatus.

Procedure

Measurement of film resistance. Since ruthenium filaments were commercially unavailable, a ruthenium film was prepared by evaporation from metal powder by electron beam gun onto a glass plate (25 × 55 mm) which had silver terminals at both ends. The thickness of the ruthenium film was estimated to be about 500 Å by multiple beam interferometry and by conventional gravimetry (*7*). The ruthenium film on the glass plate was placed in a glass vessel equipped with terminals and treated with hydrogen at 350°C for 10 hr to remove adsorbed oxygen, followed by evacuation at 350°C to give a constant value of film resistance at 350°C.

The electric resistance measurements were carried out by using electric currents below 5 mA.

Nitrogen uptake and isotopic equilibration. The nitrogen uptake and the rate of isotopic equilibration were determined in a closed circulating system, connected to a manometer, a gas burette, and a quadrupole-type mass spectrometer which permitted continuous analysis of the circulating gas. The nitrogen uptake was followed by pressure change. The procedure for determining the rate of isotopic equilibration was the same as previously reported (*2, 4*).

Analysis. The amount of potassium incorporated into ruthenium was determined by acid titration of water extract. Hydrazine formed in the water extract was determined by visible spectrophotometry for the *p*-dimethylaminobenzaldehyde adduct which absorbed at 460 nm (*8*). The amount of ammonia formed in the water extract was determined by visible spectrophotometry for a color (720 nm) developed by the reaction with sodium hypochlorite and α-naphthol (*9*).

RESULTS

Change of Resistance of Ruthenium Film upon Deposition of Cesium

Although the resistance of ruthenium film decreased with time at 350°C presumably due to sintering, it reached a stable value (365 Ω at 350°C and 258 Ω at 25°C) after 24 hr of heat treatment at 350°C. The stability was confirmed by repeated heating to 350°C and cooling to room temperature. When the cesium vapor was introduced on the ruthenium film at room temperature, the film resistance decreased to 58 to 158 Ω depending on the amount of cesium introduced; it recovered gradually to the original value (258 Ω) within 10 hr in vacuum. Even when the film with cesium was heated to 350°C, the resistance increased up to the original value (365 Ω) for the ruthenium film at 350°C. There was no indication of CsRu compound formation which should give rise to an increase in the resistance. Thus the change of film resistance was followed in the presence of nitrogen gas and compared with that in helium. When helium [150 Torr (1 Torr = 133.3 N m^{-2})] was introduced after deposition of cesium on ruthenium film, the film resistance recovered more slowly than in vacuum, suggesting that gas-phase helium retards evaporation of cesium. Although the film resistance recovered to the original value even in helium, the final value of film resistance was smaller than the original value by about 10 Ω when the film was heated to 350°C in the presence of nitrogen instead of helium. This irreversible change in the film resistance was repeatedly confirmed in the presence of nitrogen gas, demonstrating an incorporation of nitrogen into Ru–Cs system. Thus it was decided to investigate the incorporation of nitrogen by volumetric measurements.

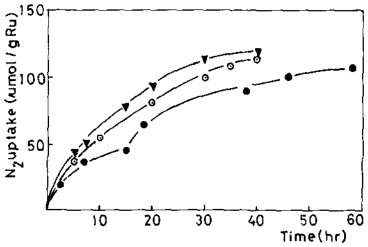

FIG. 1. Time course of nitrogen uptake: ▼, 450°C; ⊙, 350°C; ●, 250°C (0 to 15 hr) and 300°C (15 to 58 hr).

Nitrogen and Potassium Uptake by Ruthenium Metal

The nitrogen uptake by ruthenium powder was determined in the presence of potassium vapor at temperatures from 250 to 450°C. The metallic potassium (about 0.1 g) in the capillary was placed on top of a bed of the hydrogen-treated ruthenium powder (0.5 to 2.0 g) at room temperature in an atmosphere of helium. After melting, it was distributed throughout the bed. After evacuation for 2 hr, nitrogen gas (210 Torr) was introduced at room temperature, and the temperature was raised in the circulating nitrogen.

The time courses of nitrogen uptake at various temperatures are shown 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 has not reached saturation even after 40 to 50 hr. The total uptake is in a range of 100 to 150 μmol/g Ru. Since the number of surface ruthenium atoms can be estimated to be 16 μmol/g Ru from the BET area using a cross-sectional area of the ruthenium atom, 9.4 Å^2 (*10*), the sorbed N_2 is six to nine times the number of surface ruthenium atoms, suggesting an absorption or a corrosive chemisorption of nitrogen. Thus the stability of incorporated nitrogen was examined by volumetric determination of desorbed gas. When the nitrogen pressure was stepwise decreased from 339 to 0.06 Torr at 350°C, the total amount of desorbed gas was 2.2 μmol/g Ru in 6 hr which corresponded to 1.5% of the uptake, indicating that the incorporated nitrogen was essentially irreversible at this temperature.

The amount of potassium held by the ruthenium powder was determined after each uptake measurement. Although the potassium content was found to be 600 μmol/g Ru after the nitrogen uptake at 350°C (40 hr), it decreased with the time of evacuation at 350°C to a stable value of about 150 μmol/g Ru after 2 hr of evacuation as illustrated in Fig. 2. In order to examine the effect of nitrogen on the potassium content, the ruthenium powder was exposed to potassium vapor in circulating helium instead of nitrogen, at 350°C for 40 hr. The potassium content of the ruthenium powder was determined after varied times of evacuation and is shown in Fig. 2. The potassium content is much less for the helium-prepared sample than that prepared in nitrogen. It decreases to a negligible value (6 to 8 μmol/g Ru) after evacuation at 350°C for 2 hr. It is clear that the potassium taken up in helium is mostly desorbable in contrast to that taken up in nitrogen.

The potassium uptake in a nitrogen atmosphere may be classified as at least two types: desorbable and undesorbable. The former would be regarded as adsorbed potassium which can be formed even in the presence of inert helium. The latter is

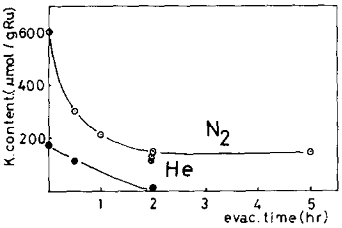

Fig. 2. Variation of potassium content with evacuation time at 350°C.

demonstrated by the stable potassium content obtained after evacuation for 2 hr at 350°C and can be traced back to the chemical nature of nitrogen because the inert helium does not result in such uptake. The uptake of potassium in the presence of nitrogen suggests that nitrogen acts as a "binder" between ruthenium and potassium.

If the role of nitrogen in uptake of the potassium is chemical in nature, there may be a stoichiometric relation between potassium and nitrogen. Since the nitrogen uptake is mostly undesorbable by evacuation at 350°C, the nitrogen content in the ruthenium powder may be regarded to be constant even after evacuation, while the potassium content decreases to a stable value during evacuation for 2 hr. Thus the potassium content was 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 potassium content is a function of the temperature and the time of potassium addition, the nitrogen uptake also changes. The molar ratio of nitrogen uptake to the stable potassium content, N_2/K, are represented as a function of the stable potassium content in Fig. 3. Although the data are somewhat scattered, they are located within a range of 1.0 ± 0.2, indicating a stoichiometric relation of dinitrogen with potassium. Since both the uptakes are much larger than the number of surface ruthenium atoms, the incorporation seems to proceed cooperatively into the bulk of ruthenium metal. The observed slow uptake is thus reasonable, if it is limited by a solid phase rearrangement. In view of the "binder" nature of nitrogen, ruthenium also should be involved in the stoichiometric reaction.

Catalytic Activity of Ruthenium Modified with Potassium and Nitrogen

It has been shown that ruthenium is promoted by addition of metallic potassium for the isotopic equilibration of nitrogen (*2*, *11*). In these studies, the potassium addition was carried out in helium and was followed by the introduction of nitrogen to be adsorbed. Since the cooperative incorporation of potassium and nitrogen into ruthenium was found in the present study, it was decided to study the effect of nitrogen incorporation on the catalytic activity. Thus the catalytic activity for the isotopic equilibration of nitrogen was determined after the potassium treatment of ruthenium powder (350°C for 40 hr) in nitrogen or helium, followed by evacuation for different periods of time at 350°C. The catalysts thus prepared were exposed to a $^{15}N_2$–$^{14}N_2$ mixture (150 Torr) at 350°C for 10 hr when prepared in nitrogen and for 24 hr when prepared in helium. Although no further uptake was observed with the sample prepared in nitrogen, the uptake of isotopic nitrogen by the sample prepared in helium was as follows: 56 μmol/g Ru right after the potassium treatment and 10 μmol/g Ru after 30 min of evacuation at 350°C.

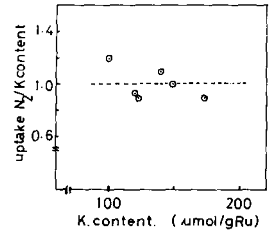

Fig. 3. Molar ratio of nitrogen uptake to stable potassium as a function of stable potassium content.

The results of the activity measurements as a function of evacuation time are shown in Fig. 4, because the potassium content changes with evacuation time as shown in Fig. 2. The rate of isotopic equilibration, or the catalytic activity, at 350°C first increases with the evacuation time and, after passing a maximum, approaches a stable value on the catalyst sample prepared in nitrogen, while the rate on the catalyst sample prepared in helium is not only smaller in the initial value, but also decreases rather rapidly by the evacuation, demonstrating that the stable potassium is required to give high activity. It is also disclosed that the weakly held potassium also gives rise to an enhanced activity.

Hydrolysis of Incorporated Nitrogen and Potassium

The fate of incorporated nitrogen on hydrolysis is of interest. During the determination of the potassium content of the ruthenium powder, it was found that the water extract gave a white precipitate on addition of Nessler reagent, suggesting that some nitrogen compound other than ammonia is formed by hydrolysis. Thus several runs were made to identify the product of hydrolysis. The sample powder was prepared by potassium treatment of the ruthenium powder in nitrogen at 350°C for 40 hr followed by evacuation at 350°C for 2 hr. It was transferred to 20 ml of water under an argon atmosphere. After standing for 24 hr at room temperature, the insoluble residue (unreacted ruthenium powder) was separated by filtration, again under an argon atmosphere, to give a pale reddish filtrate in which ruthenium was found present by emission spectroscopy. The filtrate was distilled in vacuum to dryness to give a pinkish white residue which gave two ir-absorption bands at 2160 and 2200 cm^{-1}, as shown in Fig. 5. The bands were assigned to a dinitrogen species because the analogous $^{15}N_2$ (97.5%) uptake resulted in a band shift to 2103 and 2155 cm^{-1}. The presence of nitrogen in the residue was confirmed by an elemental analysis. These results demonstrate that a water-soluble dinitrogen complex of ruthenium is formed.

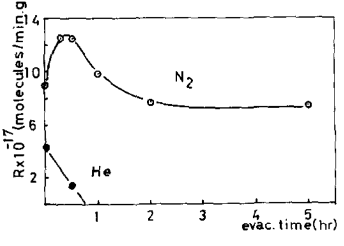

FIG. 4. Variation of catalytic activity for isotopic equilibration of dinitrogen with evacuation time at 350°C.

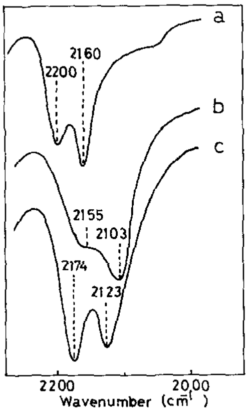

FIG. 5. Infrared spectra of the distillation residue (mixture with KBr). (a) $^{14}N_2$ hydrolysis, (b) $^{15}N_2$ hydrolysis, (c) $^{14}N_2$ ethanolysis.

On the other hand, in the distillate, both hydrazine and ammonia were found and identified by means of visible absorption at 460 and 720 nm, respectively. The amounts of hydrazine and ammonia thus found were, respectively, 11.8 ± 0.3 and 9.5 ± 1.3% of dinitrogen uptake on a mole basis. Thus only about 16% of dinitrogen uptake was found as hydrazine and ammonia. The rest of dinitrogen uptake would be either lost as molecular nitrogen or involved in the ruthenium complex mentioned above. In fact the evolution of molecular nitrogen in addition to a small amount of hydrogen was confirmed during the hydrolysis treatment by mass spectrometry of evolved gas, while no quantitative determination was made.

Analogous decomposition of the incorporated nitrogen was made by using ethanol at room temperature under an argon atmosphere. The resultant pale yellow solution was distilled in vacuum to give a yellow residue which gave, again, two ir-absorption bands at 2174 and 2123 cm^{-1} as shown in Fig. 5. Hydrazine was detected in the distillate. Thus the incorporated nitrogen can be transformed into hydrazine by reaction with either water or ethanol. It is noteworthy, however, that the 2174-cm^{-1} band is stronger than the 2123-cm^{-1} band, in contrast to the case of hydrolysis where the 2200-cm^{-1} band is weaker than the 2160-cm^{-1} band.

DISCUSSION

Formation of a Dinitrogen Complex of Ruthenium

The foregoing results indicate that potassium and nitrogen are cooperatively incorporated into metallic ruthenium, giving rise to the stable potassium. Since nitrogen appears to act as a binder between ruthenium and potassium, it appears that a ternary compound of K–N_2–Ru is formed. The observed molar ratio of the incorporated nitrogen to potassium indicates that N_2 and K are found with a one-to-one mole ratio in this compound. Although no information about the molar ratio of ruthenium to nitrogen was obtained in the present study, in which bulk metal of ruthenium was used so that the extent of conversion of ruthenium was very limited, the observed dissolution of ruthenium into the water extract demonstrates that some compound involving ruthenium was formed. In fact in a separate study with a Ru–K/Al_2O_3 catalyst, an analogous slow uptake of nitrogen was found and the molar ratio of dinitrogen uptake to total ruthenium was as high as 0.8 (*4*). If the nitrogen uptake proceeds through a corrosive sorption, the smaller the ruthenium particle, the larger the extent of corrosion expected, hence giving rise to the observed large mole ratio of dinitrogen to ruthenium in the supported ruthenium. The fact that the ratio was near unity suggests a compound having the formula $(KN_2Ru)_n$. Indeed an analogous dinitrogen compound of cobalt, $KN_2Co(PMe_3)_3$, has been found (*12*), although the method of preparation is quite different.

Similar nitrogen uptake to form a metallic compound was reported in 1928 for the Li_3FeN_2 system. The product was claimed to be a composite nitride (*13*). The retention of the N≡N bond in the sorbed state of the present case is supported by ir observations; i.e., an intense ir absorption band at 2020 cm^{-1} was obtained when Ru–K/Al_2O_3 was treated with nitrogen at 350°C for 3 hr and has been assigned to N≡N stretching frequency (*14*). This band appears to form slowly upon the nitrogen treatment above 200°C and decreases in intensity upon hydrogen treatment above 260°C forming ammonia (*15*), in agreement with the nitrogen uptake under consideration in its behavior.

Additional support for the retention of N≡N bond may come from the ir absorption at 2160 and 2200 cm^{-1} by the distillation residue of water extract. Since ruthenium is found in this residue, and since the ir band is assigned to a dinitrogen species, the precursor complex formed in the solid phase should contain dinitrogen.

It is evident that a $(KN_2Ru)_n$ type of ternary compound is formed by the reaction of potassium with ruthenium in the presence of molecular nitrogen, converting ruthenium metal to a more reactive catalyst for the nitrogen activation. The adsorbed potassium on this compound seems to act as a promoter.

Water-Soluble Dinitrogen Complex of Ruthenium

As described in the results, it is clear that a water-soluble dinitrogen complex of ruthenium is formed upon hydrolysis of the $(KN_2Ru)_n$ complex, in addition to hydrazine and ammonia. Since the hydrogen atoms in hydrazine and ammonia must come from water, it would be of interest to examine the stoichiometric relation to the complex $(KN_2Ru)_n$. Although it is obvious that potassium is oxidized by water, ruthenium also would be oxidized. Actually no dinitrogen complex of Ru(0) is known (*16, 17*). If $(KN_2Ru)_n$ is oxidized to K(I) and Ru(II), the hydrogen that will be evolved will be equivalent to 50 or 75% of the amount required for the conversion of dinitrogen to ammonia or hydrazine, respectively; i.e., at least 50% of dinitrogen may be converted to hydrogen compounds. Since the total amount of nitrogen found as ammonia and hydrazine was about 16% of the uptake, there can be more ammonia or hydrazine formed and coordinated to ruthenium, while ammonia would be more likely as a ligand to the dinitrogen complex, because no known dinitrogen complex of ruthenium has hydrazine as a ligand (*16, 17*).

Another probable ligand is water in the case of hydrolysis and ethanol in the case of ethanolysis. In fact the ir bands ascribed to coordinated dinitrogen are affected by the solvent, water or ethanol. Thus it is likely that the water-soluble dinitrogen complex has ammonia and/or water as ligand. Although two bands are found in both cases, as shown in Fig. 5, hydrolysis gives rise to higher frequencies than ethanolysis. Two bands might result from two different mono-dinitrogen complexes which give single peaks, respectively. However there can be another possibility of bis-dinitrogen complex such as $[Ru(NH_3)_4(N_2)_2]^{2+}$ which is known to give two bands at 2220 and 2185 cm^{-1} (*18*). In fact the known bands for mono-dinitrogen complexes are generally lower than the bands observed here. Although the known bis-dinitrogen complexes are reportedly rather unstable (*19*), the dinitrogen complex found in the distillation residue was quite stable in air. The sample disk preserved in a desiccator reproduced the same spectra after 1 month. The determination of their molecular formulas awaits further work.

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