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Activation of Nitrogen by Alkali Metal-Promoted Transition Metal

IV. Effect of Potassium on the Kinetics of Isotopic Equilibration of Nitrogen on Ruthenium Catalysts

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The kinetics of isotopic equilibration of nitrogen was studied on ruthenium catalysts with and without added potassium at 280–480°C and 40–200 mm Hg. The first order kinetics observed on $Ru-Al_2O_3$ is changed by the potassium addition into fractional order kinetics which approaches first order as the temperature increases. The change in kinetics is accompanied by an increase in apparent activation energy, whereas the equilibration activity is increased by two or three orders of magnitude. The kinetics are consistent with a Langmuir type rate equation for the dissociative chemisorption of nitrogen, from which the effective value of adsorption constant and thus the effective value of heat of chemisorption may be estimated. The change in kinetics as well as the estimated value of the heat of chemisorption (40 ± 6 kcal/mol on Ru–K) demonstrates that the addition of potassium intensifies the adsorption strength of ruthenium towards nitrogen.

INTRODUCTION

In the preceding paper (*1*), it has been shown that the addition of potassium to ruthenium–active carbon remarkably enhances the rate of isotopic equilibration of nitrogen,

$$^{28}N_2 + {}^{30}N_2 = 2\,{}^{29}N_2, \qquad (1)$$

as well as the rate of ammonia synthesis. The kinetics of the reaction (1) observed there was one half order with respect to nitrogen pressure, but no reasonable interpretation for the kinetics could be offered at that time, because the strong adsorption of nitrogen on ruthenium required to explain such a reaction order is in conflict with the previous results of the ammonia synthesis on Ru–Celite (*2*).

Clarification of this question is the first object of the present paper. The kinetic interpretation for the marked enhancement of the rate of isotopic equilibration by the addition of potassium should also be presented. For this purpose an active catalyst, $Ru-Al_2O_3$, was used as well as unsupported Ru.

The isotopic equilibration of nitrogen which was first observed by Joris and Taylor in 1939 (*3*) has been studied by some workers over various catalysts. However, no detailed kinetic study has been made on ruthenium.

EXPERIMENTAL METHODS

Material. Unsupported ruthenium was prepared by reducing $RuCl_3 \cdot 3H_2O$ powder (Koso Chem. Co., Ltd., 4.1 g; 1.6 g after reduction) by hydrogen from 100 to 475°C for 62 hr, and subjected to adsorption of potassium (about 0.04 g; 2.5 wt%) followed by circulation of helium and then nitrogen to distribute the potassium at 380°C. The BET total surface area (Kr or N_2 adsorption at −195°C) of unsupported Ru decreased by the addition of potassium as follows:

	Kr	N_2
Ru	2.0 m^2	2.4 m^2
Ru–K	1.8 m^2	1.7 m^2

The Ru–Al_2O_3 pellets (0.5 wt% Ru; 10.0 g) obtained from Japan Engelhard, Ltd. were reduced by circulating hydrogen from 120 to 400°C for 26 hr, and subjected to adsorption of potassium followed by circulation of helium at 70–350°C. The amount of potassium adsorbed was determined by dissolution in water followed by titration to be 3.1 wt%. The amount of CO chemisorption on the reduced Ru–Al_2O_3 at 0°C was 2.45 ml(STP)/10 g.

Heavy nitrogen was prepared by adding water to $(^{15}NH_4)_2SO_4$ (^{15}N, 70 at.%)–$Ca(OH)_2$ mixture, followed by oxidizing the liberated $^{15}NH_3$ with hot cupric oxide to form free nitrogen. All gases to be used here were freed from oxygen by passing through a copper–kieselguhr column at 180°C.

Procedure. The apparatus was a closed circulating system comprising a reactor. The isotopic mixture of $^{28}N_2$, $^{29}N_2$ and $^{30}N_2$ gases (^{15}N, about 20%) was in advance adsorbed on the catalyst without circulation at the reaction temperature until an adsorption equilibrium was established under the reaction pressure. The change in the isotopic composition of circulating gas with time was continuously followed by mass-filter type quadrupole mass spectrometry. The gas sample was taken out through a sampling leak attached to the circulating system, but the leak was negligibly small compared to the amount of reacting gas. The response time of the mass spectrometer to a sudden change in the composition of reacting gas was estimated to be less than 1 min.

RESULTS

1. Marked Enhancement of the Rate of Isotopic Equilibration by the Addition of Potassium

It was previously reported (*1*) that the Ru–AC (active carbon) was inactive for the isotopic equilibration even at 400°C, but the addition of potassium made it active even at 220°C. In order to clarify the kinetic meaning of this potassium effect, series of kinetic measurements were made on unsupported Ru and also on a more active ruthenium catalyst, Ru–Al_2O_3. The rate of isotopic equilibration, R (molecules/min), was determined from the first order plot of $^{29}N_2$ mole fraction according to Eq. (2):

$$-\log \frac{(^{29}X_e - {}^{29}X)}{(^{29}X_e - {}^{29}X_0)} = \frac{R}{2.3\ N_g}\,t, \quad (2)$$

where ^{29}X, $^{29}X_0$ and $^{29}X_e$ are, respectively, the mole fraction of $^{29}N_2$ at time t, zero and the equilibrium. N_g is the number of nitrogen molecules in the gas phase.

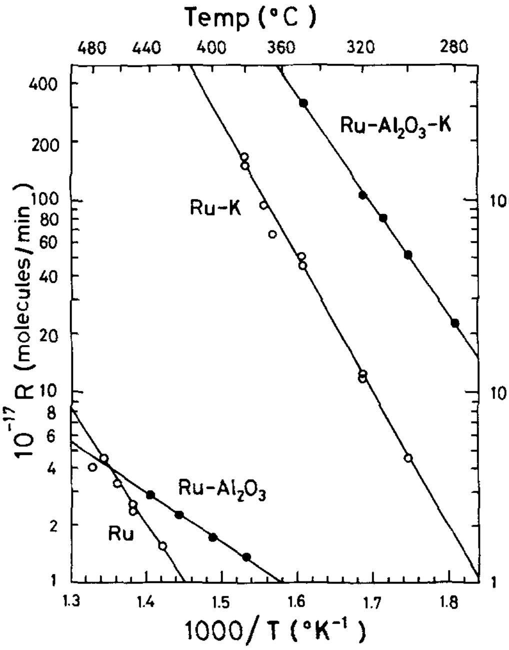

FIG. 1. Temperature dependence of the equilibration rate under 150 mm Hg on unsupported Ru and Ru–Al_2O_3 with and without potassium.

The temperature dependences of the equilibration rate under 150 mm Hg on unsupported Ru and Ru–Al_2O_3 with and without potassium are shown in Fig. 1. It is clear that those ruthenium catalysts which are less active by themselves are dramatically activated by the addition of potassium. The extent of activation is estimated to be 480 and 650 times at 400°C on unsupported Ru and Ru–Al_2O_3, respectively. It is to be noted that the activation by potassium is accompanied by an increase in apparent activation energy associated with R, E_{app}, on unsupported Ru and Ru–Al_2O_3 as shown in Table 1. In comparison with iron catalysts the specific activity (molecules/min m^2) of Ru–K at 330°C is 10 to 10^2 times more active as follows:

	Molecules/min m^2	mm Hg
Fe–Al_2O_3 (*4*a)	9.3×10^{16}	200
Fe–Al_2O_3–K_2O (*4*b)	2.0×10^{15}	378
Ru–K	1.3×10^{18}	200

2. *Kinetics of the Isotopic Equilibration; Temperature Dependence of Reaction Order*

There have been three determinations of the reaction order for isotopic equilibration on iron catalysts, i.e., on pure iron at 350°C (*5*) and on doubly promoted iron at 430°C (*6*a), and 500°C (*6*b). They are all one half order. Such kinetics are usually interpreted in terms of adsorption constant for nitrogen. The one half order was also obtained at 280°C on Ru–AC–K (*1*). If the adsorption constant for nitrogen on Ru is unaffected by the added potassium, such a reaction order would be hardly understood, because the kinetics of ammonia synthesis on Ru–celite (*2*) is independent of ammonia in conformity with the absence of deuterium isotope effect, demonstrating that the adsorption of ammonia on Ru is very weak, and suggesting that the interaction of nitrogen with Ru is weak, too.

TABLE 1

KINETIC CONSTANTS OF ISOTOPIC EQUILIBRATION OF NITROGEN

Catalyst	Reaction order	Temp range (°C)	(kcal/mol) E_{app}	 E_0	 Q
Ru	—	430–480	23 ± 3	—	—
Ru–K	0.44–0.79	320–380	32 ± 1	14 ± 3	40 ± 6
Ru–Al_2O_3	1.0	380–440	11 ± 1	11 ± 1	—
Ru–Al_2O_3–K	0.26–0.45	280–320	25 ± 2	10 ± 2	22 ± 3

Thus the nitrogen–ruthenium interaction was investigated by examining the temperature dependence of reaction order on Ru–K. It turned out that the reaction order increased from 0.44 at 320°C to 0.79 at 380°C, as shown in Fig. 2, suggesting the feasibility of interpretation in terms of adsorption constant. Since those measurements were made under the condition of adsorption equilibrium, the rate of adsorption, V_a, is equalized to that of desorption, V_d. If the Langmuir equation for the dissociative adsorption of nitrogen is applied, the equilibration rate, R, may be given by

$$R = V_a = V_d = kP/[1 + (KP)^{1/2}]^2, \quad K = k/k', \quad (3)$$

where k, K and P are, respectively, rate constant (molecules/min mm Hg), adsorption constant for nitrogen (mm Hg^{-1}) and nitrogen pressure (mm Hg). The results in Fig. 2 well fit this equation. The best values of k and K are determined from the linear plots of $1/R^{1/2}$ against $1/P^{1/2}$ by the

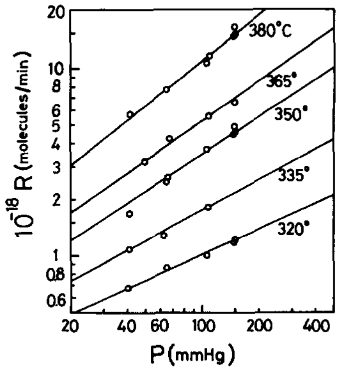

FIG. 2. Pressure dependence of the equilibration rate at 320–380°C on Ru–K.

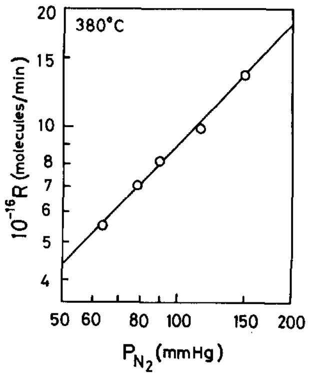

FIG. 3. Pressure dependence of the equilibration rate at 380°C on Ru-Al_2O_3.

method of least squares. Their Arrhenius plots give 14 ± 3 kcal/mol for the activation energy, E_0; and 40 ± 6 kcal/mol for the heat of adsorption, Q. The undissociative adsorption was tested by an alternative plot of $1/R$ versus $1/P$ which gave an Arrhenius plot of K broken at 350°C leading to a negative heat of adsorption. These results are consistent with the Bonhoeffer-Farkas type equilibration, while the coexistence of undissociated and dissociated species of adsorbed nitrogen may not be ruled out.

The unsupported Ru without added potassium was considerably less active so that the reaction order was difficult to be determined even at 470°C. In order to clarify the effect of potassium, another series of kinetic measurements were made on the more active catalyst, Ru-Al_2O_3, on which the reaction order before the addition of potassium could be determined to be first order with respect to nitrogen pressure at 380°C as shown in Fig. 3. After adding potassium, fractional orders were again obtained which increased with temperature as shown in Fig. 4. The results in Fig. 4 are again consistent with Eq. (3), giving E_0 and Q values shown in Table 1.

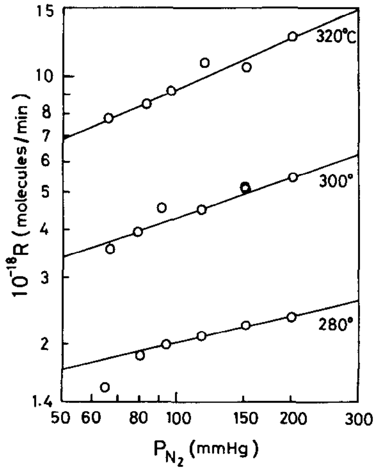

FIG. 4. Pressure dependence of the equilibration rate at 280-320°C on Ru-Al_2O_3-K.

DISCUSSION

1. *Intensification of Ruthenium-Nitrogen Interaction Caused by Potassium*

The kinetic constants obtained on these ruthenium catalysts are summarized in Table 1. It is obvious there that the addition of potassium gives rise to the fractional reaction order which is in conformity with a strong adsorption of nitrogen. The observed increase in apparent activation energy by the addition of potassium is now explained as being due to the adsorption term. It is accordingly suggested that the potassium addition intensifies the adsorption strength of nitrogen on ruthenium.

This is also indicated by the high value of heat of adsorption. The effective heat of adsorption during catalysis is usually lower than the initial value at zero coverage. Thus the effective heat of nitrogen chemisorption during ammonia synthesis on promoted iron catalyst is about 15 kcal/mol at around 300°C (*7*), while the initial heat on iron film is reportedly 70 kcal/mol (*8*). Although the corresponding value on ruthenium film is unavailable, it seems lower than on iron (*9*), as suggested by no nitride formation of ruthenium. In this respect the observed value of 40 ± 6 kcal/mol on Ru-K is remarkably high as a heat of nitrogen chemisorption on ruthenium. The heat of nitrogen adsorption appears to be affected by the alumina support, the reason of which is not clear yet.

2. *Nature of Activation by Potassium*

Pure iron has been known to chemisorb (*8*) and activate nitrogen (*5*) but pure ruthenium is less active requiring higher temperature for the isotopic equilibration. Such a less active surface of ruthenium acquires a high affinity and activity towards nitrogen by the addition of potassium as shown in this study. It is noteworthy that the observed change in activation energy (E_0) is not so extensive as to explain the remarkable enhancement which amounts to about 650 times at 400°C over Ru-Al_2O_3. Accordingly the large part of enhancement should be ascribed to the increase in frequency factor, although no further explanation may be given at present.

Our interpretation of this activation has been the electron donation from alkali metal to transition metal (*10*). A similar phenomenon has been found in the chemisorption of carbon monoxide. Dry *et al.* (*11*) found that addition of K_2O to iron increases the heat of chemisorption of carbon monoxide and interpreted this in terms of electron donation from K_2O. Since a carbon monoxide molecule tends to accept electrons from iron on adsorption, it is quite reasonable that the higher electron density on iron strengthens the Fe–C bond, resulting in an increase in the heat of chemisorption. A similar effect can be expected for the chemisorption of nitrogen because nitrogen is also electronegative in nature. Thus the increased electron density on ruthenium induced by potassium metal would strengthen the Ru–N bond simultaneously weakening the $N{\equiv}N$ bond by an electron donation to the antibonding orbital, as depicted by Blyholder (*12*) for carbon monoxide chemisorption.

It has been reported that semiconducting compounds are formed by reaction of alkali metals with gold (*13*) and platinum (*14*). In case of Cs–Au, a crystal structure of Cs–Cl type has been found. Since ruthenium has an electronegativity as high as platinum, it is likely that a Ru–K compound is formed on the ruthenium surface in which the ruthenium atoms assume an anionic nature. The anionic ruthenium and the ionic nature of surface would play a role in polarizing the adsorbing nitrogen molecule to give the activated state.

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