than that for the DAPES condensed polymer.

Conclusions

The ²⁹Si CP/MAS NMR spectra of the Cab-O-Sil silica and treated Cab-O-Sil silica with coupling agent solutions provide information on the nature of the structure of the silane coupling agents adsorbed on the silica surface similar, but not identical to, that of silica gel.¹⁸⁻²² The ²⁹Si NMR spectra of treated silica showed that the silane molecules were chemically adsorbed to the surface through the formation of a siloxane bond with the silanol on the surface. The amount of coupling agent adsorbed on the silica surface was increased with an increased concentration of treating solution.

The solid-state ²H NMR spectra as a function of the amount of silane coupling agent provide information on the molecular motion of silanes adsorbed on silica and the adsorption behavior. The simulated deuterium line shapes suggest possible motional mechanisms, rates, and the relative amounts of rigid and mobile components. The spectra are consistent with rigid and mobile fractions with the mobile fractions undergoing anisotropic rotation plus two-site jumps about a diffusion axis tilted at 54.7°. The calculated spectrum for the sample from the 2% treating solution, which may correspond to monolayer coverage, shows the highest

relative amount of rigid component and the slow reorientation rate, indicative of the most crowded surface environment.

²⁹Si NMR data and ²H NMR spectra for DAPS and DABS are consistent with the notion that silane molecules are adsorbed and reacted directly onto the silica surface until monolayer coverage and then form a polysilsesquioxane layer which is intermolecularly condensed above the monolayer and indirectly bonded to the surface. From solution concentrations above this for monolayer coverage, the molecular motion has a contribution from a highly mobile component resulting from the silane molecules of the polysilsesquioxane layer.

The ²H NMR spectra for both DAPS and DABS on a silica surface suggest that the molecular motion of silane directly adsorbed on silica is not affected by the difference in carbon chain length of amino functional silane coupling agent. It appears to be affected by the amount of coupling agent for these fairly short chain lengths. This is in contrast with that observed for longer chains. 10,25

Acknowledgment. The authors thank the Office of Naval Research for their financial support. They also thank Drs. Schneider and Freed for supplying the original program and R. B. Funchess for adapting it for deuterium line shape calculations.

Promoter Action of Alkali Nitrate in Raney Ruthenium Catalyst for Activation of Dinitrogen

Tokihisa Hikita, Yasushi Kadowaki, and Ken-ichi Aika*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan (Received: October 23, 1990)

Alkali nitrate promoted Raney Ru catalysts were prepared by decomposition of alkali nitrates (CsNO₃, RbNO₃, KNO₃, and NaNO₃) with hydrogen over Raney Ru. These catalysts were as active as Raney Ru promoted with metallic potassium at 573 K in N₂ activation (ammonia synthesis and especially isotopic equilibration reaction (IER) of N₂). The promotional behavior of alkali nitrates on Raney Ru was different from that on the supported Ru catalysts. The alkali was estimated to work as a metallic on Raney Ru, whereas it was estimated to be hydroxide on supported Ru. The more reduced form on Raney Ru-CsNO₃ was considered to give a higher turnover frequency of IER of N₂ than that over alumina-supported Ru-CsNO₃. Since the rate of IER of N_2 is a rate of tracer atom moving from N_2 to adsorbed N under the condition of adsorption equilibrium, it should be slower than the rate of ammonia synthesis whose adsorption step is rate-determining in a dynamic condition. To the contrary, the rates of ammonia synthesis were slower than IER rates of N_2 over Raney Ru-CsNO₃, suggesting hydrogen inhibition in the N₂ activation process. Indeed, the IER of N₂ over Raney Ru-CsNO₃ was proved to be retarded by the presence of hydrogen. A kinetic analysis disclosed that N(a) and H(a) compete with each other on the Ru surface where H(a) adsorption is stronger than N(a) adsorption at 473-523 K. The heats of adsorption of N_2 and H_2 were estimated from the kinetics.

Introduction

Ruthenium has been known to be quite active in ammonia synthesis when it is promoted with electron donors or basic oxides.¹ Two different forms of Ru catalysts can be prepared: supported Ru²⁻⁴ and Raney Ru.^{5,6} For supported catalysts, a metallic alkali promoter resulted in higher activity than did an alkali nitrate promoter such as CsNO₃.²⁻⁴ However, water-sensitive metallic

(5) Urabe, K.; Yoshioka, T.; Ozaki, A. J. Catal. 1978, 54, 52.
 (6) Ogata, Y.; Aika, K.; Onishi, T. J. Catal. 1988, 112, 496.

alkali is not easily handled, whereas the alkali nitrate can be safely treated for preparing the catalysts. During the activation process, alkali nitrate decomposition is promoted by the presence of Ru in hydrogen, which results in an active promoter form.³ The promoter action of alkali nitrates has been studied comprehensively on supported Ru catalysts.^{3,4} The alkali promoter is considered to interact not only with the Ru surface directly but also with the support. Thus, the direct interaction should be studied in detail on the catalyst without the support. However, a support-free Ru powder-alkali nitrate catalyst does not provide enough activity for detailed study because it has a low surface area $(1 \text{ m}^2/\text{g})$. The Raney Ru-alkali nitrate system was thus chosen as a model system, although the surface was covered partly by residual Al.⁶ The surface area was about 50 m^2/g in the last study⁷ and 40 m^2/g

⁽¹⁾ Ozaki, A.; Aika, K. In Catalysis-Science and Technology; Anderson, J. R., Boudart, M., Eds.; Springer-Verlag: Berlin, 1981; Vol. 1, Chapter 3, p 87.

⁽²⁾ Aika, K.; Hori, H.; Ozaki, A. J. Catal. 1972, 27, 424.
(3) Aika, K.; Shimazaki, K.; Hattori, Y.; Ohya, A.; Oshima, S.; Shirota, K.; Ozaki, A. J. Catal. 1985, 92, 296.

⁽⁴⁾ Aika, K.; Ohya, A.; Ozaki, A.; Inoue, Y.; Yasumori, I. J. Catal. 1985, 92, 305.

⁽⁷⁾ Aika, K.; Ogata, Y.; Takeishi, K.; Urabe, K.; Onishi, T. J. Catal. 1988, 114. 200.

in this study. Unexpectedly, the alkali nitrates were found to be as effective as metallic potassium on Raney Ru. Thus, we studied the state of alkali nitrate under the reaction condition. The isotopic equilibration reaction (IER) of dinitrogen $({}^{28}N_2 + {}^{30}N_2 = 2{}^{29}N_2)$ is a fundamental reaction that represents a catalyst's ability to rupture the N-N bond. The effect of hydrogen on the IER of N₂ was also studied in order to clarify the mechanism of ammonia synthesis.

Methods

A Raney Ru catalyst was prepared from an Ru-Al alloy (Ru/Al = 1/1 w/w) by leaching with a 5 N KOH aqueous solution at 373 K for 3 h.⁵⁻⁷ The original Ru powder was obtained from Endow-Platinum, Tokyo. The Ru-Al alloy, melted in a microwave oven, resulted in an inactive sample; however, the same sample melted again in an arc oven became an active catalyst. The leached sample was moved to the reactor, and water was evacuated for 10 h at 298 K, treated by circulating He (80 kPa) at 523 K for 5 h with a liquid N₂ trap, and adsorbed gases were evacuated for 2 h at 523 K. The sample was treated with circulating N₂ (53 kPa) at 673 K until the adsorption of N₂ ceased (40 h), before it was used for the reaction.^{6,7}

The pretreatment method was different when the sample was applied by promoter nitrates. Alkali nitrates (alkali/Ru = 6-10mol %) were added to Raney Ru in water (impregnation) in a glass reactor and allowed to stand for 5 h. After the water was removed at 298 K for 10 h, 1.3 kPa of H₂ was added consecutively in order to avoid explosion to reach a final pressure of 80 kPa at 298 K. The sample was heated gradually to 573 K for 3 h and was treated with circulating H_2 at 573 K with a liquid N_2 trap until H₂ consumption ceased (2 h). The rate of ammonia synthesis was measured at 573 K or lower temperatures by the volume decrease of $N_2 + 3H_2$ under constant pressure (80 kPa) in a closed circulation system (flow rate 80 mL/min) with a liquid nitrogen trap. The trapped product was determined to be ammonia by mass spectroscopy. IER of N₂ was carried out under 20 kPa (150 Torr) of ${}^{28}N_2 + {}^{30}N_2$ in a closed circulation system with a quadrupole mass filter (AGA-100, ANELVA, Tokyo). Reaction rates were calculated from the change of mole fraction of $^{29}\mathrm{N}_2$ with time. Usually 1 g of Ru-Al alloy (Ru/Al = 1/1 w/w), which resulted in 0.5 g of Ru and about 0.05 g of Al after the leaching, was used.⁵⁻⁷ The catalyst weight used in the text means the weight of Ru (0.5 g) for convenience. The rates of 588 K were represented on a weight basis. Turnover frequencies (TOF) of Raney Ru with and without CsNO₃ were estimated on the basis of H₂ chemisorption data which were obtained at 273 K on Raney Ru without the CsNO₃ promoter, because Raney Ru-CsNO₃ showed excess H₂ chemisorption. Before H₂ chemisorption, Raney Ru without a promoter was evacuated at 673 K for 2 h; however, Raney Ru nitrates were evacuated at 573 K for 2 h. BET area was measured with N₂. A Shimadzu ESCA 750 was used for the XPS measurements. A sealed sample was opened in an argon atmosphere in the chamber. The binding energy was determined to be 83.8 \pm 0.1 eV by comparing to the peak of gold (Au) 4f_{7/2}.

Results

Effect of the Amount of CsNO₃ Promoter on the Ammonia Activity. Rates of ammonia synthesis were measured at 573 K over Raney Ru-CsNO₃ with various amounts of CsNO₃. In Figure 1, the activity is shown as a function of Cs/Ru mole ratio. Maximum activity was shown at Cs/Ru mole ratios of 0.06-0.10 (or 6-10 mol % in Figure 1 and 0.6-1.0 mmol of Cs/g of Ru). The activity decreased with excess Cs, probably due to saturation of the surface. H_2 chemisorption (4 mL/g) on Raney Ru corresponded to 0.36 mmol surface Ru for 1 g of Ru if H/Ru is assumed to be unity and the amount of residual Al is ignored.6.7 Thus, the value Cs/Ru = 0.1 might roughly correspond to three layers of Cs or Cs compounds on Ru. Cs or Cs salt is thus suggested to be aggregated not only on the Ru surface but also on the residual Al. It is interesting to point out that the Raney Ru-CsNO₃ system did not adsorb detectable amounts of nitrogen at 673 K. To the contrary, Raney Ru and Raney Ru-K adsorbed



Figure 1. Ammonia synthesis rate as a function of the amount of $CsNO_3$ on Raney Ru. The leached sample contains 0.5 g of Ru. The catalyst weight was stated as 0.5 g because of convenience, although about 0.05 g of Al is estimated to remain. The ammonia synthesis rate was measured at 573 K under 80 kPa (600 Torr) of mixture gas $(N_2 + 3H_2)$.

TABLE I: Effect of H_2 Treatment Temperature of Raney Ru-CsNO₃ on Ammonia Synthesis at 523 K under 80 kPa of N_2 + 3 H_2

-	-	
H ₂ treatment temp, K	rate, mmol of NH ₃ /(g h)	
523	1.09	
573	1.24	
623	0.40	
673	0.40	

nitrogen at 0.42 and 0.81 mmol of N/g, respectively.⁶ However, after ammonia synthesis, adsorbed nitrogen was observed by XPS on Raney Ru–alkali nitrate, although the concentration was as small as N/Ru (0.04 \pm 0.01) in XPS area ratio.

Effect of Decomposition Temperature of $CsNO_3$ and Effect of Water Addition. The decomposition temperature of $CsNO_3$ in H₂ was changed from 523 to 673 K for Raney Ru-CsNO₃, and the ammonia synthesis activity was measured. The results are shown in Table I. The maximum activity occurred at the decomposition temperature of 573 K.

For supported Ru catalysts, the reaction of CsNO₃ with H₂ (eq 1) occurs at lower temperatures (473-543 K), and the decomposition of Cs₂O (eqs 2 and 3) occurs at higher temperatures (573-673 K).³⁸ Cs is considered to become CsOH on the support (eq 4).³ For Raney Ru-CsNO₃, reaction 4 does not seem to occur

$$2C_{s}NO_{3} + 8H_{2} \rightarrow Cs_{2}O + 2NH_{3} + 5H_{2}O \qquad (1)$$

$$2Cs_2O \rightarrow Cs_2O_2 + 2Cs \tag{2}$$

$$Cs_2O_2 + H_2 \rightarrow 2CsOH$$
 (3)

$$Cs + OH(a) \rightarrow CsOH$$
 (4)

because it involves less OH(a). Since Cs is a more effective promoter than Cs₂O and disproportionation (eq 2) may give more Cs at 573 K than at 523 K (eqs 1 and 2), the higher activity of the sample after disproportionation at 573 K may be reasonable for Raney Ru-CsNO₃. When the sample treated by H₂ at 573 K was contacted with water vapor (ca. 2.6 kPa) at 298 K for 5 min, ammonia synthesis activity decreased from 1.24 to 0.40 mmol/(g h). This suggests the existence of a metallic Cs that is oxidized by water vapor and becomes a less effective promoter. When the sample was treated by H₂ at high temperatures (623 and 673 K), the activity was decreased, probably due to the evaporation of Cs and/or Cs₂O. Indeed, a white deposit was observed on the reactor at the upper part outside of the furnace

⁽⁸⁾ Gmelins Handbuch der Anorganischen Chemie; Pietsch, E., Ed.; Verlag-Chemie: Weinheim, 1955; System No. 25, p 107.

⁽⁹⁾ Amariglio, H.; Rambeau, G. In *Proceedings of the 6th International* Congress on Catalysis; Bond, G. C., et al., Eds.; Chemical Society: London, 1977; p 1113. The activity was recalculated by assuming the total pressure dependence of order 1.5 and the apparent activation energy of 17 kcal/mol.

⁽¹⁰⁾ Ozaki, A.; Aika, K.; Morikawa, Y. In Proceedings of the 5th International Congress on Catalysis, 1972, Florida, Hightower, J. W., Ed.; North-Holland, Amsterdam, 1973; p 1251.

catalyst	activity, ^a mmol/(h g)	$TOF \times 10^4$, NH ₃ /H(a)/s	apparent activation energy, kcal/mol	ref
Raney Ru-CsNO ₃	2.73 ^b	21	19	this work
Raney Ru-RbNO ₃	2.12	16		this work
Raney Ru-KNO ₃	1.54 ^b	12		this work
Raney Ru-NaNO3	0.62 ^b	4.8		this work
Raney Ru	0.081 ^b	0.63	22	this work, 5
Raney Ru-K	1.12 ^b		22	5
4.7% Ru-K/AC ^c	2.0 ^d	130	22	2
1.96% Ru–Ćs+/MgO	0.047	11	25	4
1.96% Ru-Cs+/MgO	0.013	6.6	23	4
2% Ru-Cs+/Al ₂ O ₃	0.042	4.0	(23)	3
Ru powder	0.0013 ^d		23	1, 2, 10
Fe-Al,O,-K,O	0.21 ^d			1, 10
Fe-Al,O,-K,O-CaO	1.034			9
Fe powder	0.0018 ^d			1, 10

^a Reaction under 80 kPa of N₂ + 3H₂ at 573 K. ^bCatalyst weight (g) means weight of Raney Ru without promoter. ^cAC = active carbon. TOF is based on CO adsorption. d Catalyst weight (g) means weight of (RuCl₃-3H₂O (or Fe) + support + promoter other than K).

when heated at 623 or 673 K. Any activated alkali nitrate-Raney Ru catalysts were all pyrophoric in air, while the Raney Ru without promoter was not pyrophoric in air after use.

Activity Measurement of Ammonia Synthesis on Raney Ru Catalysts Promoted with Various Alkali Nitrates. Ammonia synthesis rates on various alkali nitrate promoted Raney Ru samples were measured. The rates at 573 K and the apparent activation energy are shown in Table II. Activity is expressed as millimoles of NH₃ per hour per weight of catalyst. The TOF is represented as the rate of ammonia synthesis per second per number of surface Ru atoms. The number of surface Ru atoms was estimated from hydrogen or CO adsorption. All the activities cited in Table II were measured on catalysts with 6-10 mol % nitrates where the activity was the maximum in the case of Raney Ru-CsNO₃. The activity of KNO₃-promoted Raney Ru (1.54 mmol/(hg)) was found to be similar to that of Raney Ru-K (1.12) $mmol/(h g))^5$ or that of 4.7% Ru-K/AC (2.0 mmol/(h g)), which were the most active ammonia catalysts below atmospheric pressure.² On CsNO₃-promoted Raney Ru, the ammonia synthesis rate was found to be highest (2.73 mmol/(h g)) at 573 K, and it was measurable even at around 373 K. The activity was more than 2000 or 30 times higher than the activity on Ru powder or Raney Ru, respectively. The activity of these catalysts did not change for a week during the measurement of activation energy (443-573 K). The apparent activation energy on Raney Ru-CsNO₃ (19 kcal/mol) was similar to that on Raney Ru-K (22 kcal/mol). The activity of Raney Ru-CsNO3 was also higher than that reported for commercial Fe-Al₂O₃-K₂O-CaO (1.03 mmol/(hg)) or Fe-Al₂O₃-K₂O (0.21 mmol/(hg)) iron catalysts under the same conditions. Among alkali nitrates, the heavier the alkali element, the more effective was the promotion of the activity (Cs > Rb > K > Na). This tendency was consistent with the order of electron-donating ability of alkali metals. These results suggest electron donation from a metallic alkali to the Ru metal surface. The electron-donated surface or electrostatic field effect of metallic alkali-Ru surface¹¹⁻¹³ is considered to promote N_2 dissociation. Although the per-weight activity was highest, the TOF of ammonia synthesis on Raney Ru–CsNO₃ (21×10^{-4}) was still lower than that on 4.7% Ru-K/AC (active carbon) (130 \times 10⁻⁴) at 573 K; however, it was higher than that on supported Ru catalysts with CsOH promoter $((4.0-11) \times 10^{-4})$, as shown in Table II. The TOF of IER on Raney Ru-CsNO₃ was higher than that on 5% Ru-K/AC, as will be described later.

XPS Spectra of the Catalysts. XPS spectra of these catalysts were measured after the reaction without exposure to air and are shown in Figure 2. The binding energies of Ru, Al, and N are summarized in Table III. The binding energy of Ru 3d_{5/2} was found to shift to lower energy by 0.1-1.3 eV compared to that of Ru metal powder or Raney Ru (280.0 eV). The value for Ru





Figure 2. X-ray photoelectron spectra of activated alkali nitrate-Raney Ru samples.

TABLE III: Binding Energy (eV) of Various Raney Ru Catalysts

	Ru 3d _{5/2}	Ru 3p _{3/2}	Al 2s _{1/2}	N 1s _{1/2}
pure Ru powder	280.4ª	462.0		
Raney Ru	280.0	461.9	118.8	397.8
Raney Ru-NaNO ₃	279.9	461.5	118.9	397.9
Raney Ru-KNO ₁	279.9	461.1	118.4	397.2
Raney Ru-RbNO ₁	278.7	460.5	117.5	396.6
Raney Ru-CsNO ₃	279.3	461.0	117.9	396.7
Al metal			117.50	
AlN				396.7°

^a Most values reported are 280.0 eV.¹⁵ ^b Data in ref 7. ^c Data in ref 16.

TABLE	IV:	XPS	Binding	Energy	of Alk	ali-Me	etal E	lement	s of A	lkali
Nitrate	and	Those	of Alka	li Eleme	ents on	the A	ctive l	Raney 1	Ru-Al	kali
Nitrate	Cat	alyst								

	BE of alkali element of alkali nitrate, eV	BE of alkali element on the active catalyst, ^a eV
Na 1s1/2	1073.2	1073.2
K 2p _{3/2}	293.4	293.1
Rb 3d _{5/2}	110.7	108.7
Cs 3d _{5/2}	726.0	725.2

^a After activation of Raney Ru-alkali nitrate with H₂ at 573 K.

 $3p_{3/2}$ also became lower by 0.5-1.0 eV. One of the causes of this shift is considered to be the electron transfer from the "metallic" alkali element to the Ru surface.¹⁴ The nitrates undergo dis-

⁽¹¹⁾ Luftman, H. S.; White, J. M. Surf. Sci. 1984, 139, 369.

TABLE V: BET Surface Area and Amount of H₂ Chemisorption

	BET area, m ² /g	H_2 chemisorbed at 273 K, mL/g
pure Ru powder	1	0.20
Raney Ru	40	4.0
Raney Ru-NaNO3ª	38	11.9
Raney Ru-KNO3 ^a	22	11.0
Raney Ru-RbNO ₁ ª	34	9.7
Raney Ru-CsNO ₃ ª	28	11.5

^aAlkali/Ru mole ratios are 0.06-0.10.

proportionation on Raney Ru through eqs 1-3 and some to eq 4. The binding energies of the alkali element in each alkali nitrate before and after the disproportionation were also measured and are shown in Table IV. It was found that the binding energy was decreased by the disproportionation reaction, although all the absolute values for alkali nitrates were somewhat higher than those reported in the literature.¹⁵ The change of the binding energy might also be correlated with the presence of the "metallic" alkali element on the active catalyst.

It has been reported that surface Al in Raney Ru changes from Al⁰ (Al 2s binding energy of 117.4 eV) to Al³⁺ (119.1 eV) during heat treatment at 573 K.7 Here Al is shown to be reduced again or kept at a reduced state through disproportionation of alkali nitrate, especially of Rb or Cs. The binding energy of Al $2s_{1/2}$ of Raney Ru was 118.8 eV (Al³⁺), whereas that of Raney Ru-RbNO3 or CsNO3 was 117.5 or 117.9 eV (Al⁰), respectively. The peak area of Al compared to that of Ru decreased from 0.35 to 0.11 ± 0.04 by adding alkali nitrates. Alkali nitrates are considered to reduce the amount of surface aluminum and partly to cover it. This is more proof that alkali nitrates are turned to metallic states.

Nitrogen adsorbed during the reaction gave an XPS spectrum binding energy of 297.8 eV for N 1s1/2 on Raney Ru, which has been identified to be adsorbed N on Ru (397.4 eV).¹⁶ When RbNO3 or CsNO3 was applied, the peak shifted to 396.6 or 396.7 eV, which is the same value for AlN (396.7 eV).¹⁶ It seems to be more probable that once Al is reduced to Al⁰, it is easy to react with the surface-dissociated nitrogen to give AlN. Another possibility is a formation of anovel surface dinitrogen compound with alkali metal,¹⁷ although no XPS data are available. The adsorbed amount of N is small, with the XPS peak area ratio of $N/Ru \text{ being } 0.04 \pm 0.01.$

Adsorption Measurements. BET surface areas and the amounts of H₂ chemisorption on the catalysts are shown in Table V. The BET area of Raney Ru was decreased when Raney Ru was promoted with alkali nitrates. The resultant alkali metals or metal hydroxides are thought to be incorporated into the fine pores of Raney Ru.

From hydrogen chemisorption, the number of surface Ru atoms (N_h) was calculated, assuming H/Ru is 1. The number of surface Ru atoms (N_s) can also be calculated from BET measurements, assuming the average crystal faces of Ru.¹⁸ N_h/N_s ratios were 1.0 for Ru powder and 0.4-0.5 for Raney Ru, which are reasonable values. However, $N_{\rm h}/N_{\rm s}$ for alkali-promoted Raney Ru exceeded unity. Apparently, hydrogen was adsorbed on the promoter, too. For this reason, the TOFs on Raney Ru-alkali nitrates were based on hydrogen adsorption on the sample without the promoter. Since metallic alkali reacts with H₂ making hydride, hydrogen may be adsorbed on the metallic alkali promoter. Al reduced by alkali might also adsorb hydrogen.

Isotopic Equilibration Reaction of N_2 . Since the ammonia activity of Raney Ru-CsNO3 was the highest among the alkali



Figure 3. Plot of IER rate of N₂ as a function of H₂ pressure at various temperatures on Raney Ru under 20 kPa of N₂. Rate (μ mol/(g h)) at 603 (△), 623 (□), 638 (●), and 653 K (O).

nitrate promoted Raney Ru, the IER of N₂ was studied over the catalyst. The rate of IER of N_2 , R (mmol/(h g)), was obtained from the equation

$$\ln \left[(X_{\rm e} - X_{\rm i}) / (X_{\rm e} - X_{\rm i}) \right] = -Rt/n \tag{5}$$

where X_e , X_i , and X_i are mole fractions of ²⁹N₂ at equilibrium, at time *t*, and at the beginning, respectively; *n* is millimoles of $\binom{28}{2}N_2 + \binom{29}{2}N_2 + \binom{30}{2}N_2$ in the system.

The results at 588 K and the apparent activation energies are shown in Table VI, with the reported data. The rate of this reaction over Raney Ru-CsNO₃ was extraordinarily fast and comparable to the data on Raney Ru-K. However, the reported activity of Raney Ru⁶ without promoter was not reproduced here. The reason is not clear at present but may be related to the fact that the Ru-Al alloy used here was obtained from a batch different from that used in the former work.⁶ The activity, this time, was about 60 times less active. However, the activity of Raney Ru-CsNO3 was high, and it was one of the highest values reported so far. The activity of IER of N₂ was observed even at around 373 K. TOF values are also shown in Table VI. The TOF on Raney Ru-CsNO₃ is of the same order as the TOFs on the other Ru catalysts that were promoted with metallic potassium (Ru-K/AC, Ru-K/MgO). This also suggests the existence of Cs metal in the Raney Ru-CsNO₃ system. It is also interesting to point out that the TOF of ammonia synthesis on Raney Ru-CsNO₃ was lower than that on Ru-K/AC.

All the past work suggests that the rate-determining step of ammonia synthesis on Ru catalysts is the dissociative adsorption of dinitrogen.^{1,29,30} If the surface condition made no difference, twice the value of the IER rate should be comparable to the rate of ammonia synthesis. Table VII represents the comparison of both rates under the same conditions. In fact, the surfaces are different. Under IER, nitrogen covers more sites, while hydrogen is adsorbed during the synthesis. If no hydrogen would be adsorbed, the rate of synthesis would be faster because of more bare sites (less nitrogen coverage) in a dynamic condition. This may be the case for Ru-K/AC, although the catalysts were prepared in different batches. However, the results were contrary for two Raney Ru catalysts, as shown in Table VII; the synthesis rates are much lower than the IER rates. We concluded that hydrogen retardation occurred during the synthesis over Raney Ru-CsNO3.

Recently, $SrN_{0.5}$ was found to be an effective catalyst for IER of N_2 (Table VI); however, this sample was irreversibly poisoned by hydrogen, which formed a hydride during ammonia synthesis, and finally became inactive.²⁸

⁽¹⁴⁾ Shyu, J. Z.; Goodwin, Jr., J. G.; Hercules, D. M. J. Phys. Chem. 1985. 89. 4983.

⁽¹⁵⁾ Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. Handbook of X-ray Photoelectron Spectroscopy; Perkin-Elmer: Eden Prairie, MN, 1978. (16) Ogata, Y.; Aika, K.; Onishi, T. Chem. Lett. 1985, 207.

⁽¹⁷⁾ Aika, K.; Midorikawa, H.; Ozaki, A. J. Phys. Chem. 1982, 86, 3263. (18) Anderson, J. R. Structure of Metallic Catalysts; Academic Press: London, 1975.

⁽¹⁹⁾ Ogata, Y.; Aika, K.; Onishi, T. Chem. Lett. 1984, 825.
(20) Urabe, K.; Aika, K.; Ozaki, A. J. Catal. 1974, 32, 108.
(21) Urabe, K.; Aika, K.; Ozaki, A. J. Catal. 1975, 38, 430.

⁽²²⁾ Ohya, A.; Aika, K.; Ozaki, A. J. Chem. Soc., Chem. Commun. 1984, 321

	activity, mmol/(g h)	$TOF \times 10^4$, N ₂ molecules/H(a)/s	act. energy, kcal/mol	BET area, m ² /g	ref
Raney Ru-CsNO3 ^a	24.0	(187) ^b	22	28	this work
Raney Ru ^a	0.28	$(2.2)^{b}$	23	40.0	this work
Raney Ru	17.0	88.2	27	51.4	6, 19
Raney Ru-K	48.5	252	27	(51.4)	6, 19
5% Ru-K/AC	0.51	24.1	23		19, 20
5% Ru-K/BeO	2.5	175	24	18	19, 22
5% Ru–K/MgO	0.66	147	26	9.9	19, 22
4.2% Ru-K/ČaO	0.49	139	25	12	19, 22
Ru powder	0.0002	0.020	23	2.0	19, 21
Fe-Al ₂ O ₃ -K ₂ O	0.0019	0.027	29	19.3	19, 23, 25
Fe powder	0.00005	0.0021	50	2.3	19, 24, 25
Os	0.061	0.040	21	30.8	19, 26
5% Ni-K/AC	0.0004		31		19, 27
5% Co-K/AC	0.0012		38		19, 27

12

13

"Raney Ru in the same batch. ^bEstimated from hydrogen adsorption data on Raney Ru. ^cEstimated from the rate and kinetic data.²⁸

TABLE VII: Comparison of Rates between Ammonia Synthesis (N2 + 3H₂, 80 kPa) and IER of Dinitrogen (N₂, 20 kPa) at 573 K^a

0.031

(0.55)^c

(12.5)

5% Os-K/AC

BaN_{0.62}

SrN_{0.5}

	Raney Ru	Raney Ru-CsNO ₃	Ru-K/ AC	Fe-Al ₂ O ₃ -K ₂ O
IER of N_2 , mmol of $N_2/(h g)$	0.17	14.7	0.30*	0.0010
mmol of N/(h g)	0.33	29.4	0.60*	0.0020
NH ₃ synthesis, mmol of NH ₃ /(h g)	0.081	2.73	2.04	0.21

^aData taken from Tables II and VI. ^bRu content is 5% (Table VI). ^cRu content is 4.7% (Table II).



Figure 4. Plot of IER rate of N₂ as a function of H₂ pressure at various temperatures on Raney Ru-CsNO₃ under 20 kPa of N₂. Rate (μ mol/(g h)) at 473 (●), 493 (□), 508 (△), and 523 K (O).

IER of N_2 as a Function of N_2 and H_2 Pressure. In order to clarify the hydrogen inhibition effect on IER, the rates of IER were measured in the presence of hydrogen over Raney Ru (Figure 3) and Raney Ru-CsNO₃ (Figure 4). As was expected in the former description, IER of N_2 was proved to be retarded by hydrogen on both catalysts. The rate of IER was also measured as a function of N_2 pressure. One set of data at 563 K is shown in Figure 5, where the pressure dependency was of order 0.42.

- (23) Morikawa, Y.; Ozaki, A. J. Catal. 1968, 12, 145.
 (24) Morikawa, Y.; Ozaki, A. J. Catal. 1971, 23, 97.
 (25) Morikawa, Y.; Naka, Y.; Ozaki, A. Nippon Kogaku Kaishi 1972, 1023
- (26) Guyer, W. R. F.; Joris, G. G.; Taylor, H. S. J. Chem. Phys. 1941, 9. 287
- (27) Urabe, K.; Ohya, A.; Ozaki, A. J. Catal. 1978, 54, 436.
 (28) Panov, G. I.; Kharitonov, A. S. In Proceedings of the 9th International Congress on Catalysis, 1984; Dechema, Eds.; Verlag Chemie: Vein-
- hohar Congress on Catagas, 1997, Dechenna, Eds., Verlag Chenne. Venl-heim, 1984; Vol. 3, p 371.
 (29) Aika, K.; Kumasaka, M.; Oma, T.; Kato, O.; Matusda, H.; Watan-abe, N.; Yamazaki, K.; Ozaki, A.; Onishi, T. Appl. Catal. 1986, 28, 57.
 (30) Urabe, K.; Aika, K.; Ozaki, A. J. Catal. 1976, 42, 197.



0.1

0.1

Figure 5. Nitrogen pressure dependence of rate of IER of N₂ on Raney Ru-CsNO3 at 563 K.



Figure 6. Plot of $R^{-0.5}$ as a function of $P_{N_2}^{-0.5}$ (eq 11). R is the rate of IER of N₂ without hydrogen over Raney Ru–CsNO₃. Raney Ru, 0.5 g. Rate $(\mu mol/(g h))$ at 423 (\bullet), 453 (Δ), 473 (\blacksquare), 493 (O), 523 (∇), and 573 K (□).

We assumed that adsorbed hydrogen and nitrogen were competing with each other to occupy the same sites (Ru surface). Under the equilibrium of two adsorption processes (eqs 6 and 7), the coverages of N (θ_N) and H (θ_H) are represented as a function of pressures according to the Langmuir equation.

$$N_2 + 2 \text{ sites} \rightleftharpoons 2N(a)$$
 (6)

$$H_2 + 2 \text{ sites} \rightleftharpoons 2H(a)$$
 (7)

$$(K_{\rm N}P_{\rm N_2})^{0.5} = \theta_{\rm N}/(1-\theta_{\rm N}-\theta_{\rm H})$$
(8)

$$(K_{\rm H}P_{\rm H_2})^{0.5} = \theta_{\rm H}/(1-\theta_{\rm N}-\theta_{\rm H}) \tag{9}$$

The rate of IER of $N_2(R)$ is expressed as follows:^{21,30}

$$R = kP_{N_2}(1 - \theta_N - \theta_H)^2$$
(10)

$$R^{-0.5} = (kP_{\rm N_2})^{-0.5} + (K_{\rm N}/k)^{0.5} + (K_{\rm H}P_{\rm H_2}/kP_{\rm N_2})^{0.5}$$
(11)

The rates measured as a function of P_{N_2} without hydrogen on Raney Ru-CsNO₃ at various temperatures are rearranged in

19, 27

28

28



Figure 7. Arrhenius plot of k and K_N of eq 11. Catalyst: Raney Ru(0.5 g)-CsNO₃, IER of N_2 without hydrogen (from Figure 6).



Figure 8. Plot of $R^{-0.5}$ as a function of $P_{H_2}^{0.5}$ at various temperatures on Raney Ru-CsNO₃ under 20 kPa of N₂. R: IER of N₂ (μ mol/(g h)) at 473 (●), 493 (□), 508 (△), and 523 K (O).

Figure 6 in the form of eq 11. The slope gives k, and the intercept at $P_{N_1}^{-0.5}$ equals 0 gives K_{N_1} . The Arrhenius plots of these values are shown in Figure 7. The activation energy of k is given to be 15.0 kcal/mol, and the heat of adsorption of N_2 is given to be 11.6 kcal/mol. For same kinetic analysis was done for Ru-K at 593-653 K and for $Ru-K/Al_2O_3$ at 553-593 K. The activation energies were 14 ± 3 and 10 ± 2 kcal/mol, and the heats of adsorption were 40 ± 6 and 22 ± 3 kcal/mol for Ru-K and $Ru-K/Al_2O_3$, respectively.²¹ The heat of adsorption on Raney Ru-CsNO₃ in this study was lower than these values. The heat of adsorption of N_2 on Ru is not known because the amount of adsorbed nitrogen on clean Ru is too low for heat measurement. The calculated value is reported to be -28 kcal/mol (negative value).31

The effect of hydrogen for Raney Ru-CsNO₃ (Figure 4) was replotted in the form of eq 12, which is transformed from eq 11.

$$(kP_{\rm N}, /R)^{0.5} = 1 + (K_{\rm N}P_{\rm N})^{0.5} + (K_{\rm H}P_{\rm H})^{0.5}$$
(12)

The results are shown in Figure 8, where k and K_N obtained above are applied. Thus, $K_{\rm H}$ was obtained for each temperature. The Arrhenius plot of $K_{\rm H}$ gave the heat of adsorption to be 19.3 kcal/mol (Figure 9). These kinetic analyses show that hydrogen and nitrogen atoms compete for the Ru surface atoms under reaction conditions, where H (19.3 kcal/mol) adsorption is stronger than N adsorption (11.6 kcal/mol) at 473-523 K. The same kinetic analysis has been carried out on Ru-K at 593 K, where k and K_N were decreased when hydrogen was adsorbed.²¹ In this study, this effect was ignored for convenience; however, hydrogen was found to be adsorbed strongly both on Ru-K and on Raney Ru-CsNO₃.

Discussion

The State of Alkali Nitrates. The process of disproportionation of alkali nitrate on Raney Ru was not studied in detail here; however, the temperature-programmed reaction has been studied on Ru/Al_2O_3 , where CsNO₃ is thought to be converted to Cs₂O and/or CsOH on Ru/Al₂O₃, as shown in eqs 1-4.^{3,8} Similar reactions are suggested for Raney Ru, although eq 4 is inferred to proceed to a less extent than for the supported catalyst system where more surface OH exists. A part of the alkali element is thought to be "metallic" by eq 2. The following facts suggest this. (1) Any kind of activated alkali nitrate-Raney Ru catalysts are very pyrophoric in air, while the Raney Ru without promoter was not pyrophoric in air after use. (2) The catalyst was irreversibly deactivated by the addition of water. (3) Raney $Ru-CsNO_3$ has a similar activity to Raney Ru-K in ammonia synthesis and IER of N_2 . (4) The promoter effect decreases in the order CsNO₃, RbNO₃, KNO₃, and NaNO₃. (5) XPS results show that the binding energy of Ru is decreased by the disproportionation of alkali nitrates (Table III), although alkali oxide addition also makes the binding energy shift.¹⁴ (6) XPS binding energy of alkali under the working state is lower than that of alkali nitrate (Table IV). (7) Surface aluminum is reduced by the disproportionation of RbNO₃ or CsNO₃ (Table III). (8) Hydrogen is adsorbed much more than the number of surface Ru atoms might allow.

Thus, the disproportionation of CsNO₃ on Raney Ru is suggested to produce some metallic Cs (eqs 1 and 2) in addition to Cs_2O or CsOH (eqs 3 and 4). It is no wonder we get "metallic" alkali from the nitrate thermodynamically. The free energy data about CsNO3 are not available, but the data for KNO3 are known. The following reaction can occur thermodynamically.

$$KNO_3 + \frac{9}{2}H_2 \rightarrow K + NH_3 + 3H_2O$$
 ($\Delta G = -73.87$ kcal)
(13)

Of course K₂O formation must be easier, though no thermodynamic data of K_2O are available.

$$KNO_3 + 4H_2 \rightarrow \frac{1}{2}K_2O + NH_3 + \frac{5}{2}H_2O$$
 (14)

Once "metallic" alkali is formed (eq 2), it might react with the product H₂O to give CsOH. However, the product H₂O is trapped in the liquid nitrogen through the circulated hydrogen gas in our system. If H₂O evolved is controlled to keep quite low pressure (for example, to raise the temperature slowly during the hydrogen treatment as is shown in the "method"), metallic alkali can be protected. Even KOH has been known to be reduced to K by carbon at 1073 K.32,33

The Role of Promoter. The main purpose of this work is (1) to report the activeness of alkali nitrate promoted Raney Ru catalyst for N_2 activation, (2) to suggest the existence of "metallic" alkali on the Raney Ru catalyst, and (3) to report the hydrogen inhibition on this system due to the competitive adsorption between N_2 and H_2 . However, the general role of alkali promoter, which has been already reported, ^{1-4,22} is summarized here, citing the other recent works, too.¹¹⁻¹⁴

The activity of N_2 activation (NH₃ synthesis and IER of N_2) on Ru surface is promoted by the presence of electropositive elements or basic oxides.¹⁻⁴ Although the effectiveness of promotion depends on how the promoter compound interacts with Ru surface (morphological aspect or preparation method), the electronegativity of elements or compounds³⁴ is a useful measure of promotion as has been shown in Figure 2 of ref 4. The turnover frequencies of ammonia synthesis over Ru-K/Al₂O₃, Ru-CsOH/Al₂O₃, and Ru/Al₂O₃ are roughly 10^{-2} , 10^{-3} , and 10^{-4} at 588 K, respectively.⁴ This is in accordance with the values of electronegativity of K (0.80), CsOH (1.73), and Al_2O_3 (2.49).⁴ The reason why the activated Raney Ru-alkali nitrate catalyst is active is that the system probably contains "metallic" alkali in the system.

It has been discussed that dissociation of N_2 on Ru is accelerated by electron donation to adsorbed N₂ through Ru atom from the

⁽³²⁾ Wennerberg, A. N.; O'Grady, T. M. U.S. Patent 4,082,694, 4 April, 1978

⁽³³⁾ Otowa, T.; Yamada, M.; Tanibata, R.; Tanaka, G. 64th Catalysis Society of Japan Meeting Abstracts; No. 2A11, 1989. (34) Sanderson, R. T. J. Chem. Educ. 1952, 29, 539; 1954, 31, 2; J. Am.

Chem. Soc. 1952, 72, 272.



Figure 9. Arrhenius plot of $K_{\rm H}$ (eq 12). Catalyst: Raney Ru(0.5 g)-CsNO₃. From Figure 8.

promoter.¹⁻⁴ This is in accordance with the activation of CO molecules on a transition metal with an alkali promoter.^{35,36} Recently, a slightly different explanation has been proposed for the CO activation on metal surfaces with metallic alkali. Metallic alkali changes the adsorption site potential, which changes the electronic energy levels in the CO-metal system.¹¹⁻¹³ Such discussion can be applied to the N₂-metal system. Metallic alkalis can give their electrons up to the Ru surface, causing a change in adsorption site potential. Although alkali-metal "salts" cannot give electrons in principle, the dipole of the salts might change the circumstances of the electrostatic field at the adsorption site.¹⁴ The activation of N₂ on Ru could be promoted by alkali-metal oxides or hydroxides in such a way. Of course, "metallic" alkali is more effective.

Surface States of Ru and Al. The Raney Ru surface is partly covered with Al^0 and $Al^{3+,7}$ The higher activity of the Raney Ru itself is due to the high surface area and to the residual Al on the surface, where Al is suggested to be a structural promoter.⁶ Quantitative analysis by XPS suggests that the intensity of Al is decreased by the addition of alkali. This suggests that the alkali compounds might localize more on Al than on Ru atoms on the Raney catalyst surface. Potassium has been reported to react with Al_xO_y on an iron single crystal.³⁷ Thus, the electron transfer from metallic alkali to Ru may be indirectly through Al in addition to direct interaction. The catalyst surface is heterogeneous and seems to be composed of several compounds of alkali and Al.

Fe-Al₂O₃-K₂O catalyst is composed of mostly reduced Fe, about 3% Al₂O₃, and about 1% K₂O. Both Al₂O₃ and K₂O exist mainly on the catalyst surface. It has been understood that Al₂O₃ is a structural promoter and K₂O is an electronic promoter.¹ For alkali nitrate promoted Raney Ru catalysts, it is suggested that the remaining Al acts as a structural promoter that stabilizes the Ru fine structure⁷ and alkali compounds act as electronic promoters that change the circumstances of the electrostatic field of the Ru surface. In this sense, alkali nitrate promoted Raney Ru catalysts resemble Fe-Al₂O₃-K₂O and should be called "doubly promoted Ru catalysts", although the states of Al and the alkali might be more reduced in the case of the promoted Raney Ru catalyst.

Why does alkali nitrate work better on Raney Ru than on supported Ru? The alkali nitrate is suggested to give some alkali metal (eq 2), which could react with surface hydroxyls on the support (eq 4). Since Raney Ru has fewer hydroxyls, the alkali metal might survive and act as a strong promoter. Why does alkali nitrate work better than alkali metal (potassium vapor) on Raney Ru? Alkali-metal nitrate may penetrate more effectively into the micropore structure during impregnation of the Ru than potassium does during preparation of the catalyst by alkali-metal vaporization.

Hydrogen Retardation Against N_2 Activation on Raney Ru-CsNO₃. It was found that hydrogen retarded the reaction, as

TABLE VIII: Hydrogen Effect on N₂ Activation (IER or Adsorption of N₂)

- · 2			
	cause	effect	case
1.	direct cause		
	(competitive adsorption)	-	Raney Ru-CsNO ₃ (this work), Ru-K/AC, ²⁰ Ru-K, ³⁰ Ru, ³⁸ Ru/Al ₂ O ₃ , ³⁰ Ru-K/Al ₂ O ₃ ³⁰
2.	indirect cause		
	(change of surface state or adsorbed species from N to NH)	+	Ru, ³⁰ Fe-Al ₂ O ₃ -K ₂ O ¹

shown in Figures 3 and 4 and in Table VII. This behavior is not seen with the Fe catalyst system.^{1,10} The IER of N₂ is slower than ammonia synthesis on Fe-Al₂O₃-K₂O, as shown in Table VII. It is also seen that IER of N₂ is much faster on the Ru system than on the Fe system, while the ammonia synthesis rate on the Ru system is not much faster than on the Fe system (Table VII). This is because hydrogen usually retards N₂ activation on the active Ru surface, whereas it sometimes promotes N₂ adsorption on Fe-Al₂O₃-K₂O.¹

Hydrogen is strongly adsorbed on the Ru surface, and hydrogen inhibition against N₂ activation seems a general trend for Ru catalysts.^{20,26,30,38} However, there are opposite cases in which hydrogen promotes the IER of N₂ (Ru powder³⁰) or the adsorption of N₂ (Fe-Al₂O₃-K₂O¹). In this case, hydrogen should change the surface states or the adsorbed form of nitrogen such as from N to NH. The effect of hydrogen is summarized in Table VIII, and the cause has been discussed precisely in every work. The discrepancy of the hydrogen effect on two Ru powder samples may be due to the Ru source.^{30,38} French Ru powder was proved to have no impurity by AES,³⁸ while our Ru powder might contain Cl ion.^{30,39}

Hydrogen retardation was well explained by a model of competitive adsorption between adsorbed hydrogen and nitrogen on Raney Ru-CsNO₃ in this study. However, if we consider all the kinds of Ru catalysts, the hydrogen effect is not simple and presents a controversial problem. Generally, there should be the two causes, and the relative importance of the two causes should depend on the surface states or the kinds of promoter. The problem of a hydrogen effect should be very important for ammonia synthesis on Ru catalyst under industrial conditions.²⁹ Thus, if we could control the hydrogen effect over the Ru catalyst, we would get a better ammonia catalyst because the rate of IER of N₂ without H₂ is extraordinarily faster compared to that of other catalysts (Table VI).

Conclusions

1. The Ru metal surface is extraordinarily active for dissociation of dinitrogen if an electron is donated or electrostatic field is applied strongly and effectively. Raney Ru-CsNO₃ was found to be one of the two most active catalysts, the other of which is Raney Ru-K, for isotopic equilibration of N₂. CsNO₃ was found to become the most effective electron-donating promoter.

2. $CsNO_3$ was presumed to become partly metallic Cs during disproportionation over Raney Ru. This is one reason for the high activity. Other alkali nitrates were also effective promoters; however, their effectiveness was in the order of electron-donating ability to the metal, i.e., Cs > Rb > K > Na.

3. The dissociative adsorption process was retarded by hydrogen on Raney Ru-CsNO₃. The retardation can be explained by a competitive adsorption model of N_2 and H_2 . Hydrogen was adsorbed more strongly than nitrogen on Raney Ru-CsNO₃.

4. Despite the hydrogen retardation, per-gram activity of ammonia synthesis on Raney Ru-CsNO₃ was almost the same as that of Ru-K/AC, because of the high surface area of Ru per gram, whereas the TOF was lower than that of the latter catalyst.

Registry No. Ru, 7440-18-8; CsNO₃, 7789-18-6; RbNO₃, 13126-12-0; KNO₃, 7757-79-1; NaNO₃, 7631-99-4; N₂, 7727-37-9; H₂, 1333-74-0.

⁽³⁵⁾ Blyholder, G. J. Phys. Chem. 1964, 68, 2772

⁽³⁶⁾ Dry, M. E.; Shingles, T.; Boshoff, L. J.; Oosthuizen, G. J. J. Catal. 1969, 15, 190.

⁽³⁷⁾ Bare, S. R.; Strongin, D. R.; Somorjai, G. A. J. Phys. Chem. 1986, 90, 4726.

⁽³⁸⁾ Rambeau, G.; Amariglio, H. J. Catal. 1981, 72, 1.

⁽³⁹⁾ Don, J. A.; Pijpers, A. P.; Scholten, J. J. F. J. Catal. 1983, 80, 296.