Isotopic Equilibration Reaction of Dinitrogen over Raney Ruthenium: Importance of the Structural Factor

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The isotopic equilibration reaction of dinitrogen ($^{28}N_2 + {}^{30}N_2 = 2^{29}N_2$) was studied over three Ru catalysts: stabilized Raney Ru, Al–Ru alloy, and Ru powder. The turnover frequency (TOF) at 588 K ranges from 10^{-6} to 10^{-2} and depends on the Al/Ru ratio and the microcrystal size of Ru. The highest TOFs are obtained over samples leached at 373 K from alloys having an atomic percent of Ru from 6 to 33. These samples have a smaller average Ru crystal size and a lower Al content, ranging from 8 to 18 mol% as measured by X-ray photoelectron spectroscopy (XPS). We also suggest that the high activity is related to strongly adsorbed nitrogen, the uptake of which exceeds hydrogen adsorption. Almost no XPS chemical shift is observed for any leached Raney Ru, whereas the Ru $3d$ binding energy in Al–Ru alloys is about 1 eV lower than that in Ru metal powder. In spite of the pronounced chemical shift, the TOF on Al–Ru alloy is quite low. Results suggest that structural factors are most important in this system, rather than the electronic factor that has been emphasized for supported Ru catalysts. © 1988 Academic Press, Inc.

INTRODUCTION

Ruthenium is known to be a promising catalyst for ammonia synthesis (*1–5*). Among active catalysts, Raney Ru has been reported to be one of the most effective for ammonia synthesis and the isotopic equilibration reaction (IER) of dinitrogen ($^{28}N_2 + {}^{30}N_2 = 2^{29}N_2$) when promoted with metallic potassium (*6–8*). Recently, Raney Ru itself was found to be quite active for the IER of N_2 (*9*). The turnover frequency (TOF) is close to that of potassium-promoted Raney Ru. This high activity was ascribed to the residual Al inside the Raney Ru. Since metallic aluminum is a weaker electron donor than potassium, the high activity was not expected. In our previous letter, we proposed that the reason for the high activity is the intimate combination of Al and Ru in this catalyst (*9*).

Two factors—electronic and structural—have been reported to be important for catalytic activation of N_2. The electronic fac-

tor involves donation of electrons from a K or CsOH promoter to Fe and Ru surfaces (*1–3, 10*). The structural factor involves influences on the activity by the faces of single crystals in Fe and Re, as has been pointed out by Ertl *et al.* (*11*), Somorjai and colleagues (*12, 13*), and Boudart and colleagues (*14*). For supported Ru catalysts, the electronic factor is more important than the structural (*10*). However, as mentioned above, unsupported Ru catalysts such as Raney Ru do not seem to be explained by the electronic factor alone. Thus, in this work, various unsupported Ru catalysts were prepared and characterized by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), electron probe microanalysis (EPMA), X-ray diffraction (XRD), and adsorption measurements. The results are used to analyze the roles of the electronic and structural factors in the activity of the catalysts for the N_2 IER. Since both ammonia synthesis and the N_2 IER have a common rate-determining step (dissociative adsorption of N_2), the

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study of the N_2 IER is fundamental to the study of ammonia synthesis.

METHODS

Several alloy samples with different Al/Ru ratios were manufactured. Only $Al_{55}Ru_{45}$ alloy was difficult to leach under standard conditions (5 N KOH, 373 K, 2 h) (*15*). Several samples were leached from $Al_{79}Ru_{21}$ at lower temperatures for a shorter period in order to control the Al/Ru ratio of Raney Ru. Si–Ru alloy (Si–Raney Ru) was also leached and was used for comparison. Raney Ru leached, washed, and kept in water was transferred to a glass reactor together with water, which prevented oxidation. The leached sample weight was estimated as the weight of Ru in the starting alloy (normally 1 g), thereby neglecting the weight of Al removed. Ruthenium powder was obtained from Tanaka Precious Metals Ltd. The reactor was attached to a closed circulation system with a mass filter. After the sealing water was evacuated, the Ru surface was stabilized by N_2 adsorption at 623 K, which caused sintering. Before the rate measurement of the N_2 IER, the BET area (77 K) and H_2 chemisorption (273 K after 623 K evacuation) were measured. The adsorbed state of nitrogen was studied by using temperature-programmed desorption (TPD) and isotopic techniques, as described in the previous letter (*16*). A part of the sample was moved to a side arm of the reactor and sealed off for XPS measurements.

Raney Ru–K was prepared by evaporating potassium onto the Raney Ru surface in the reaction apparatus (*6*). The instruments used for the characterizations were as follows: XRD, Philips Model PW-1050; SEM, Hitachi SEM Model HFS-2; EPMA, Philips EDAX Model 707B (Ru and Al peaks were calibrated using pure metals on the same sample holder); XPS, Shimadzu ESCA 750 (concentrations of elements were calculated using the cross section data); TEM, Hitachi H-1250 (1000 kV); and mass filter, NEVA AGA 100.

RESULTS

XPS Spectra of Al–Ru Alloys

Al–Ru alloys were found to have lower binding energy for the Ru $3d$ state than pure Ru metal. Three of the five alloys with different Al contents were analyzed by XRD. The following major phases were identified:

$Al_{55}Ru_{45}$ sample, AlRu phase

$Al_{79}Ru_{21}$ sample, $Al_{13}Ru_4$ and Al_6Ru phases

$Al_{94}Ru_6$ sample, Al, $Al_{13}Ru_4$, and Al_6Ru phases.

Neither an Al metal nor a Ru metal phase was observed by XRD except in the last sample. Quantitative analysis of XPS spectra of Ru ($2p_{1/2}$) and Al ($2s$) showed that the alloy surface was mostly covered by Al^{3+}, especially in the cases of $Al_{79}Ru_{21}$ and $Al_{94}Ru_6$, but that the Al/Ru ratio approached the bulk composition after Ar sputtering for 5 min. Under this condition, Al was found to be mostly metallic ($2s$ 117.5 eV, $2p$ 72.3 eV) and partly oxide ($2s$ 119.0 eV, $2p$ 74.2 eV). The partial oxidation of Al may be caused by OH during an Ar sputtering or by a charge withdrawal to Ru.
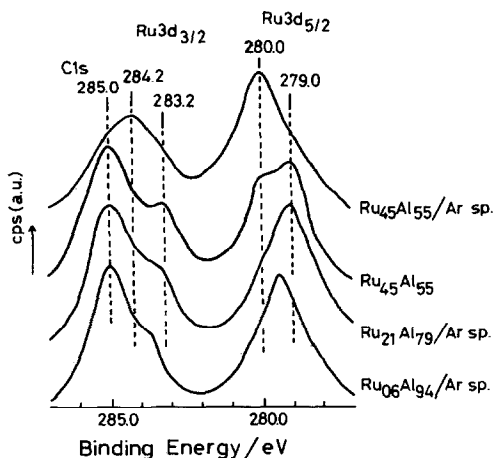
Ru $3d$ XPS spectra are shown in Fig. 1. It

FIG. 1. XPS spectra of Al–Ru alloys. Because the original Ru signal is so low on the surface, some samples were sputtered in an Ar atmosphere for 5 min to eliminate surface Al (Ar sp.). Binding energy of Al $2s$ was 117.5 eV (Al^0) with a shoulder of 119.0 eV (Al^{3+}).

TABLE 1

Characterization of Raney Ru Catalyst

Sample No.	Alloy Ru mol%	Leaching conditions			N_2 uptake[a] at 623 K (ml/g)	Surface characterization[b]				IER of N_2 at 588 K log TOF (molecules/s/site)
		Temp. (K)	Time (h)	KOH conc. (N)		BET (m^2/g)	Ru%[c] by H_2 ad.	Ru%[d] by XPS	Ru%[d] by EPMA	
1	45	373	2	5	1.3	2.0	6	60	55	−4.27
2	33	373	2	5	3.0	20.9	7	92	88	−1.79
3	21[e]	373	2	5	9.4	51.4	38	79	85	−2.06
4	14	373	2	5	15.4	41.6	10	80	85	−2.10
5	6	373	2	5	7.5	42.8	18	72	—	−2.35
6	21	273	0.1	0.5	0.8	5.6	5	34	35	−5.00
7	21	273	0.5	0.5	2.6	11.1	17	62	56	−4.25
8	21	273	2	0.5	4.3	25.5	13	70	78	−3.60
9	21	273	2	2	4.0	20.0	10	72	79	−3.68
10	21	298	2	0.5	—	40.3	11	73	83	−3.60
11	100	—	—	—	0.0	2.0	—	100	100	−5.70

[a] For 40 h.
[b] After stabilization by N_2 uptake at 623 K.
[c] Ru surface area percentage (S_{Ru}/S_T) assuming 1.63×10^{19} Ru atoms/m^2 (17).
[d] Ru/(Al + Ru) mole ratio (%).
[e] Standard sample.

is to be noted that the $3d_{5/2}$ peaks show lower binding energies (~279.0 eV) than that of Ru metal (280.0 eV). These results suggest the possibility of charge transfer from Al to Ru in an Al-rich alloy. Unexpectedly, these alloys show a quite low TOF for IER of N_2. For $Al_{55}Ru_{45}$, an Ar sputtering resulted in a shift to the normal value for Ru metal. The reason for this shift is not clear; however, an Ar sputtering might cancel the excess reduction of Ru atoms by the presence of a foreign OH group. This shift was not found with $Al_{79}Ru_{21}$ and $Al_{94}Ru_6$.

Characterization of Stabilized Raney Ru

The Raney Ru samples prepared under various leaching conditions were heat-treated in N_2 at 623 K for 40 h to prepare them for reaction at higher temperatures. The surface of the heat-treated samples was characterized. H_2 chemisorption and BET surface area were measured; the ratio of these values is a measure of the percentage of Ru on the surface (S_{Ru}/S_T) (27). These values are listed in Table 1. The Ru atomic ratios (Ru)/(Ru + Al) obtained by XPS and EPMA are also given in Table 1. The value of S_{Ru}/S_T is much smaller than the (Ru)/(Ru + Al) value obtained by XPS or EPMA. It has been suggested that this difference is due to surface enrichment of Al (15). The (Ru)/(Ru + Al) values obtained by XPS are very close to those obtained by EPMA. That is not surprising, because XPS with kinetic energy of about 1000 eV averages over about five layers of Ru surface. Si–Raney Ru has a low surface area of 2.2 m^2 g^{-1} and a Ru surface fraction of 18% (S_{Ru}/S_T).

Figure 2 shows the progress of the leaching with time and temperature. H_2 chemisorption increases as with increasing time and/or temperature of leaching. Other measurements shown in this figure are described in the next section. A drastic change is seen when the leaching temperature is increased to 298 or 373 K. BET area and Ru content also increase, as shown in Table 1.

Nitrogen Adsorption

If the N_2 IER were studied on fresh leached Raney Ru at 523 to 623 K, sintering and N_2 adsorption would affect the rate measurements. Treatment with N_2 is also
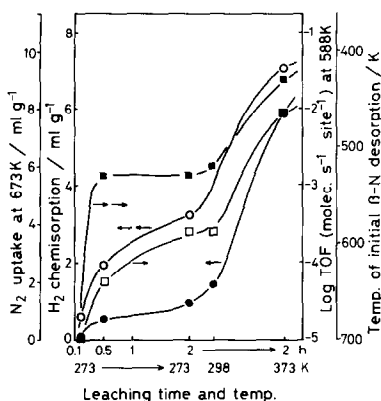
FIG. 2. N_2 adsorption (open circles), H_2 adsorption (closed circles), nitrogen desorption temperature (closed squares), and TOF of the N_2 IER (open squares) as functions of leaching time and/or temperature. The used sample is leached from $Al_{79}Ru_{21}$ alloy with 0.5 to 5 N KOH solution.

FIG. 3. XPS spectra of N $1s$ in the following. (1) Nitrogen adsorbed on Rany Ru (400 Torr N_2 at 623 K for 40 h). (2) NH_3 adsorbed at 298 K on Raney Ru slightly oxidized (NH_3 is decomposed on reduced Raney Ru). (3) Commercial AlN. Spectra are identified as adsorbed N (397.4), NH_x (398.7), adsorbed NH_3 (399.6–399.7), and AlN (396.7 eV) (19).

known to activate Fe surfaces (1, 18). To stabilize and activate the surface of our samples, N_2 was adsorbed at 623 K for 40 h at about 400 Torr (1 Torr = 133.3 N m^{-2}). The amount of adsorbed N_2 on various Raney Ru samples is shown in Table 1. The adsorbed N_2 of some samples is shown as a function of leaching time and/or temperature in Fig. 2. Both N_2 uptake and H_2 uptake increase with leaching, but N_2 uptake is always greater than H_2 uptake. This finding suggests that nitrogen atoms are adsorbed by parts of the catalyst that do not adsorb H_2 (16).

XPS spectra of adsorbed nitrogen are shown in Fig. 3, together with the reference spectra. These spectra indicate that adsorbed nitrogen is mostly atomic (N) and partly hydrogenated (NH, NH_2) and is not AlN (19). Figure 4 shows the concentration of adsorbed N by XPS on various samples compared with the concentrations of Ru and Al by XPS. The concentration of N is linearly related to that of Ru and is independent of the residual Al in the Raney Ru. Nitrogen is, therefore, considered to be combined with the Ru atom but not with Al. This situation is rather different from the system Ru–K, where the amount of ad-
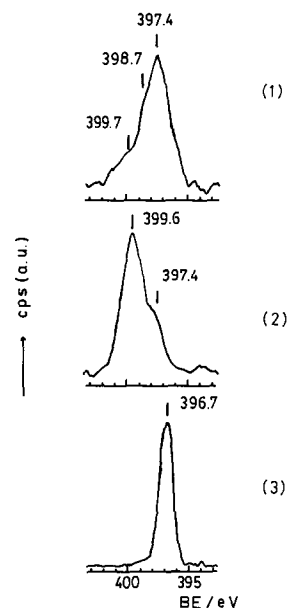
sorbed N is related to the amount of K (20, 21). No N_2 adsorption was observed on 1.0 g of Si–Raney Ru by a volumetric measurement.

Identification of Adsorbed Nitrogen by Isotopes and TPD

After $^{28}N_2$ adsorption for 40 h, the IER of N_2 ($\sim$40% $^{30}N_2$ + 60% $^{28}N_2$) was carried out
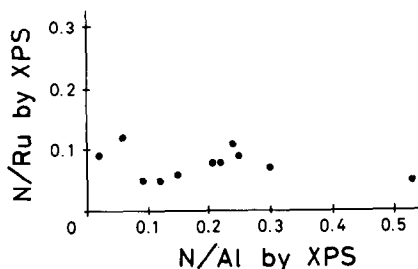

FIG. 4. Concentration ratio of adsorbed N to Ru as a function of ratio of adsorbed N to Al. Values are measured by XPS. Nitrogen was adsorbed on Raney Ru at 623 K for 40 h.

at 573 K over various Raney Ru samples to label the exchangeable ^{15}N on the surfaces (16). The reaction was continued until the *degree of equilibration* DE reached about unity, where

$$DE = (^{29}N_2)^2(^{28}N_2)^{-1}(^{30}N_2)^{-1}.$$

A TPD run of the adsorbed nitrogen was then carried out from 77 to 873 K at a heating rate of 4 K min^{-1}, after the N_2 gas phase was evacuated at 77 K for 3 h. The desorbing gas was continuously detected by a mass filter as described previously (16). The results for every sample are shown in Fig. 5. At low temperatures (below 200 K), nitrogen is adsorbed molecularly (γ state), as shown by the fact that DE remains approximately 1. At higher temperatures (above 400 K) nitrogen is adsorbed in atomic form (β and δ state) as seen because isotopic randomization gives a DE value of about 4.0. At still higher temperatures, desorbing N_2 is diluted by the initially adsorbed ^{14}N which is strongly adsorbed. A peak or shoulder that is not diluted by ^{14}N is assumed to be weakly adsorbed (β state) and the desorbing N_2 not diluted by ^{14}N is assumed to be strongly adsorbed (δ state). The samples that had higher surface area or were leached more thoroughly (samples 2, 3, 4, and 5) had more δ-state nitrogen. Samples 1 and 6 had no δ-state nitrogen. Weakly adsorbed (β-state) nitrogen is considered to be the intermediate state of the N_2 IER because it desorbs through randomization (16). δ-Nitrogen does not take part in the IER: the desorbed gas has isotopic compositions different from those of the IER condition. However, the two states (weakly and strongly adsorbed) cannot be distinguished by XPS spectra (19). The temperatures at which β-nitrogen begins to desorb are shown in Fig. 2 as a function of leaching time and/or temperature. It decreases as leaching conditions become more severe. This tendency is in accordance with the N_2 IER activities of the samples, as is discussed in the next section. Thus, the desorbing temperature of β-nitro-
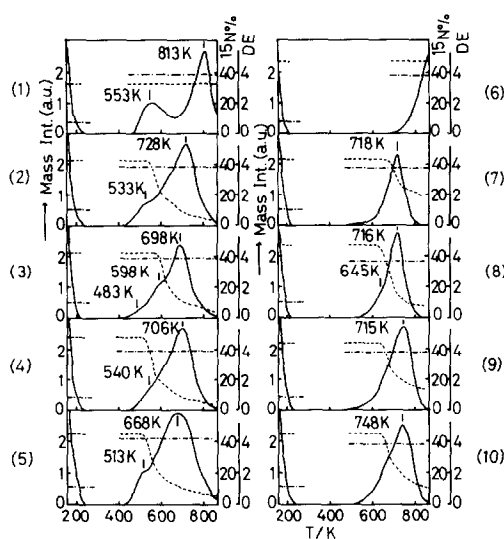

FIG. 5. TPD spectra of adsorbed N_2 on various stabilized Raney Ru samples. (—) Total dinitrogen; (---) ^{15}N % in dinitrogen; (-··-) DE of desorbed dinitrogen. Before TPD, $^{28}N_2$ was adsorbed at 623 K for 40 h; the IER was carried out using 60% $^{28}N_2$ + 40% $^{30}N_2$ at 573 K until DE reached 1.0. Samples numbered as in Table 1.

gen is also a measure of the catalyst activity.

TOF of N_2 IER

The rate of the N_2 IER was measured at a pressure of 150 Torr at 523 to 623 K, and for some samples to 723 K. The rate was analyzed by the first-order plot (22, 23), and the rates at 588 K were normalized as TOF on the basis of H_2 chemisorption, as shown in Table 1. The rates seem to depend on the preparation conditions and surface states, as discussed later. As is shown in Fig. 3, the activity increases with the severity of the leaching conditions, as does the desorption temperature of β-nitrogen.

The highest TOF on Raney Ru (sample 2, 8.8×10^{-3}) is 4000 times that on Ru metal (2.0×10^{-6}) (22). This value must reflect either the striking effectiveness of the skeletal structure or a promoter action of residual Al metal. The activation energies are 27 and 23 kcal mol^{-1}, respectively. Al has been shown by an XPS study to exist

mainly in the oxidized state and partly in the reduced state (15). The maximum TOF on Raney Ru is also higher than that on conventional Ru catalysts at 588 K (TOF below 10^{-7} on Ru/AC (22); 2.4 × 10^{-3} on Ru–K/AC (22); 1.2 × 10^{-5} on Ru/Al$_2$O$_3$ (23); and 2.4 × 10^{-3} on Ru–K/Al$_2$O$_3$ (23)), but it is slightly lower than TOFs on the superbase-supported Ru catalysts, which have been reported to be the most active catalysts for this reaction (24). The values over Raney Ru are also much higher than those for Os (4.0 × 10^{-5} at 588 K) (23, 25) which had been known to be the most active element for IER of N$_2$. Si–Raney Ru was quite inactive (TOF below 10^{-7} at 588 K). Whether the high activity of Raney Ru is due to the skeletal structure or to Al as a promoter is discussed in the next section.

DISCUSSION

Possible Charge Transfer from Al to Ru in Al–Ru Alloy

Chemical shifts of XPS binding energy of Ru 3d have been reported on alkali-added Ru catalyst (−1.1 eV) (26) and on CaO-supported Ru catalyst (−0.5 eV) (10). These data suggest some electron transfer from alkali or alkali earth oxides to Ru metal. Since Al metal has a lower electronegativity than alkali oxides (10), metallic Al can be expected to transfer its electron to Ru metal in Al–Ru alloy. A chemical shift to lower binding energy is observable when Al content is higher than 79%, as is shown in Fig. 1. Such a chemical shift is not observed for freshly leached Raney Ru, even though it contains some metallic Al. This is probably due to the low Al/Ru ratio, which makes electron transfer negligible.

Strongly Adsorbed Nitrogen on Ru

N$_2$ uptake is greater than H$_2$ chemisorption over these samples. It is assumed that reversibly adsorbed β-nitrogen is located on the Ru surface where hydrogen can be adsorbed. The strongly adsorbed δ-nitrogen is suggested to be dissolved in the bulk Ru

phase near the surface or located under Al(OH)$_3$ layer. The strongly adsorbed nitrogen is considered to be formed during the sintering of the sample under N$_2$ atmosphere.

Active Ru catalysts such as Ru–K/AC (20, 22) and Ru–K/Al$_2$O$_3$ (21, 23) absorb more nitrogen atoms than the number of Ru surface atoms. We suggested that this adsorbed nitrogen was related to potassium, such as KN$_x$ complexes on the Al$_2$O$_3$ surface (21). If Al played the same role as K, adsorbed nitrogen could be expected to interact with Al in Raney Ru. However, an XPS study discloses that the absorbed N is not present as AlN, and the amount is related to the concentration of Ru, but not to that of Al. As seen in Fig. 5, δ-nitrogen (main peak with high ^{14}N concentration) desorbs almost completely at 800 K. If this peak represented N in AlN, the reversible adsorption would be impossible, although in some cases conversion to AlN occurs only at very high temperatures (873 K) in the presence of H$_2$ (19). The state of Ru containing δ-nitrogen might be one factor in the high activity of this system; this problem needs to be studied. Activation of iron surfaces by N$_2$-containing gases has been reported (18).

Importance of Structural Factor in Activation of N$_2$ over Raney Ru

The main purpose of this study is to compare the catalytic activity with the surface characteristics of the catalysts and to identify the most important factors controlling the activity. The specific rates (molecules per second per gram) and TOFs (molecules per second per site) of the N$_2$ IER over the various Raney Ru samples are plotted as a function of Ru content measured by XPS in Figs. 6 and 7. The Ru content by XPS is close to the value of EPMA (bulk analysis). Although a small fraction of the Ru may be oxidized, most surface Ru is metallic (15). This conclusion is proved by the following findings: (i) H$_2$ is chemisorbed; (ii) N$_2$ is adsorbed atomically (XPS); and (iii) the rate
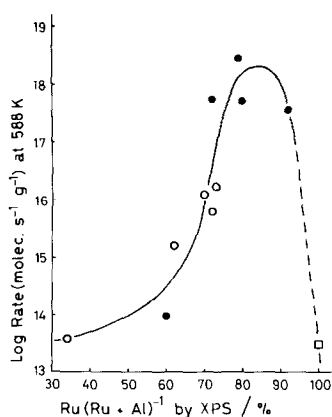
FIG. 6. Specific rate (molecules per second per gram) of the N_2 IER at 588 K over various Raney Ru samples as a function of Ru mol% (XPS). Open circles, leached at 273 or 298 K; closed circles, leached at 373 K; squares, Ru powder. XPS spectra were measured after the reaction following N_2 uptake at 623 K.

of the N_2 IER is quite fast. The activity increases with increasing Ru content in the Raney Ru samples, but Ru metal powder has a low activity. Figure 8 shows the TOF as a function of BET area. Generally, the finer skeletal structures with higher BET area give the higher activity.

The highest activity samples were obtained by leaching Al-rich alloys (6 to 33%

Ru) at high temperatures (373 K), which gives a finer Ru skeleton and low Al content. The TOF value ranged from 10^{-6} to 10^{-2} at 588 K, depending on the sample state. The TOF of the sample from $Al_{79}Ru_{21}$ is shown as a function of leaching time and/ or temperature in Fig. 2. The activity increases with the degree of leaching and the fineness of the crystals. The desorption rate (temperature of β-nitrogen desorption) also correlates with the IER activity in Fig. 2.

The drastic change of activity is considered to be mainly due to surface structural effects. Metallic Al remaining inside the Ru catalysts does not seem to act as a chemical (electronic) promoter, because the samples with higher Al content had lower activity. Even Al–Ru alloys, in which Ru has lower binding energy in Ru $3d$ XPS spectra, have quite low TOFs for this reaction. We do not intend to deny the electronic factor totally. The lower activity of Si–Raney Ru may be due to the higher electronegativity of Si than Al. When metallic potassium is added to Raney Ru, the activity at 588 K approximately doubles, probably because of an electronic effect (9). However, the effect is quite small compared to the TOF changes effected by controlling the Al/Ru ratio and/ or particle size. Thus, it is natural to con-
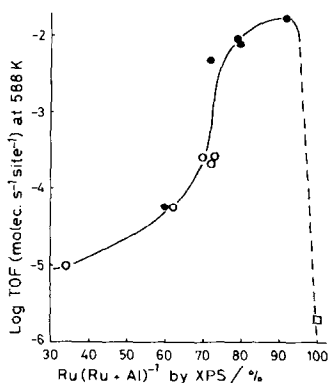

FIG. 7. TOF (molecules per second per site) of the N_2 IER at 588 K over various Raney Ru samples as a function of Ru mol% (XPS). Open circles, leached at 273 or 298 K; closed circles, leached at 373 K; squares, Ru powder. XPS spectra were measured after the reaction following N_2 uptake at 623 K.
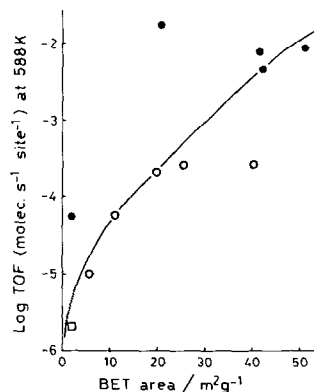

FIG. 8. TOF (molecules per second per site) of the N_2 IER at 588 K over various Raney Ru samples as a function of BET area. Open circles, leached at 273 or 298 K; closed circles, leached at 373 K; squares, Ru powder. BET area was measured after the reaction following N_2 uptake at 623 K.

clude that activation of N_2 over Raney Ru is strongly affected by structural factors; i.e., the activity depends on different single crystal faces and/or on active centers (surface imperfections, edges, corners, Al-bound Ru, N-bound Ru). TEM pictures show that Raney Ru has many lattice imperfections (15). Iron prepared from an amorphous $Fe_{91}Zr_9$ precursor has been reported to be active for ammonia synthesis (27). It has been proposed that this result is also due to a structural effect. Further model studies are necessary to solve these problems.

The reason why the electronic effect is weaker for the Raney Ru than for supported Ru catalysts should be discussed. Recently, Lu and Tatarchuk pointed out that reduced $RuCl_3/Al_2O_3$ catalysts retained Cl ion over the Ru surfaces and that Cl ion might withdraw electrons from surrounding Ru atoms (28). Such surfaces would be less active for activated adsorption of N_2. Addition of alkali metals to supported Ru catalysts made from $RuCl_3$ could neutralize the effect of Cl ion, thereby markedly increasing the activity of ammonia synthesis or of the N_2 IER. Chloride-free Ru catalysts such as Raney Ru can be sufficiently active without alkali metal addition. The starting Al–Ru alloys we used were thought to be free from Cl ion because the Ru powder was melted (melting point of Ru, 2523 K) (17). Ru powder catalyst may retain some Cl ion as has been pointed out by Scholten and colleagues (29); this may be one reason why the activity of Ru powder is so low (Figs. 6 to 8). This hypothesis is also supported by the fact that alkali addition also increases Ru dispersion, that is, H_2 chemisorption on Ru catalyst (30). Thus, the remarkable electronic promotion over supported Ru catalysts may partly result from the neutralization of surface Cl ion. This possibility needs to be studied. However, there should still be some electronic promotion, as is found in the Raney Ru–K system.

CONCLUSIONS

Raney Ru was found to be quite active for the IER of N_2 ($^{28}N_2 + {}^{30}N_2 = 2^{29}N_2$). This catalyst is prepared by leaching $Al_{94}Ru_6$, $Al_{86}Ru_{14}$, $Al_{79}Ru_{21}$, or $Al_{67}Ru_{33}$ alloy at 373 K. This condition gives a high surface area and low Al content. The active catalyst adsorbs atomic nitrogen on the surface, which is the intermediate for the IER, and also strongly adsorbs nitrogen somewhere that hydrogen cannot be adsorbed. The active and skeletal state of Ru contains Al inside the catalyst. The high activity of this state is inferred to have a structural cause (imperfections, Al-bound Ru, N-bound Ru, etc.) and not to be due to an electronic effect of Al metal.

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