Activation of Dinitrogen over Various Raney Type Metal Catalysts

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Synopsis. Raney Ni, Rh, Re, and Ir adsorbed molecular nitrogen which was stable up to about 300 K. Raney Fe, Co, Ni, Ru, Rh, Ir, and Pt adsorbed atomic nitrogen which was desorbed around 700 or 800 K. The XPS spectra of atomically adsorbed nitrogen was observed on Co, Ni, and Ru samples. While the per-weight activity of Raney Ru for isotopic equilibration of N_2 is much higher than that of 5% Ru-K/AC, those of other Raney metals are lower than those of 5% metal-K/AC.

Supported Ru catalysts are known to be promoted with metallic potassium,[1,2] however, Raney Ru, which has no potassium promoter, was found to be as active as potassium-promoted Ru catalysts.[3] Thus, other transition metals of Raney-type catalysts might be active without a potassium promoter. The adsorption characteristics and the activity of isotopic equilibration (IE) reaction of the N_2 are compared for various Raney catalysts.

Experimental

Raney catalysts were prepared by leaching metal-Al alloys (weight ratio; 1/1) with a 5 M of KOH solution at 373 K for 2 h.[4] The weight of the leached sample was estimated to be that of the starting transition metal (normally 1 g), thereby neglecting the weight of remaining Al (ca. 10%). After the sealing water was evacuated in the reactor at room temperature for 10 h the sample was dryed under circulating He at 523 K with a liquid-nitrogen trap for 5 h, and then evacuated at 523 K for 2 h. After the BET surface area was measured by N_2 at 77 K, the sample was stabilized under a N_2 atmosphere at 623 K for 40 to 50 h. This treatment caused N_2 adsorption and sintering of the sample. After evacuation at 623 K (here, ca. one third of N_2 was still irreversibly adsorbed in the case of Ru sample) H_2 chemisorption (273 K) and the BET area (77 K) were again measured. The rate of the IE reaction of N_2 was measured this time at 473 to 773 K. Another series of samples were sealed in glass tubes after N_2 adsorption at 623 K, and were then transfered into the XPS spectrometer.

Results

Characterization of Various Raney Metal. Most of the metal-Al alloys were leached smoothly, except for the Fe sample (10 h for the leaching). The resultant solution of the Fe sample was dark greenish, which suggested that a part of the Fe was dissolved. The leached Raney Fe was treated exceptionally with H_2 at 723 K for 100 h since the surface might have been oxidized. The BET surface area of all the samples measured before N_2 uptake are shown in Table 1. The leached samples have a high surface area (27 to 142 m^2g^{-1}), except for Pd (5 m^2g^{-1}) and Fe (14 m^2g^{-1}), compared to the starting alloy (ca. 1 m^2g^{-1}). The surface area (Table 1) was decreased by sintering during the N_2 treatment at 623 K, except for the Fe sample, in which case nitride formation was suggested.[1]

The metallic atom percentage on the surface was calculated by assuming the relation: (number of H chemisorbed)/(number of surface metal estimated by BET area)[5] (Table 1). The metallic atom percentage on the surface was also measured by XPS, assuming the molar ratio Me/(Me+Al); see Table 1. The XPS results show that Al remained on the surface, except for Raney Re. The surface metallic atom percentage measured by H_2 chemisorption is generally lower than that measured by XPS. Several reasons have been suggested: 1) The surface dencity of Al atoms is lower than that of Ru, because oxidized Al requires a wider space for the counter anion (oxygen); 2) irreversibly adsorbed nitrogen might partly remain; and 3) a part of the surface transition metal, such as Fe or Re, is oxidized. An XPS study showed that about 20% of Re and 70% of Fe were oxidized; however, other samples were all metallic. The residual Al was metallic (Al_{2s}=117.5 eV) over Rh, Pt, and Ir samples, though, it was almost oxidized (Al_{2s}=119.0 eV) over other sam-

Table 1. Characterization of Various Transition Metal Raney Catalysts

Raney catalyst sample	BET before N_2 uptake[a]	BET after N_2 uptake[a]	N_2 uptake[a]	H_2 ads.[b]	Surf. metal atom% by ads.[c]	Surf. metal atom% by XPS[d]
	m^2g^{-1}	m^2g^{-1}	$ml\,g^{-1}$	$ml\,g^{-1}$		
R-Fe[e]	14.0	46.6	2.0	0.23	2	53
R-Co	—	22.7	5.2	0.57	9	52
R-Ni	82.7	63.0	7.0	3.8	21	37
R-Ru	98.4	51.4	9.4	6.0	51	79
R-Rh	141.7	31.5	—	1.6	21	60
R-Pd	5.0	0.8	Neg	—[f]	—	47
R-Re	83.6	11.1	Neg	1.10	34	100
R-Ir	41.2	22.3	0.5	0.98	18	44
R-Pt	26.7	6.8	Neg	1.50	96	57

a) With 400 Torr N_2 (1 Torr≈133.322 Pa) at 623 K for 40 h. b) Measured at 273 K. c) Calculated using H_2 ads. and BET area by the method in Ref. 5, p. 296. d) M/(M+Al). e) Sample after H_2 reduction at 723 K for 100 h. f) Calculation was not carried out for Raney Pd because of the excess hydrogen dissolution to Pd metal phase.

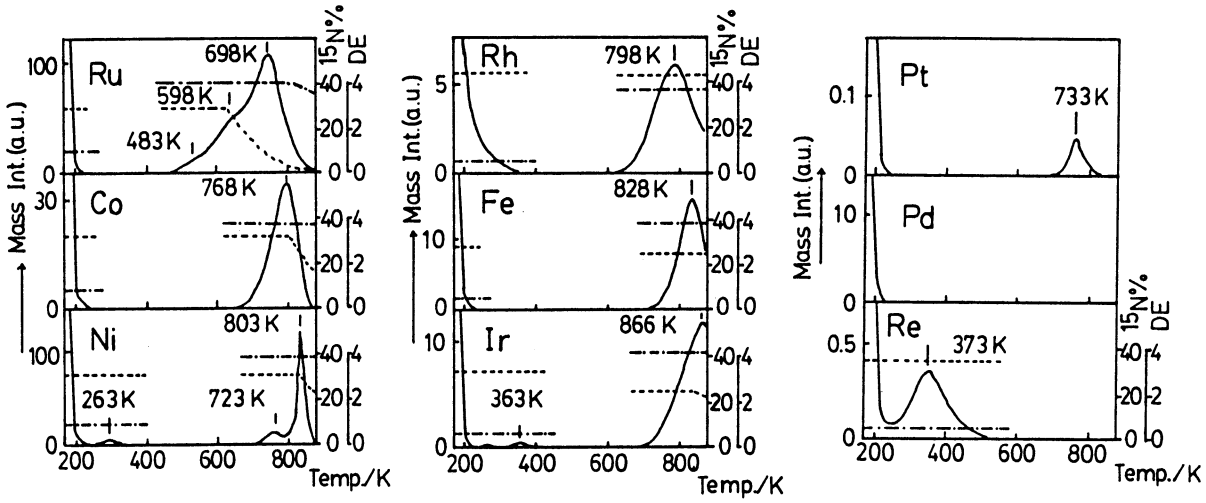

Fig. 1. TPD spectra of adsorbed nitrogen after some extent of isotopic randomization over various Raney type metals. The kind of metal is shown in the figures. ——; total nitrogen ($^{28}N_2+^{29}N_2+^{30}N_2$), ·····; ^{15}N% ($^{29}N_2/2+^{30}N_2$), -·-·-; DE in the text.

ples (Co, Ni, Ru, and Pd).

TPD Study Using ^{15}N Isotope. About one half of the gas-phase nitrogen ($^{28}N_2$) was replaced with $^{30}N_2$ at 573 K. At this point the IE reaction was carried out at 573 K in order to supply an isotopic mixture of surface nitrogen until the degree of equilibration (D.E.) reached approximately unity.

$$\text{D.E.} = (^{29}N_2)^2(^{28}N_2)^{-1}(^{30}N_2)^{-1} \quad (1)$$

An adequate value of D.E. could not be obtained for Pd, Re, and Pt, because of the low activity. The adsorbed nitrogen was quenched and the gas-phase nitrogen was evacuated at 77 K for 3 h; then, a TPD run was carried out to 873 K at a rate of 4 K min^{-1}.

In Fig. 1, the solid lines indicate the total amount of all isotopes of nitrogen during TPD, and the dots and lines show the value of D.E. If no isotopic randomization in N_2 molecule occurs during the desorption (i.e., molecular adsorption), the value of D.E. of the desorbing gas should be kept unchanged from the initial D.E. (ca. 1.0). If isotopic randomization occurs (i.e., atomic adsorption), the value of D.E. should reach about 4.0. Therefore, peaks below 195 K were all assigned to the molecular species (γ-type) because of the low D.E. value (ca. 1.0). Molecular species which were stable at around room temperature (α-type) were observed on Ni, Re, Ir, and probably on Rh catalyst. Peaks above 500 K were all assigned to atomic species since the D.E. values were near 4. It is interesting that Pt, Ir, and Rh samples have β-type, despite the fact that these metals are known to be poor catalysts for N_2 activation, and that there has been no report concerning atomic adsorbed nitrogen from N_2.[1)]

The ^{15}N% of the desorbing gas is also shown as dotted lines in Fig. 1. If pre-adsorbed nitrogen (containing ^{14}N) is completely mixed during the IE reaction at 573 K, the ^{15}N% should be constant during a TPD run. However, the value becomes lower at high temperature for Ru, Co, and Ni samples. This means that some pre-adsorbed nitrogen did not take part in the IE reaction at 573 K, and that the atomic nitrogen was adsorbed at various heats of adsorption (surface heterogeneity).

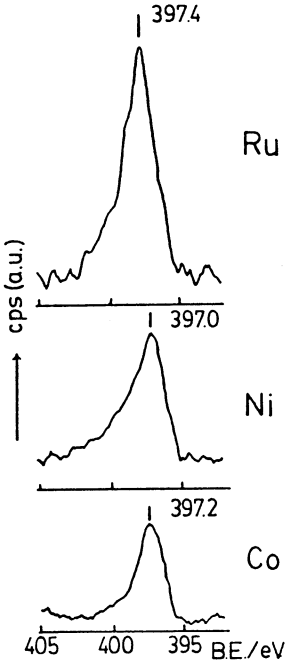

Fig. 2. XPS spectra of N_{1s} region of adsorbed nitrogen on Raney Ru, Ni, and Co.

XPS Spectra of Adsorbed Nitrogen. Only Ru, Ni, and Co samples showed XPS spectra of nitrogen (Fig. 2). The binding energies are 397.4 for Ru, 397.0 for Ni, and 397.2 eV for Co sample, respectively. Since the binding energy of AlN is 396.7 eV, these spectra have been identified to be adsorbed nitrogen on transition metals. Since molecularlly adsorbed nitrogen was evacuated in the XPS chamber at room temperature, the observed XPS spectra should correspond to atomic nitrogen (β-type) for Ru, Ni,[6)] and Co catalysts. The relative XPS intensities of nitrogen against metal are 0.07 for Ru, 0.05 for Ni, 0.04 for Co sample, respec-

Table 2. Kinetic Data of Isotopic Equilibration Reaction over Raney Catalysts

Catalyst	10^4×TOF[a]	10^{-16}×Activity[a]		Act. energy		Desorption temp[d]
	10^4×molec. s^{-1} $site^{-1}$	10^{-16}×molec. min^{-1} g^{-1}		kcal mol^{-1}		K
R-Fe	0.0031	0.023	(4.6)[e]	33	(35)[f]	828
R-Co	0.035	0.64	(1.5)[e]	40	(38)[f]	768
R-Ni	0.0014	0.17	(0.35)[e]	34	(31)[f]	723
R-Ru	88.2 (24.1)[b]	17000	(503)[e]	27	(23)[f]	483
R-Rh	0.0088	0.45	(1.2)[e]	21	(25)[f]	798
R-Pd	0.000[c]	—	—	—	—	—
R-Re	0.000[c]	—	(1.3)[e]	—	(40)[f]	—
R-Ir	0.0147	0.46	(0.75)[e]	15	(26)[f]	866
R-Pt	0.000[c]	—	—	—	—	733

a) At 588 K under 150 Torr. b) TOF over 5% Ru-K/AC.[4] c) Rate is not measurable even at 773 K. d) The lowest peak temperature for the desorption of β-nitrogen. e) 10^{-16}×Activity over 5% Me-K/AC.[2] f) Activation energy over 5% Me-K/AC.[2]

tively. These values are lower than the surface metallic atom percentages listed in Table 1, probably because of an overestimation of the bulk metal by XPS.

Isotopic Equilibration Reaction of Dinitrogen. The rates of the IE reaction were observable at a temperature where the β-type started to be desorbed. Kinetic data of the reaction are shown on Table 2. The activities are rearranged as TOF in which the number of sites is based on H_2 chemisorption. The activities of all the catalysts were stable during runs for several days at 473 to 773 K.

Discussion

TPD of Adsorbed Nitrogen and TOF of IE Reaction. Molecularly adsorbed nitrogen (α-type) was found at around room temperature on Raney Ni, Re, Ir, and probably on Rh catalysts. Molecularly adsorbed nitrogen has been also observed by ir on Ni-SiO_2 (2202 cm^{-1}), Rh-SiO_2 (2236 cm^{-1}), and Ir (2185 cm^{-1}).[1]

Atomically adsorbed nitrogen should be related with an IE reaction. The desorption peak temperature of the β-type nitrogen is compared with the TOF of an IE reaction at 588 K in Table 2. Raney Ru, which has the lowest desorption temperature, is extraordinarily active. Since the desorption process is one of the steps in the IE reaction, the above two data should be related to each other. The surprizing thing is the activity difference among the catalysts. Only Raney Ni and Ru have multiple TPD peaks for atomic nitrogen. All of the other samples give sharp and single TPD spectra of the β-type. Raney Ni and Ru seem to have multiple active sites. The β-type species must be the intermediate for the IE reaction. The activation energy of IE reaction is equal to that of the adsorption step when the coverage is low and is equal to that of desorption step when the coverage is high. Among Fe, Co, Ni, and Ru on which nitrogen coverage seems to be high (see the mass intensity in Fig. 1), Ru gives the lowest activation energy (Table 2). Rh and Ir give low activation energies, probably, because the coverages are low. Of course, the activation energy data is not decisive in explaining the extraordinal activeness of Raney Ru. It is suggested that a relatively high concentration of the special active site is formed.[3]

Comparison of the Activity of Raney Metal with That of Potassium Promoted Metals. Activity data of potassium promoted metals on AC (Me-K/AC) are only available for comparing the activity of various metal catalysts.[2] The activity is, however, described on the bases of catalyst weight, shown in Table 2. The per-weight activity over Raney Ru is quite high (17000×10^{16} molec. min^{-1} g^{-1}), compared to that (503×10^{16} molec. min^{-1} g^{-1}) over 5%Ru-K/AC.[2,4] The major reason is that Raney Ru has 6% dispersion, i.e., (0.06 g-surface Ru) (g-catalyst)$^{-1}$, and that the 5%Ru/AC has only 12.7% dispersion i.e., (0.0064 g-surface Ru) (g-catalyst)$^{-1}$. Thus, if the two catalysts have the same TOF, the per-weight activity of Raney catalyst must be about ten-times higher than that of 5% Me-K/AC. In this respect, the TOFs of Raney Co, Ni, Rh, and Ir seem to be less than one tenth of those of 5% Me-K/AC. This is because these Raney catalysts have an even lower per-weight activity than Me-K/AC catalysts (Table 2).

Inactiveness of Fe and Re. Fe and Re single crystals have been reported to be quite active for ammonia synthesis.[7] XPS results showed that our Fe and Re samples were partly oxidized because the Raney-type catalyst is prepared in water. This must be the reason why the activities of these samples are low.

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