CHEMISTRY LETTERS, pp. 825 - 828, 1984.

ISOTOPIC EQUILIBRATION REACTION OF DINITROGEN OVER RANEY RUTHENIUM WITH AND WITHOUT POTASSIUM

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Turn over frequency (TOF) of isotopic equilibration reaction of N_2 over Raney-Ru was as high as those over supported Ru catalysts with K, showing the striking effectiveness of the residual Al metal as a chemical promoter. Raney-Ru when promoted with K had the highest TOF for this reaction among the data so far reported.

Isotopic equilibration reaction of dinitrogen ($^{28}N_2$ + $^{30}N_2$ = $2{}^{29}N_2$) is a fundamental reaction which represents a catalyst ability to rupture the N-N bond. The dissociation of dinitrogen is well-known to be the rate determining step of ammonia synthesis.1) Several works have been done on Fe,2-6) Os,7) and other metals1) such as Co, Ni, Re, W, and Mo. It has been reported that the title reaction over supported Ru catalysts are promoted by an addition of alkali metal,8, 9) and that those Ru catalyst systems are more active than any systems with other transition metals.10) The promoter action has been discussed to be due to the electron donation from alkali metal to Ru.10, 11) Since Al in Raney-Ru is also considered to be a promising promoter for ammonia synthesis,12) the title reaction was carried out.

Raney-Ru and Si-Raney-Ru alloys were kindly manufactured by professor A. Suzuki and Mr. Y. Ohya of Research Laboratory of Precision Machinery and Electronics, Tokyo Institute of Technology. Raney-Ni and -Co were supplied from Kawaken Fine Chemicals. Raney-Ru catalyst was prepared with a similar method to that reported previously except the use of leaching solution of KOH in stead of NaOH, and Al content in Raney-Ru after leaching was estimated to be 10 wt%.12)

The preparation method of Raney-Ni and -Co was similar to that of Raney-Ru. Si-Ru alloy was also leached and was referred to Si-Raney-Ru. Results of the BET areas and %-dispersions by hydrogen chemisorption for the catalysts used in this work are listed in Table 1. Raney-Ru-K was prepared by evaporating potassium on Raney-Ru in the reaction apparatus.

An adsorption run of N_2 (ca. 400 Torr) was carried out at 623 K for about 40 h in order to stabilize the surface. An amount of the adsorbed N_2 was 0.42, 0.23 and 0.31 mmol/g on Raney-Ru, Raney-Co, and Raney-Ni respectively, while no N_2 adsorption was observed on 1.0 g of Si-Raney-Ru by a volumetric measurement. An isotopic equilibration reaction with the total pressure of 150 Torr (1 Torr = 133.3 Nm^{-2}) was carried out at 523 to 723 K in a conventional circulating system with a quadrupole mass spectrometer (NEVA NAG 515), and the rate was derived by using the first order plot.[8)] The rates at 588 K were normalized as TOF on the basis of hydrogen chemisorption measurements at 273 K. The results are shown in Table 1 together with the reported data. Some TOFs at 588 K in other works were recalculated by using their surface areas and activation energies.

TOF of Raney-Ru was more than 4000 times higher than that of Ru metal, showing the striking effectiveness of the residual Al metal as an electronic promoter. Al was proved to exist in the reduced state by an XPS study which would be published elsewhere. TOF of Raney-Ru was higher than that of the conventional Ru catalyst (Ru-Al_2O_3, Ru-AC) with K, but it was slightly lower than those of the superbase-supported Ru catalysts which had been reported to be the most active catalysts for this reaction.[13)] The superiority of Al as a promoter is considered to be due to the intimate contact among the both components in the leached alloy, although the electronegativity value of Al is higher than that of K. Si-Raney-Ru was quite inactive for this reaction.

When Raney-Ru was added with potassium, it revealed to have the highest TOF of this reaction under these conditions among the data so far reported including iron and osmium catalysts as are seen in Table 1.

Raney-Co and -Ni showed some activity, however, the levels were quite low and seemed to be lower than that of Co(Ni)-AC-K judging from the activity per gram catalyst. It is interesting to see that the activation energies of the Raney catalysts are almost the same as those of the AC-K systems.

Raney-Ru was revealed to be quite effective for the title reaction rather than for ammonia synthesis. Although an activity per gram catalyst of Raney-Ru is almost the same as that of Ru-K in ammonia synthesis,[12)] the former is about 300 times higher than the latter in the title reaction. It is also interesting to

Table 1. Characterization of catalysts and activities of isotopic equilibration of N_2 at 588 K

	Sample code[a)]	Weight /g[b)]	BET area[e)] $/m^2 g^{-1}$	Total metal /mmol	% disp. of metal[g)]	N_2 equilibration activity[k)] TOFx10^4 at 588 K[m)]	Activity/ bulk Me[n)]	Act.E kcal mol^{-1}
Raney-Ru	Og-1	0.9[c)]	51.4	8.02	6.0	88.2	5.3	27
Raney-Ru-K	Og-2	0.7[c)]	51.4	6.24	6.0	252	15.1	--
Si-Raney-Ru	Og-3	2.0[c)]	2.2	17.8[f)]	0.12	0.00	0.00	--
Raney-Co	Og-4	2.0[c)]	--	30.6[f)]	0.64	0.035	0.00022	40
Raney-Ni	Og-5	2.0[c)]	63.0	30.7[f)]	2.2	0.0014	0.00003	34
Ru-BeO-K	O-1k	2.00	18	0.916	8.6	175	15.1	24
Ru-MgO-K	O-2k	2.00	9.9	0.848	2.9	147	4.3	26
Ru-CaO-K	O-3k	2.00	12	0.778	2.5	139	3.5	25
Ru-Al_2O_3	U-2	10.0	89	0.494	22.1[h)]	0.12	0.026	11
Ru-Al_2O_3-K	U-2k	10.0	--	0.494	22.1[h)]	24.0	5.3	25
Ru-AC-K	U-1c	3.00	1000	1.37	12.7[h)]	24.1	3.1	23
Ru	U-3	1.58[d)]	2.0	15.8	0.25[i)]	0.020	0.00005	23
Ru-K	U-3k	1.58[d)]	(1.8)	15.8	0.25[i)]	6.9	0.017	32
Os	GJT	2.47[d)]	30.8	13.0	8.0	0.40	0.032	21.8
Fe	M-1	15.4[d)]	2.3	276	0.35[i)]	0.0021	0.000007	50
Fe-Al_2O_3	M-2	9.1[d)]	12.5	160	1.89[i)]	0.43	0.0081	38
Fe-Al_2O_3-K_2O	M-3	15.3[d)]	19.3	257	1.17[i, j)]	0.027	0.00032	29
Fe	GB-1	21.7[d)]	0.5	389	0.076[i)]	0.00002	--	39
Fe-Al_2O_3	GB-2	22.0[d)]	11.6	371	1.75[i)]	0.00028	0.000005	43
Fe-Al_2O_3-K_2O	GB-3	22.0[d)]	3.6	371	0.22[i, j)]	0.0012	0.000003	41.5
Co-AC-K	U-4	1.0	1000	0.71	--	--	0.0063	38
Ni-AC-K	U-4	1.0	1000	0.71	--	--	0.0014	31

a) Data cited from; Ref. 13 for O: Ref. 9 for U-2: Ref. 8 for U-1 and U-3: Ref. 10 for U-4: Ref. 14, 15, and 16 for M-3, M-1, and M-2 respectively: Ref. 4 for GB: Ref. 7 for GJT. b) Weight of (Metal chloride + support). c) Weight after leaching. d) Weight after reduction without K. Some estimated (Sample M and GB). e) Measured after reduction. f) 10 wt% of Al is assumed to be left. g) Based on H_2 chemisorption at 273 K after reduction if not cited. h) Based on CO chemisorption. i) Estimated by BET data. j) Fe is assumed to cover 40% of the total surface. k) Measured at 588 K under the total presure of 150 Torr. Data on Os is estimated. m) 10^{-4} N_2 molec./surface metal atom/s. n) 10^{-4} N_2 molec./bulk metal atom/s.

point out that the TOF of this reaction on iron catalysts are quite low, although the activity of ammonia synthesis on the total weight base is comparable with Ru catalysts at about 500 K.[11] Two facts should be pointed out with respect to these phenomena; (1) Although the title reaction is promoted by the existance of hydrogen on Fe catalysts,[15] it is depressed on Ru catalysts with K:[17] (2) The ammonia synthesis rate on Ru catalyst has an negative order with respect to hydrogen,[18] while that on iron catalyst does a positive order.[1]

An intrinsic activeness of Ru for N-N bond rupture without the presence of hydrogen was demonstrated when promoted with a strong electron donor.

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(Received February 23, 1984)