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Support and Promoter Effect of Ruthenium Catalyst

II. Ruthenium/Alkaline Earth Catalyst for Activation of Dinitrogen

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The turnover frequency (TOF) of the ammonia synthesis on Ru was promoted by using alkaline earths as supports. The TOF of this reaction on Ru/MgO and Ru/CaO was as high as those on Ru–CsOH/Al_2O_3 catalyst. The activity was shown to be correlated with the electronegativity of oxide support. XPS results seem to support the electron transfer from alkaline earth to Ru. Activity of Ru/MgO was further promoted with CsOH, which increased not only TOF but also Ru dispersion. On the other hand, Ru/alkaline earth with K, which may be called "superbase-supported Ru catalysts," proved to have excellent activities for N_2 activation. TOF of ammonia synthesis over those catalyst was as high as that on Ru–K/AC (activated carbon) which has been known to be the best catalyst under these conditions. Furthermore, TOF of N_2 isotopic equilibration reaction on these catalyst were several times as high as those on Ru–K/Al_2O_3 or Ru–K/AC which have been believed to be the most active catalysts for this reaction.

INTRODUCTION

Ruthenium has been proved to be an excellent catalyst for activation of dinitrogen when it is promoted by alkali metal (*1, 2*) or alkali metalhydroxide (*3*). However, the Ru catalysts so far studied mostly contain Al_2O_3 or activated carbon (AC) as supports whose surfaces are rather acidic. The activities of such catalysts are not high unless alkali is added (*1, 3*). Thus it is interesting to apply basic compounds to the Ru catalysts as the supports.

In this study, several kinds of Ru/alkaline earths catalysts were prepared and characterized, and the activities of ammonia synthesis and isotopic equilibration were measured. On the other hand, it has been reported that alkaline earths became extremely basic when these are added along with metallic alkali and these systems are called superbases (*4*). Thus it will be interesting to apply the superbase as supports of Ru catalysts. The activity of Ru/superbase support was also studied.

EXPERIMENTAL

Alkaline earths, BeO (99.7% pure), MgO (98.5%), and CaO (99.99%), were obtained from Soekawa Rikagaku. Sources of other materials has been listed in the previous report (*3*). The preparation method of the supported catalysts also follows the previous report (*3*). BeO was treated in a draft chamber with the caution that it not be inhaled. During the impregnation process Ru^{3+}, Cl^-, Mg^{2+}, Ca^{2+} ions were analyzed and it was concluded that the ion-exchange reaction was completed.

$$2RuCl_3 + 3MgO + 3H_2O \rightarrow 2Ru(OH)_3 + 3MgCl_2$$

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$$2RuCl_3 + 3CaO + 3H_2O \rightarrow 2Ru(OH)_3 + 3CaCl_2$$

The activation and the characterization was carried out in a way similar to that reported previously. Ammonia synthesis rate at total pressure of 600 Torr (80.0 kPa) was measured with the same method reported in the previous paper. Activity of molecular equilibration reaction of dinitrogen ($^{30}N_2 + {}^{28}N_2 = 2\,{}^{29}N_2$) was measured under a total pressure of 150 Torr (20.0 kPa) at various temperatures. The isotopes of dinitrogen were analyzed by NEVA NAG-515 mass filter which was directly connected to the reaction system by means of a leak valve.

XPS spectrum of the catalyst was measured with the Hewlett–Packard 5950A-ESCA spectrometer. Catalysts with high Ru loading were used for XPS measurement (10% Ru/BeO, 11% Ru/MgO, 11% Ru/CaO, and 10% Ru/Al_2O_3). Reduction was carried out in the spectrometer with H_2 (1 Torr) at 480°C for 1 h. Standard condition of the measurement was as follows: vacuum of 2×10^{-8} Torr, Al–K_α X-ray source with 800-W, electron gun at 0.2 mA and 4.0 eV. Samples were always set neighboring the Al_2O_3 standard sample. Impurities of C 1*s* (284.8 eV) and Al $2s_{1/2}$ (119.4 eV) were used as the standard peak for the determination of the binding energy (B.E.).

RESULTS

Reduction behavior of Ru/alkaline earth. During the reduction of these catalysts, hydrogen was consumed more than that expected from the stoichiometry of Ru^{3+} reduction for 24 h at 460°C, i.e., 126% for Ru/BeO (O-1), 226% for Ru/MgO (O-2), 270% for Ru/CaO (O-3), and 125% for 5.1% Ru/Al_2O_3 (Alon-C). The sample code in parentheses is cited from Table 2. The products collected in a liquid-nitrogen trap adjacent to the reactor were H_2O, CH_4, and CO_2. CH_4 was thought to be produced at above 200°C from adsorbed CO_2. Ru metal was necessary for the decomposition of adsorbed CO_2 on MgO. The excess H_2 consumption was due to the reaction with surface carbonate on the support. Several kinds of carbonate species have been identified by ir spectrometry on Ru/MgO and Ru/CaO (*5*).

In order to examine the oxidation state of Ru before and after reduction, XPS spectra of Ru/BeO and Ru/CaO were measured and the results are shown in Fig. 1. As seen in this figure, unreduced Ru/MgO and Ru/CaO samples which have consumed a great deal of excess H_2 give a peak around 289 eV, which is identified to be due to C 1*s* of adsorbed CO_2 (i.e., CO_3^{2-}). This XPS peak disappeared after the reduction; this corresponds well to the nature of a surface carbonate studied by ir (*5*). B.E. values of C 1*s* in carbonate compounds have been reported to be 288 to 290 eV for Cu, Ag, Cd, or Ni compounds (*6*).

Besides C 1*s* peak at around 284.8 eV due to carbon impurity in the apparatus, there are twin peaks divided by a distance of 4.1 or 4.2 eV in every sample. Those were

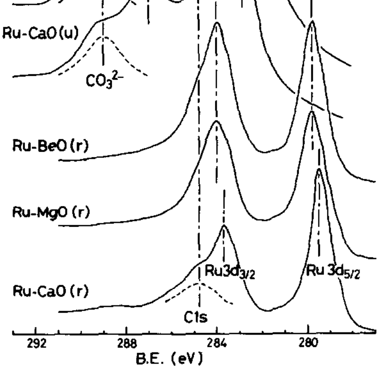

FIG. 1. XPS spectra of 10% Ru/BeO, 11% Ru/MgO, and 11% Ru/CaO before reduction (u) and after reduction (r). Reduction was carried out in a spectrometer apparatus at 480°C for 1 h.

identified to be Ru $3d_{5/2}$ and Ru $3d_{3/2}$. The B.E. values are shown in Table 1. Since the B.E. of Ru $3d_{5/2}$ of the samples before reduction are in the range from 282 to 283 eV, Ru valency could be determined to be 6 if the B.E. of RuO_3 (282.5) were applied (*7*). However, H_2 consumption during the reduction of Ru/BeO or Ru/Al_2O_3 indicated the maximum valency of Ru to be about 3.8. This number is clearly overestimated because of the excess H_2 consumption by the surface carbonates. Thus the valency of Ru is considered to be mostly +3 with a small probability of having higher valency. The higher value of B.E. than that reported by Kim and Winograd (*7*) may be due to the difference of coordinated compound. Indeed, coordination of H_2O to RuO_2 increases the B.E. value as shown in Table 1.

The XPS spectra of reduced catalysts showed that Ru on any of the alkaline earths was reduced to its metal state, which was contrary to the results by Bossi *et al.* (*8*). It is to be noted that the B.E. of Ru $3d_{5/2}$ on these supports were less than 280.0 eV that has been reported for Ru/Al_2O_3 (*3*) or Ru powder (*7*). In the case of Ru/CaO, the value was 0.5 eV lower than that for Ru powder, and moreover the B.E. of Ru $3d_{3/2}$ was clearly lower than that of the C 1*s* peak (Fig. 1). Generally the B.E. of a metal is affected by the particle size due to the relaxation effect (*9*). Ru dispersion was not measured as with the four kinds of samples (10 to 11 wt% of Ru) used here in the XPS study, however, the corresponding samples (5 wt% of Ru) have rather low dispersions ranging from 2.5 to 11.5% (Table 2). The particle diameters are not extremely small. Thus the difference of B.E. of Ru on those samples are considered mostly to be the chemical shifts due to metal–support interaction. Ru is assumed to have received an electron from the alkaline earth.

TABLE 1

Binding Energy (eV)[a] of Ru 3*d* on Supported Ru Catalysts

	Before reduction		After reduction at 480°C	
	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$
Ru/Al_2O_3	282.3	286.5	280.0	284.2
Ru/BeO	282.7	286.8	279.8	284.0
Ru/MgO	282.5	286.6	279.8	284.0
Ru/CaO	282.9	287.0	279.5	283.7
Ru metal[b]			280.0	284.2
RuO_2[b]	280.7			
$RuO_2 \cdot xH_2O$[b]	281.4	285.5		
RuO_3[b]	282.5			

[a] With a resolution of ±0.1 eV.

[b] By Kim and Winograd (*7*).

Ammonia synthesis over Ru/BeO, Ru/MgO, or Ru/CaO. Ammonia synthesis activities per surface Ru atom (TOF) on those supported catalyst are listed on Table 2. The second half of this table also includes the data already reported (*2, 3, 10–12*) for comparison purposes. Activity sequence of supported catalyst without alkali promoter is as follows: Ru/CaO > Ru/MgO > Ru/BeO > Raney Ru > Ru/Al_2O_3 > Ru powder > Ru/AC. It is interesting to note that this sequence is closely related with the Ru$3d_{5/2}$ value in Table 1. The activation energy on Ru/alkaline earth was lower than that on the other catalyst, which will be discussed elsewhere (*14*).

Since alkaline earths used here have small BET area (10 to 20 m^2/g) and the impregnation in aqueous solution causes an ion exchange only on an outer face of the sample, the percentage dispersion values of Ru are not high (below 10%). If acetone is used instead of water in the impregnation process (H-7) or if the oxide is made by pyrolysis of hydroxide (H-9), the Ru dispersion increases.

Ru–CsOH/MgO catalyst. CsOH, which has been found to be an effective promoter for Ru/Al_2O_3 (*3*), was added to the Ru/MgO system. Although the starting precursor is different ($CsNO_3$ for H-8 and H-9 or $CsCO_3$ for H-6), the final state is considered to be CsOH as has been discussed for Ru/Al_2O_3 catalyst (*3*). CsOH addition not only in-

TABLE 2

Characterization and Activity of Ru Catalysts

	Sample code[t]	Weight[a] (g)	BET area[d] (m^2/g)	wt% of Ru[e]	Total Ru (mmol)	% Dispersion of Ru[f]	Ammonia synthesis[j]			N_2 equilibration[m]		
							TOF ×10^4 at 588 K[k]	Activity/bulk Ru[l] × 10^4	Act. *E* (kcal/mol)	TOF ×10^4 at 588 K[n]	Activity/bulk Ru[o] ×10^4	Act. *E* (kcal/mol)
Ru/BeO	O-1	2.00	18	5.0	0.916	8.6	1.63	0.14	18			
Ru–K/BeO	O-1k	2.00	—	5.0	0.916	8.6	204	17.5	24	175	15.1	24
Ru/MgO	O-2	2.00	9.9	4.6	0.848	2.9, 4.4[g]	14.3	0.41	10			
Ru-K/MgO	O-2k	2.00	—	4.6	0.848	2.9	197	5.71	16	147	4.3	26
Ru/CaO	O-3	2.00	12	4.2	0.778	2.5, 4.2[g]	18.7	0.47	7.9			
Ru-K/CaO	O-3k	2.00	—	4.2	0.778	2.5	74.7	1.87	11	139	3.5	25
Ru-CsOH/MgO	H-6[p]	2.64	—	1.96	0.380	8.5	19	1.6	25			
Ru/MgO	H-7[q]	1.98	9.9	1.96	0.372	8.4	7.2	0.60	16			
Ru-CsOH/MgO	H-8[r]	3.51	—	1.96	0.481	4.1	11	0.45	23			
Ru/MgO	H-9[s]	2.12	126	1.96	0.399	12.5	3.0	0.38	16			
Ru-CsOH/MgO	H-10[s]	1.37	—	1.96	0.189	35	27	9.5	24			
Ru/Al_2O_3	S-2	2.00		2.0	0.381	5.0	0.67	0.034	17			
Ru-K/Al_2O_3	S-3	2.00		2.0	0.381	5.0	100	5.0	27			
Ru/Al_2O_3	U-2	10.0	89	0.50	0.494	22.1[h]				0.12	0.026	11
Ru-K/Al_2O_3	U-2k	10.0	—	0.50	0.494	22.1[h]				24.0	5.3	25
Ru/AC	A-9	1.00	1068	4.7	0.435	10.3[h]	Neg	Neg				
Ru-K/AC	A-9k	1.00	—	4.7	0.435	10.3[h]	205	21.1	22			
Ru-K/AC	U-1c	3.00	1000	5.0	1.37	12.7[h]				24.1	3.1	23
Ru	A-1	0.385[b]		100	3.81	0.30[h]	0.54	0.0016	23			
Ru-K	A-1k	0.385[b]		100	3.81	0.30[h]	28.8	0.086	26			
Ru	U-3	1.58[b]	2.0	100	15.8	0.25[i]				0.020	0.00005	23
Ru-K	U-3k	1.58[b]	(1.8)	100	15.8	0.25[i]				6.9	0.017	32
Ru	Y-1	1.12[b]	1.02	100	11.1	0.18	0.41	0.0007	25			
Ru-K	Y-1k	1.12[b]	(0.54)	100	11.1	0.18	24.6	0.044	26			
Raney Ru	Y-3	1.49[c]	30.7	91	13.5	3.1	1.40	0.044	19			
Raney Ru-K	Y-3k	1.49[c]	(10.2)	91	13.5	3.1	17.5	0.54	19			

[a] Weight of ($RuCl_3 \cdot 3H_2O$ + support + promoter other than K) if not cited.

[b] Weight after reduction without promoter.

[c] Weight after leaching.

[d] Measured after reduction; weight based on *a*, *b*, or *c*.

[e] Ru/(Ru + support).

[f] Based on H_2 chemisorption if not cited.

[g] Based on X-ray line broadening.

[h] Based on CO chemisorption.

[i] Estimated by BET data.

[j] $N_2 + 3H_2 = 600$ Torr.

[k] NH_3 molec./surface Ru atom/s at 315°C.

[l] NH_3 molec./bulk Ru atom/s at 315°C.

[m] $^{28}N_2 + {}^{29}N_2 + {}^{30}N_2 = 150$ Torr.

[n] N_2 molec./surface Ru atom/s at 315°C.

[o] N_2 molec./bulk Ru atom/s at 315°C.

[p] Precursor; $RuCl_3 \cdot 3H_2O$, MgO, Cs_2CO_3 (Cs/Ru = 10).

[q] Precursor; $RuCl_3 \cdot 3H_2O$(acetone), MgO.

[r] Precursor; $(Ru(NH_3)_5N_2)Cl_2$, MgO, $CsNO_3$ (Cs/Ru = 10).

[s] Precursor; $RuCl_3 \cdot 3H_2O$(acetone), MgOH, and $CsNO_3$ (Cs/Ru = 10).

[t] Data cited from Ref. (*1*) for A, Ref. (*3*) for S, Refs. (*10, 11*) for U, and Ref. (*2*) for Y.

creased TOF of ammonia synthesis several times but also increased the Ru dispersion for these catalyst (see Table 2) as in the case of Al_2O_3-supported catalyst (*3*).

Ammonia has been reported to be formed also from CO, H_2O, and N_2 at a steady rate over Ru–CsOH/MgO without forming any hydrocarbons at 370 to 430°C under 1 atm (*13*).

Ammonia synthesis on K-promoted catalyst. Ru/BeO, Ru/MgO, and Ru/CaO were added with K and the ammonia synthesis activities were measured. TOF at 315°C on Ru–K/MgO or Ru–K/BeO were as great as that on Ru–K/AC which has been the best catalyst under these conditions (see Table 2). Since the activation energy on Ru–K/MgO (16 kcal/mol) is much lower than that on Ru–K/AC (22 kcal/mol), the former should have the greatest TOF at lower temperatures. Kinetic problems will be discussed elsewhere (*14*). The promotion effect by K was greater than alkaline earth.

N_2 isotopic equilibration over Ru K/BeO, Ru–K/MgO, and Ru–K/CaO. This reaction is perhaps the most important reaction for N_2 activation because hydrogen effect can be neglected. The activity of this reaction was measured and is shown in Table 2. It was found that TOF of this reaction on Ru–K/BeO, Ru–K/MgO, and Ru–K/CaO was six times greater than that on Ru–K/AC or Ru–K/Al_2O_3 which have been the best catalysts for this reaction.

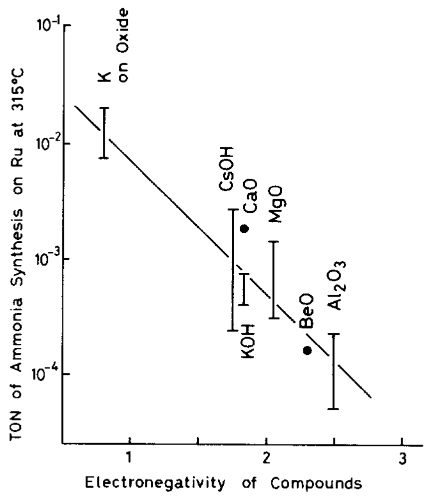

FIG. 2. TOF of ammonia synthesis at 315°C under 600 Torr on various Ru catalyst as a function of the electronegativity of support or promoter compounds. Data are cited from Table 2 in this work and Table 1 in the previous paper (*3*).

DISCUSSION

Electron donation by support and promoter. In order to discuss the role of the support and promoter, the TOF of ammonia synthesis at 315°C under 600 Torr (80.0 kPa) was rearranged from Table 2 in this paper and from Table 1 in the previous paper (*3*). The values were plotted as a function of the electronegativity of a predominant-promoter compound (*15*) as shown in Fig. 2. Although the values are scattered in some extent due to some other factors, we can observe a definite trend. The lower the electronegativity of a support or a promoter, the greater the activity of ruthenium catalyst. It is concluded that N_2 dissociation which is the rate-determining step of ammonia synthesis is promoted by electron donation from support or promoter to Ru. The XPS results also support this hypothesis qualitatively. The effectiveness of MgO has already been pointed out by others (*16*).

Structure insensitiveness in this system. The (111) surface of an iron single crystal is known to be the most active for ammonia synthesis among any iron surfaces with simple indexes (*17*). TOF for this reaction on Fe/MgO has been reported to decrease with increasing dispersion (*18*). The structure sensitivity has been explained by a change in the fraction of active sites on the surface (*19*). TOF of this reaction over various Ru catalyst were plotted as a function of percentage dispersion of Ru from Table 2 in this study and Table 1 in the previous paper (*3*) as shown in Fig. 3. Systematic relations were not found between them. This means that the structure sensitiveness is not more important than the electronic effect as for a Ru catalyst.

Comparison of activity of ammonia synthesis. Figure 3 shows TOF of this reaction

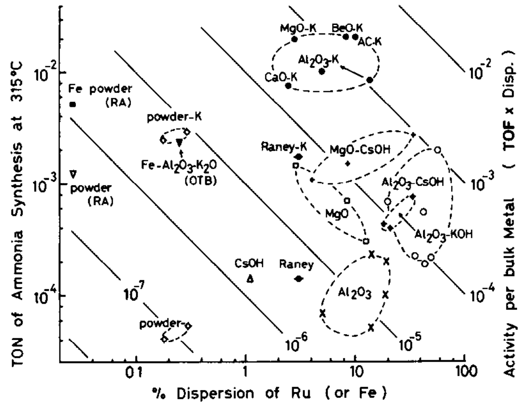

FIG. 3. TOF of ammonia synthesis at 315°C under 600 Torr of $N_2 + 3H_2$ on various Ru and Fe catalyst as a function of percentage dispersion of metals. Activity per bulk metal is also scaled as declined lines. Data in dotted circle is cited from Table 2 in this paper and Table 1 in the previous paper (*3*). The other data are cited from our previous paper (*20*) or others (*21*).

at 315°C under 600 Torr as a function of percentage dispersion of metal. The declined line in this figure also shows the activity per bulk metal which is important industrially. A catalyst effectiveness is well illustrated in this way. K-Promoted catalysts have the highest TOF, while CsOH-promoted catalysts have compared well to the K-promoted catalyst in view of the per-bulk activity. Under these conditions a doubly promoted iron catalyst (*20*) shows lower activity (one-tenth of TOF of Ru–K/AC, one-hundredth of the per-bulk activity of Ru–CsOH/Al_2O_3). However, this does not mean that the Ru catalysts are extraordinarily better than the iron catalysts even under commercial conditions, because the kinetics are much different from each other (*14, 20, 21*). The data on Fe and Ru powder by Rambeau and Amariglio were transformed to TOF by using their BET area (*21*). Their values were greater than ours. The reason is not clear, however, it has been pointed out recently that Cl may remain on a reduced Ru powder in some cases (*22*).

K-Promoted Ru or Raney Ru seems to have lower TOF than the supported catalyst with K. Since the real surface Ru number after K addition should be smaller than the number measured before K addition, the real TOF should be greater than the value listed here. It should be noted that 1 g of Raney Ru–K (*12*) is as effective as 1 g of 5% Ru–K/AC.

Remarkable support of "superbase" for N_2 isotopic mixing. TOF of this reaction over Ru and Fe catalysts was plotted as a function of Ru dispersion and the activities per bulk metal were also plotted in Fig. 4. The activity difference between Ru powder (*11*) and Ru–K/MgO is about 10^4 times in this reaction while it is about 10^3 times in ammonia synthesis reaction. It should be noted that alkaline earth with K (superbase) promote this reaction 10 times more than K/AC or K/Al_2O_3 does. The remarkable promoter action of this superbase may be due to its strong electron donation property (*4*). Ertl *et al.* has pointed out that the promoter action of K is to stabilize the molecularly adsorbed nitrogen on Fe surface (*23*). Since the change of activation energies is not decisive of the reasoning for the 10^5 times promotion of activity, the entropy

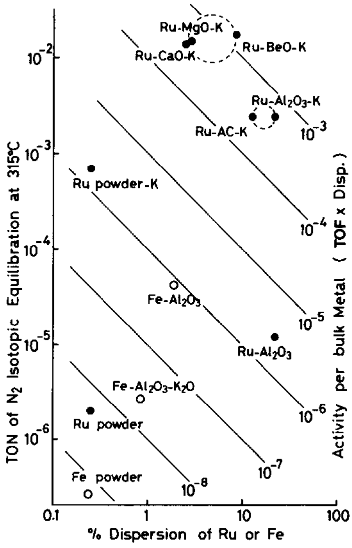

FIG. 4. TOF of N_2 isotopic equilibration at 315°C under 150 Torr of total pressure of dinitrogen on various Ru and Fe catalyst as a function of % dispersion of metals. Data are cited from Table 2 and our previous paper (*25–27*).

factor, which is related with the stabilization of the activated complex, might be more important. A further study is necessary for a more detailed discussion.

Another novel aspect of this system is that Ru–K/MgO and Ru–K/CaO adsorb a great deal of N_2 as $K(N_2)_x$ on an oxide surface (*24*).

Activities of iron catalysts (*25–27*) for this reaction are also shown in Fig. 4. It is interesting to point out that the TOF of this reaction on iron catalysts is quite low, while the activity of ammonia synthesis is comparable with Ru catalysts at lower temperatures (see Fig. 3). This is probably because the rate on Ru catalysts has a negative order with respect to hydrogen in ammonia synthesis (*21*), whereas that on iron catalysts has a positive order (*20*). An intrinsic activeness of Ru for N–N bond rupture without the presence of hydrogen is demonstrated.

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