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Support and Promoter Effect of Ruthenium Catalyst

I. Characterization of Alkali-Promoted Ruthenium/Alumina Catalysts for Ammonia Synthesis

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Ru/Al_2O_3 catalysts promoted with various alkali precursors were prepared and characterized by various methods including XPS and TPR (temperature-programmed reduction) techniques. The activation of the promoted catalyst was studied in detail. The addition of an alkali precursor, especially $CsNO_3$, promoted the turnover frequency (TOF) of ammonia synthesis, and also increased the Ru dispersion. It is suggested that the alkali precursor became converted to hydroxide after reduction at 400°C. The promotion of TOF by alkali corresponded to the electron-donating tendency ($CsOH > KOH$). Ru-alkali(KOH)/Al_2O_3 was found to be tolerant to CO and/or H_2O poisoning, and treatment in H_2 led to restoration of the original catalytic activity.

INTRODUCTION

Alkali metal-promoted ruthenium has been found to be one of the most active catalysts for ammonia synthesis under atmospheric pressure (*1*, *2*). However, alkali metals are converted to hydroxides, and the activity may decrease if the reactant gas implies impurity of water or oxygen-containing compounds. This problem is important under commercial operation. Thus, the stable promoter which acts as strong electron donor should be developed instead of the metallic alkali. Several combinations of support and promoter precursor were studied in an attempt to find the best Ru catalyst. $CsNO_3$ proved to be an effective promoter precursor for the Ru/Al_2O_3 catalyst. Although Mittash has already reported that "potassium oxide is an excellent promoter for osmium and ruthenium" (*3*), details were not published. Moreover the activation process of the supported metal catalyst including promoter precursor decomposition has not been studied well. In this work, several model systems were studied by TPR technique in order to clarify the activation process. Oxidation states of Ru before and after reduction were also studied by using H_2 consumption measurement and XPS measurements.

EXPERIMENTAL

During the impregnation process for preparation of 2% Ru/Al_2O_3, redish Ru ions were readily adsorbed on Al_2O_3, so that the aqueous solution was decolorized. However, when KNO_3 or $CsNO_3$ solution was added to $RuCl_3/Al_2O_3$, a black deposit was formed. The deposit was found to contain Ru, Cl, N, C, and H by elemental analysis. The deposit was also forced to adhere to the catalyst in the evaporation process. A dried and weighed catalyst was reduced with circulated H_2 (600 Torr) at 150°C for 2 h, 300°C for 2 h, and finally at 450°C for 24 h or 500°C for 2 h. After the catalyst was evacuated at 400°C for 2 h, hydrogen

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chemisorption was measured at 0°C (*4*). The results are shown in the form of Ru dispersion in Table 1.

The ammonia synthesis rate was measured at 200 to 400°C with 600 Torr of N_2 + $3H_2$ gas by using a closed circulation system with a liquid-nitrogen trap (*1*). The flow rate was estimated to be ca. 4.5 liters (STP)/h. TOF of the reaction was defined as the rate of ammonia production (mol/s) at 315°C divided by the amount of chemisorbed hydrogen atom (mol).

XPS spectrum of the catalyst was measured with the Hewlett–Packard 5950A-ESCA spectrometer. The reduction of the sample was carried out with H_2 at 480°C for 1 h in the spectrometer.

Temperature-programmed reduction (TPR) of the catalyst was carried out in a stream of H_2/He (1/10) gas with a flow rate of 83 ml/min. ULVAC-TGD-3000RH-N was attached to this flow system in order to measure a differential thermal gravimetry (DTG) and a differential thermal analysis (DTA). A weight change of the supported Ru catalyst during the reduction was so small that an effective measurement was not possible. Thus the samples without support were used for the TPR experiment. $RuCl_3 \cdot 3H_2O$ and $CsNO_3$ were mixed in an aqueous solution (wet mixing) or the powder were mixed in an agate mortar (dry mixing). Thirty to sixty milligrams of sample was placed on Pt-made sample holder in the TPR apparatus. Temperature was raised at a rate of 100°C/h from room temperature to 400°C, and the gravity change and the amount of heat evolved were measured.

RESULTS

$RuCl_3 \cdot 3H_2O$-$CsNO_3$ Reduction as a Model

In order to investigate the ruthenium reduction and the precursor decomposition, the following model compounds without alumina support were studied by the TPR technique. The main results are shown in Figs. 1 to 4.

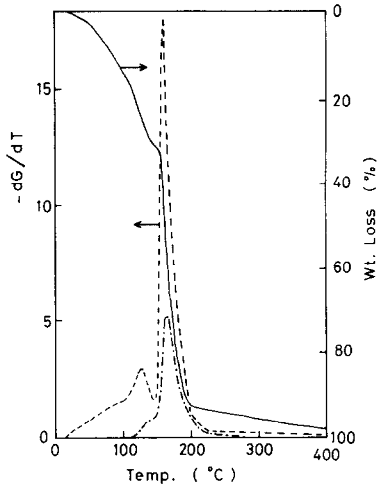

FIG. 1. TPR spectra of $RuCl_3 \cdot 3H_2O$ (23.7 mg). Weight loss calculation is based on Reaction (1) in the text. Dot and dash shows HCl detected mass spectrometrically.

(*a*) *$RuCl_3 \cdot 3H_2O$*. Coordinated H_2O was released at 125°C and $RuCl_3$ was reduced at 175°C releasing HCl which was identified mass spectrometrically. The sample lost weight almost to the theoretical value based on Reaction (1) as shown in Fig. 1.

$$RuCl_3 \cdot 3H_2O + 1.5H_2 = Ru + 3HCl + 3H_2O \quad (1)$$

(*b*) *$CsNO_3$*. No weight loss during TPR was observed up to 400°C, while two endothermal peaks were observed at 152°C (phase transition) and 370°C (melting point) by DTA. $CsNO_3$ was not decomposed unless Ru metal was present.

(*c*) *Ru powder–$CsNO_3$*. With the presence of Ru powder (ca. 1 m^2/g) $CsNO_3$ decomposition occurred mostly at above 200°C giving NH_3 (tested by Nessler's reagent) during TPR. However, the decomposition reaction was not completed by 400°C (55% of Reaction (2)) because of the incomplete contact between the mixed powders. DTA spectra showed the $CsNO_3$ transition at 152 and 370°C, which proved the existence of undecomposed $CsNO_3$ at these temperatures.

TABLE 1

Characterization and Activity of Ru/Al_2O_3 Catalysts

	Catalyst No.	Ru wt% in Ru/Al_2O_3	Total Ru (mmol)	Alumina source	Promoter precursor[a]	Original catalyst weight (g)	Ru dispersion before reaction (%)	Activity TOF[b] × 10^4	Activity per bulk Ru[c] × 10^4	Activation energy (kcal/mol)
Ru/Al_2O_3	S-2	2.0	0.383	TK[d]		2.0	5	0.67	0.034	17
	A-6	0.5	0.238	E[e]		4.86	14[h]	2.36	0.33	14
	H-1	0.5	0.245	E		5.0	19	2.0	0.38	17
	K-1	0.5	0.487	E		9.92	19	1.0	0.19	15
	O-4	5.1	0.934	Alon C[f]		2.0	11.5			
	S-4	2.0	0.330	TK-C[g]	NH_4NO_3	2.0	14	0.51	0.071	17
Ru–KOH/Al_2O_3	S-1	2.0	0.367	TK	KNO_3	2.30	21, 21[i]	3.8	0.80	28
	S-5	2.0	0.319	TK-C	KNO_3	2.0	34, 33[i]	7.5	2.55	28
	S-7	2.0	0.381	TK	K	2.0[j]	18	4.2	0.76	
Ru–CsOH/Al_2O_3	S-6	2.0	0.302	TK-C	$CsNO_3$	2.08	58, 61[h], 60[i]	20	11.6	28
	H-5	2.0	0.302	TK-C	$CsNO_3$	2.08	20	7	1.4	
	H-4	0.5	0.243	E	$CsNO_3$	5.4	42	5.6	2.35	26
	K-2	0.5	0.155	E	$CsNO_3$	3.44	43	1.9	0.82	27
	H-2	0.5	0.243	E	Cs_2CO_3	5.4	35	2.2	0.77	27
	H-3	0.5	0.243	E	CsOH	5.4	49	2.2	1.08	24
Ru–K/Al_2O_3	A-6k	0.5	0.238	E	K	4.86[j]	14[h]	84	11.8	23
	S-3	2.0	0.381	TK	K	2.0[j]	5, 18[i]	100, 28[i]	5.0	27
Ru powder[k]	K-3	100	98.4			9.95	0.25	0.80	0.002	28
Ru–CsOH[k]	Y-1	100	7.62		$CsNO_3$	3.49	1.1	1.41	0.016	22

[a] Atomic ratio of precursor against Ru is 10 except for S-7, A-2, S-3, and Y-1(1/1).

[b] Ammonia synthesis rate at 315°C expressed as NH_3 molec./surface Ru atom/s (see text for other conditions).

[c] Ammonia synthesis rate at 315°C expressed as NH_3 molec./bulk Ru atom/s.

[d] From Tokai Konetsu (TKR-95651); pelleted; 170 m^2/g.

[e] 0.5% Ru/Al_2O_3 from Japan Engelhard; pelletted; 8 mesh; 89 m^2/g.

[f] From G. L. Cabot; 82 m^2/g after pelletting as Ru/Al_2O_3.

[g] From Tokai Konetsu; crashed to 10 to 20 mesh; 170 m^2/g.

[h] Measured with CO chemisorption at 0 or 23°C.

[i] Dispersion measured after reaction.

[j] Weight without K.

[k] See Ref. (*9*).

$$CsNO_3 + 4H_2 = 0.5Cs_2O + NH_3 + 2.5H_2O \quad (2)$$

(*d*) *$RuCl_3 \cdot 3H_2O$–$CsNO_3$ mixed in a solution.* Hydrogen consumption of the sample with Ru/Cs molar ratio of 1/1 was measured in a closed-circulation system during TPR and shown as a solid line in Fig. 2. At around 160°C (first peak) Reaction (1) was suggested to occur, because HCl was detected in $AgNO_3$ solution at the exit. At around 200 to 250°C Reaction(2) was suggested to occur, because NH_3 was detected by the Nessler reagent test. Total hydrogen consumption by 400°C corresponded to 95% of the value based on Reactions (1) and (2). Although DTG was measured in the other (flow) system, the weight loss curve of the same sample (dotted line in Fig. 2) was quite similar to the hydrogen consumption curve (solid line). Slight differences of the peak positions observed were probably due to the scale effect of the sample. It is to be noted that the total weight loss was appreciably smaller than the theoretical value, which means a heavy atom such as Cl is left on the sample. X-Ray diffraction analysis of the sample before and after the TPR run gave peaks due to CsCl. This means an anion exchange between $RuCl_3$ and $CsNO_3$ has occurred in this sample:

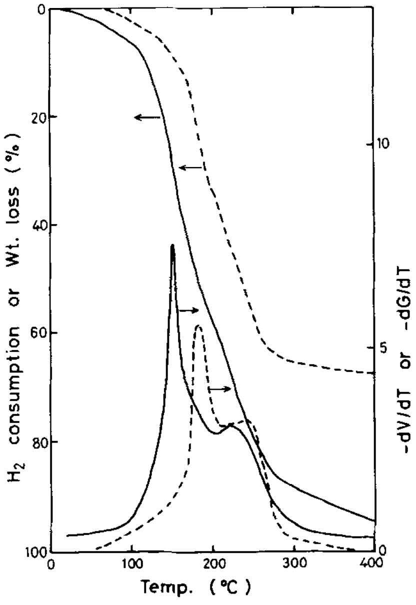

FIG. 2. TPR spectra of a mixture of $RuCl_3 \cdot 3H_2O$ and $CsNO_3$ (1/1). The sample was mixed in an aqueous solution. Solid line shows H_2 consumption measured with closed-circulation system and dotted line shows weight loss measured with DTG flow system. Percentage is based on Reactions (1) and (2) in the text.

$$RuCl_3 + 3CsNO_3 = Ru(NO_3)_3 + 3CsCl \quad (3)$$

(*e*) *$RuCl_3 \cdot 3H_2O$–$CsNO_3$ mixed in solid states.* In order to cut down the extent of anion exchange, the two salts were mixed mechanically in an agate mortar in their solid states and were studied by TPR. Weight loss of the sample (Cs/Ru = 1/1) increased from 67 to 82% by changing a mixing method from wet mixing to dry mixing. However, the anion exchange still occurred and was confirmed by X-ray diffraction (CsCl peak) of the sample before reduction. Samples mixed in their solid states with various Cs/Ru ratios were analyzed by DTG and DTA. The results are shown in Figs. 3 and 4. Decomposed products of the (1/1) sample were HCl (150 to 250°C) and NH_3 (180 to 280°C). By comparison of the DTG data with the DTA data, the reduction process of $RuCl_3 \cdot 3H_2O$–$CsNO_3$ mixture was analyzed as follows: Phase transition of $CsNO_3$ was observed at 152°C in every DTA spectra (Fig. 4). DTG peak 1 corresponding to DTA peak 1 was assigned to Ru reduction (Reaction (1)). With increasing Cs/Ru ratio, DTG peak 1 was broadened and shifted to higher temperature (160 to 208°C). Since both NH_3 and HCl were released around the temperature of DTA peak 2, any reactions in 1, 2, or 4 may account for the peak 2. An elaborate analysis was impossible.

$$Ru(NO_3)_3 + 10.5H_2 = Ru + 3NH_3 + 9H_2O \quad (4)$$

DTG peak 3, where NH_3 was observed as a product, was identified to be due to Reaction (2). Exothermic nature of this reaction is observable in DTA peak 3 in Fig. 4.

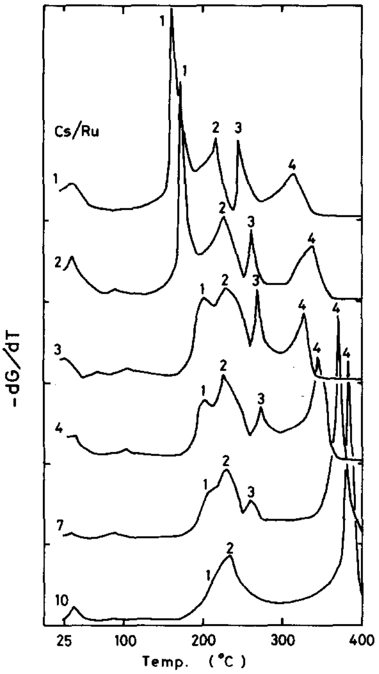

FIG. 3. Differential thermal gravimetry of various samples composed of $RuCl_3 \cdot 3H_2O$ and $CsNO_3$ (Cs/Ru = 1 to 10) in TPR runs. The samples were mixed in their solid states.

DTG peak 4 was suggested to be due to the Cs salt reaction because neither NH_3 nor HCl was observed at the outlet. Cs_2O is known to decompose into Cs_2O_2 and metal at these temperatures (*6*).

$$2Cs_2O = Cs_2O_2 + 2Cs \qquad (5)$$

A weight loss at peak 4 is suggested to be due to Cs evaporation. A strong exotherm (DTA peak 4) is considered to be due to a formation of CsOH by H_2 (Reaction (6)) or adsorbed water (Reaction (7)).

$$Cs_2O_2 + H_2 = 2CsOH \qquad (6)$$

$$2Cs + 2H_2O = 2CsOH + H_2 \qquad (7)$$

Thus the final state of $RuCl_3 \cdot 3H_2O$–$CsNO_3$ sample after the activation is considered mostly to be a mixture of Ru–CsOH partly with the presence of CsCl. The composition may depend on the Cs/Ru ratio and the mixing method. X-Ray diffraction of this sample showed the existence of Ru metal and CsCl. The activated sample was quite deliquescent in the air. Ammonia synthesis activity of the sample without a support (Cs/Ru = 1/1) prepared in this manner is shown in Table 1 (Y-1).

Reduction Behavior of Promoted Ru/Al_2O_3 Catalyst

Hydrogen consumption during the catalyst reduction was measured. $RuCl_3 \cdot 3H_2O/Al_2O_3$ (O–4; 5.1% Ru/Al_2O_3) was almost completely reduced below 150°C. Total hydrogen consumption was almost equivalent (actually 1.25 times) to that expected from the Reaction 1. Cesium nitrate-added (H-4) or cesium carbonate-added catalyst (H-2), of which Cs content was 10 times of Ru in molar scale, consumed much more hydrogen than the catalyst without a promoter. Hydrogen was consumed mostly by the hydrogenolysis of precursor promoter salt; this process was catalyzed by Ru metal as explained above. Actual hydrogen consumption for the activation of the sample

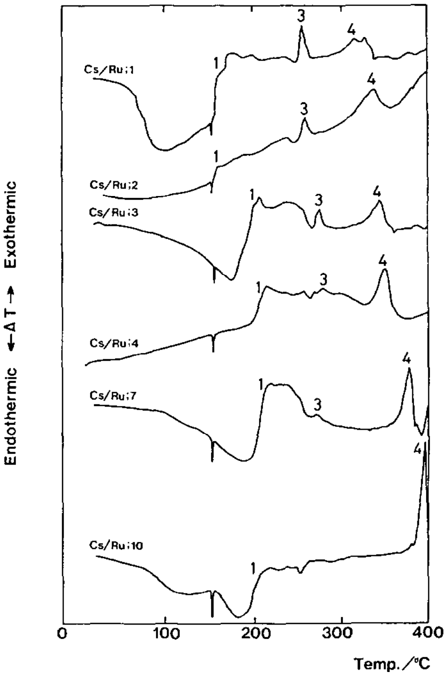

FIG. 4. Thermal analysis of various samples composed of $RuCl_3 \cdot 3H_2O$ and $CsNO_3$ (Cs/Ru = 1 to 10) in TPR runs. The samples were mixed in their solid states.

H-4 amounts to 70% of the value expected for Reaction (2) and for sample H-2 it is 82% of the value of Reaction (8). Cesium hydroxide-added catalyst (H-3) also consumed an amount of hydrogen similar to that of H-2, which suggests H-3 had adsorbed a great deal of CO_2 before reduction.

$$Cs_2CO_3 + 4H_2 = Cs_2O + CH_4 + 2H_2O \quad (8)$$

XPS Study

XPS spectra of $RuCl_3 \cdot 3H_2O$/Alon C-Al_2O_3 (Ru/Al_2O_3 = 10/90 w/w) was measured and the results are shown in Fig. 5. The binding energy (B.E.) of the peak at 282.3 eV for the sample before reduction (Fig. 5B) was assigned to be Ru $3d_{5/2}$ and a broad peak around 285 to 286 eV is considered to be composed by both Ru $3d_{3/2}$ (286.5) and C 1*s* (284.8). The B.E. of this sample is near the value of RuO_3 obtained by Kim (*7*). However, the oxidation state of Ru/Al_2O_3 before reduction is considered to be +3 because hydrogen consumption of 5.1% Ru/Al_2O_3 (O-4) was almost equivalent to Reaction (1). The high B.E. of this sample may be due to the coordination of H_2O as in the case of RuO_3 with H_2O (*7*). The above sample was reduced with hydrogen (1 Torr) in the XPS spectrometer at 480°C for 1 h. The spectra are shown in Fig. 5A.

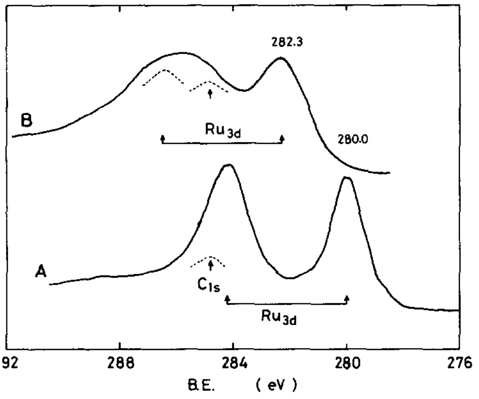

FIG. 5. XPS spectra of $RuCl_3 \cdot 3H_2O/Al_2O_3$ (Ru/Al_2O_3 = 10/90 w/w). (A) Spectra of the sample after reduction (480°C), and (B) spectra before reduction.

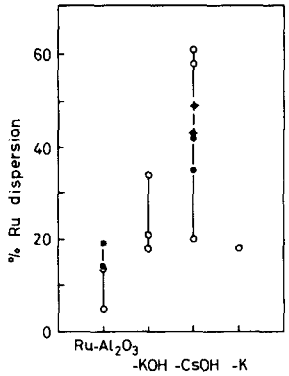

FIG. 6. Percentage Ru dispersion of Ru/Al_2O_3, Ru-KOH/Al_2O_3, Ru-CsOH/Al_2O_3, and Ru-K/Al_2O_3.

B.E. of Ru $3d_{5/2}$ (280.0) and $3d_{3/2}$ (284.2) were identical to that of Ru metal (*7*). Ru was shown to be reduced completely on Al_2O_3, which is contrary to the results of Bossi *et al.* (*8*).

Ru Dispersion

Ru dispersion based on hydrogen chemisorption of various Ru/Al_2O_3 catalysts is shown in Table 1 and Fig. 6. It was observed that the Ru catalyst with KOH or CsOH had higher dispersions than the catalyst without such promoters. The reduction process of the Ru precursor salt is considered to be affected by alkali salt.

Ammonia Synthesis Activity

Ammonia synthesis activities and activation energies of various ruthenium catalysts were measured and the results are shown in Table 1. The activities were also represented as turnover frequency (TOF) on the basis of hydrogen chemisorption (Fig. 7) and specific activity per bulk ruthenium (Fig. 8). Activities of Ru metal catalysts without support (K-3, Y-1) are also listed in Table 1, which will be discussed elsewhere (*9*). TOF on Ru powder was almost the same as that of Ru/Al_2O_3. As is shown in Fig. 7, TOF on Ru/Al_2O_3 increased upon addition of alkali promoter in the order: no addition < KOH < CsOH < K. CsOH also promoted TOF on Ru metal (Y-1) although the extent of the promotion was not re-

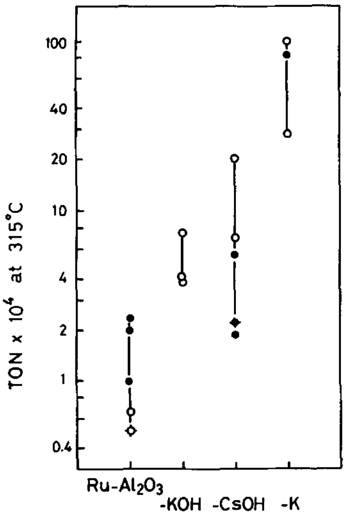

FIG. 7. TOF of ammonia synthesis on Ru/Al_2O_3, Ru-KOH/Al_2O_3, Ru-CsOH/Al_2O_3, and Ru-K/Al_2O_3 at 315°C under 600 Torr.

markable. Since CsOH- or KOH-promoted Ru/Al_2O_3 catalyst have higher Ru dispersion, the specific activities per bulk metal were high enough to be comparable with the K-promoted catalyst (Fig. 8). Addition of NH_4NO_3 instead of $CsNO_3$ seems to cause an increase of Ru dispersion but has no relation with the activities (see S-2 and S-4). The activation energies for all Ru/Al_2O_3 catalysts were lower than that for the promoted Ru/Al_2O_3 catalysts, which will be discussed in detail elsewhere (*9*).

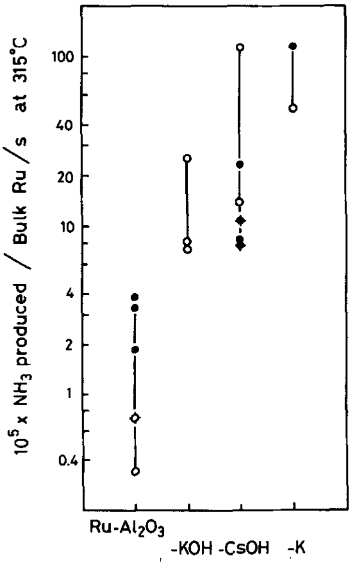

FIG. 8. Activity of ammonia synthesis per Ru bulk metal on Ru/Al_2O_3, Ru-KOH/Al_2O_3, Ru-CsOH/Al_2O_3, and Ru-K/Al_2O_3 at 315°C under 600 Torr.

Poisoning by Water Vapor

2% Ru-K/Al_2O_3 catalyst (S-3 in Table 1) was placed in contact with water vapor (16 Torr) in the closed-circulation system, then the specific activity was measured as shown in Table 2. Water reacted with K to form KOH, which resulted in the activity decrease. However, the activity was restored, to some extent by the H_2 treatment at 450°C for 40 h. It is to be noted that the restored activity was almost in the same level as that of 2% Ru-KOH/Al_2O_3 (S-1). Water vapor treatment on 2% Ru-KOH/Al_2O_3 (S-1) also decreased the activity, as shown in Table 2, which was also recovered by H_2 treatment at 450°C. It is interesting to note that Ru dispersion increased from 5 to 18% through the series of processes of K addition, activity measurement of ammonia synthesis, and both H_2O and H_2 treatments (see S-2, S-3, and S-7 in Table 1). Activity decrease of 2% Ru-KOH/Al_2O_3 with CO poisoning was also recovered by H_2 treatment at 450°C.

DISCUSSION

State of Ru

Although $RuCl_3$ is known to be easily reduced thermodynamically $((\mathrm{Ru})(\mathrm{HCl})^3(\mathrm{Ru}$-

TABLE 2

Effect of Water Vapor (16 Torr) against Ru/Al_2O_3 Catalyst for Ammonia Synthesis

	Treating gas	Specific activity at 315°C (ml NH_3/h/g-cat)
2% Ru-K/Al_2O_3 (S-3)	—	8.0
	H_2O, 20°C, 1 h	5.3
	H_2O, 450°C, 14 h	0.50
	H_2, 450°C, 40 h	1.2
2% Ru-KOH/Al_2O_3 (S-1)	—	1.1
	H_2O, 20°C, 5 min	0.38
	H_2, 450°C, 40 h	1.1

$Cl_3)^{-1}(H_2)^{-1.5} = 10^{17}$) (*10*), the oxidation state of Ru has been reported to depend upon the surrounding condition even after H_2 reduction (*8*). XPS results of 10% Ru/Al_2O_3 in this study show that ruthenium is reduced completely to the metallic state over Al_2O_3. Activity level of ammonia synthesis on Ru/Al_2O_3 is another proof that Ru is reduced to metal. Ru on active carbon which is known as a strong electron acceptor has no activity (*1*).

Metal dispersion is known to be controlled by the preparation method and/or surface properties of the support (*10*). In this study it was found that the existence of promoter precursor salt increased the Ru dispersion (Fig. 6). Ru atom coagulation during the reduction process might possibly by prevented by the surrounded precursor salt. Further study will be necessary for this problem.

State of Alkali

Cesium nitrate was almost completely decomposed with the presence of Ru as was proved by hydrogen consumption or DTA data (Fig. 4) which showed no peak at 370°C ($CsNO_3$ mp). A part of Cl ion was left on the catalyst, forming CsCl (Reaction (3)) which was not a promoter. The decomposition (Reaction (2)) occurs by the aid of Ru metal (a catalyst for solid-phase reaction) giving Cs_2O as a product. DTA and DTG experiments suggested that the Cs_2O was decomposed and a part of Cs was lost by the evaporization (Reaction (5)), and that CsOH was formed (Reactions (6) and (7)). These conclusions on the system without a support are considered to be applied for the system with Al_2O_3 support. On alumina, Cs_2O may be turned to CsOH more easily by a reaction with surface OH.

A similar conclusion is thought to be applied to potassium system. KNO_3-based catalyst had the same TOF as that of Ru-KOH/Al_2O_3 which was formed from Ru–K/Al_2O_3 by H_2O addition, that was another proof that KNO_3 was turned to KOH. Cs_2CO_3 and CsOH, whose surface was essentially Cs_2CO_3 when exposed to air, decomposed to CsOH with the aid of Ru.

Alkali and Support Action

The activity (TOF) of Ru catalyst is related to the basicity or the electron-donating tendency of a support or a promoter. The activity sequence is in the order of the average electronegativity of compound, that is 0.8 for K, 1.75 for CsOH, 1.83 for KOH, and 2.5 for Al_2O_3 as shown in Fig. 7. The reason of the scattering of the values in Fig. 7 is considered mostly to be due to the difference of source of alumina. These catalysts will be studied kinetically elsewhere (*9*) and the support action will be studied further by using other kinds of oxide (*5*).

CONCLUSION

Alkali-promoted Ru/Al_2O_3 catalysts were proved to be effective for ammonia synthesis. Alkali promotes not only the intrinsic activity of Ru, but also improves the Ru dispersion. Alkali was suggested to be present in a form of hydroxide under the reaction condition. Alkali metal hydroxide acts as a stable promoter against poisons such as H_2O or CO. Although Ru-alkali metal hydroxide/Al_2O_3 catalyst decrease the activity by those poisons, it restores the activity by a treatment in H_2/N_2.

REFERENCES

1. Aika, K., Hori, H., and Ozaki, A., *J. Catal.* **27,** 424 (1972).

2. Aika, K., Yamaguchi, J., and Ozaki, A., *Chem. Lett.* 161 (1973).

3. Mittasch, A., "Advances in Catalysis," Vol. 2, p. 95. Academic Press, New York, 1950.

4. Dalla Betta, R. A., *J. Catal.* **34,** 57 (1974); Taylor, K. C., *J. Catal.* **38,** 299 (1975).

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

6. "Gmelins Handbuch der Anorganischen Chemie" (Pietsch, E., Ed.), System-Number 25, p. 107. Verlag Chemie, Weinheim, 1955.

7. Kim, K. S., and Winograd, N., *J. Catal.* **35**, 66 (1974).
8. Bossi, A., Garbassi, F., Orlandi, A., Petrini, G., and Zaderighi, L., *in* "Preparation of Catalysis. II. Scientific Bases for the Preparation of Heterogeneous Catalysts" (D. Delmon *et al.* Eds.), p. 405. Elsevier, Amsterdam, 1979.
9. Aika, K., *et al.*, to be published.
10. Anderson, J. R., "Structure of Metallic Catalysts," p. 167. Academic Press, New York, 1975.