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Preparation and Characterization of Chlorine-Free Ruthenium Catalysts and the Promoter Effect in Ammonia Synthesis.

1. An Alumina-Supported Ruthenium Catalyst

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Ru/Al_2O_3 catalyst prepared from Cl-free Ru carbonyl was much more active for ammonia synthesis under 1.01 bar of $N_2 + 3H_2$ than that prepared from $RuCl_3$. The high activity was related to the high dispersion and lack of Cl. Alkali metal ion (oxide or hydroxide of Cs^+, Rb^+, and K^+) was an effective promoter for the Cl-free Ru catalyst, suggesting that the alkali acted as an electronic promoter for Ru. The synthesis rate was maximum when the Cs/Ru ratio was as high as 10. Alkali had a strong interaction with the Al_2O_3 surface and a weak interaction with the Ru surface.

INTRODUCTION

Ruthenium catalysts are considered as second generation ammonia catalysts after the iron catalysts (*1*). Ruthenium has been reported to be quite sensitive to the catalyst support and the promoter in ammonia synthesis (*2*). In a previous paper, the Cl element was observed by XPS on Ru/MgO prepared from $RuCl_3$. The amount of Cl was decreased when the reduction temperature was increased, while H_2 adsorption and ammonia activity were increased. It was concluded that chlorine left on Ru/MgO catalyst retarded ammonia synthesis and that alkali could remove it (*3*). Thus, the following questions arise. (1) Is Cl-free Ru precursor a more effective catalyst? (2) Does the alkali promote activity only by neutralizing Cl or does it even promote Cl-free Ru?

In past work, $RuCl_3$ was used as the precursor because it is a stable common compound (*4–6*). Few works on the effect of precursor and the preparation method have been reported. Brief data are available on the ammonia synthesis rate on Ru/MgO prepared from $Ru(NO)(NO_3)_3$ (*7*), although we observed that this catalyst had little activity. $Ru_3(CO)_{12}$ has been reported to give fine particles when supported on Al_2O_3. Several works have been published on the interaction between the $Ru_3(CO)_{12}$ and the Al_2O_3 surface (*8–12*). In the present study, two other Cl-free precursors ($Ru(acac)_3$ and K_2RuO_4) were examined. The catalysts prepared from various precursors give various Ru dispersions. Structure sensitivity can also be examined by using these Cl-free and alkali-free catalysts. Results in the literature indicate that structure sensitivity on Ru is not as important as that on Fe (*13–15*).

Because the promoter can interact with both Ru and the support, it is important to control how the promoter interacts exclusively with Ru. Thus, the effects of both decomposition temperature and the amount of promoter on ammonia synthesis were also studied.

METHODS

Five kinds of Ru precursors were used: $RuCl_3 \cdot 3H_2O$ (Koso Chemical Co.), Ru

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TABLE 1

Summary of Ammonia Synthesis Rate and Hydrogen Chemisorption on Various 2 wt% Ru/Al_2O_3 Catalysts[a] Prepared from Various Precursors

Code No.:	1	2	3	4	5	6	7	8
Precursor:	$RuCl_3 \cdot 3H_2O$	Ru(acac)$_3$	K_2RuO_4	Ru(NO)(NO$_3$)$_3$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$	$Ru_3(CO)_{12}$
Solvent:	Acetone	THF	H_2O	3N–HNO_3	THF	THF	THF	THF
Ru (wt%):	1.9	2.0	2.0	2.0	2.1	1.0	4.8	7.4
Rate:[b]	8 (32)[c]	20	33	53	62	35	202	271
H(*a*)/Ru:	0.23	0.28	0.03	0.35	0.43	0.65	0.39	0.37
TOF[d] × 10^4:	0.5	1.3	18.5	2.2	2.2	1.5	3.2	2.8
Size (nm):[e]	5.7	4.7	44	3.8	3.1	—	—	—
BET S.A.:[f]	202	184	190	194	184	—	—	—

[a] All catalysts were treated with H_2 at 873 K for 4 h.
[b] μmol h^{-1} g^{-1} at 673 K under 101 kPa of $N_2 + 3H_2$.
[c] The reduced sample was washed with 0.1% ammonia aqueous solution (300 ml).
[d] NH_3/s/H(*a*) at 673 K.
[e] Calculated from H(*a*)/Ru using the average surface density of Ru metal [Ref. (*19*)].
[f] m^2 g^{-1}.

(acac)$_3$ (Merck), K_2RuO_4 (Fluka), Ru(NO)(NO$_3$)$_3$ (Japan Engelhard Co.), and $Ru_3(CO)_{12}$ (Aldrich). γ-Al_2O_3 (reference catalyst of Catalysis Society of Japan, JRC-ALO-4), which had been baked at 773 K, was impregnated with Ru precursor in solution as shown in Table 1. The Ru loading was 2 wt%. After evaporation and drying, a sample other than the $Ru_3(CO)_{12}$ system, which corresponds to 1 g reduced 2 wt% Ru/Al_2O_3, was transferred to the reactor and reduced by hydrogen at 873 K. The Ru(acac)$_3$–THF–γ-Al_2O_3 system was evacuated using a rotary evaporator. The $Ru_3(CO)_{12}$–THF–γ-Al_2O_3 system was also evacuated in the rotary evaporator, but it was subsequently moved to a reactor, evacuated at 723 K for 2 h, and finally reduced with hydrogen at 873 K.

Promoted catalysts were prepared from $Ru_3(CO)_{12}$/γ-Al_2O_3. After evacuating $Ru_3(CO)_{12}$/γ-Al_2O_3 at 723 K for 2 h, 1 g of the sample was impregnated with aqueous alkali nitrate solution. KNO_3, $RbNO_3$, and $CsNO_3$ were obtained from Kanto Chemical Co., Mitsuwa Chemical Co., and Soekawa Chemical Co., respectively. After standing for several hours, a sample was dried at 373 K and reduced with hydrogen, usually at 623 K in a reactor. The ratio of alkali metal to ruthenium metal was changed.

The rate of ammonia synthesis was measured below 673 K using a conventional flow system at 1.01 bar (*6, 16*). $N_2 + 3H_2$ gas (60 ml min^{-1}), deoxidized through Pd/Al_2O_3 and active carbon trap at 195 K, was used for the ammonia synthesis. Hydrogen was passed for the reduction of the catalyst at a rate of 60 ml min^{-1}. In flowing hydrogen, temperature was increased for 90 min to the programmed treatment temperature and stood at the temperature for 4 h. The ammonia synthesis rate was determined by the decrease rate of electron conductivity of diluted sulfuric acid solution which fixed the produced ammonia (*6, 16*).

After the catalyst was treated with hydrogen at 673 K for 2 h and evacuated at 673 K for 1 h, hydrogen chemisorption was measured at 273 K in a closed circulation system. A sample with alkali promoter was treated with hydrogen at 623 K. The amount of adsorbed hydrogen was calculated by extrapolating a linear portion of an adsorption isotherm measured above 20 Torr to zero pressure. BET surface area was measured by using nitrogen.

XPS spectra of each catalyst were measured with an ESCA-750 (Shimadzu) spectrometer. The catalyst was treated with hydrogen at each temperature for 4 h and kept away from air to obtain the spectra. Impurities of C 1*s* (284.6 eV) and Au $4f_{7/2}$ (83.8 eV) were used as the standard values for determining binding energies.

RESULTS

The first three sections describe the results on promoter-free Ru catalysts, while the last two sections show mainly the effect of alkali promoters.

Effect of Ru Precursor

The ammonia synthesis rate was measured at 673 K and hydrogen adsorption was measured on 2 wt% Ru/Al_2O_3 catalysts prepared from various precursors. Results are shown in Table 1. Among five kinds of precursors, $Ru_3(CO)_{12}$ and $Ru(NO)(NO_3)_3$ gave high dispersion (H(*a*)/Ru) and high rate. Dispersion of the sample from K_2RuO_4 was extraordinarily low; however, the rate was comparable with those of the others. It resulted in the highest TOF (turnover frequency), which was due to the presence of the K^+ promoter. A sample from $RuCl_3 \cdot 3H_2O$ gave low dispersion, low activity, and low TOF, probably because of residual chlorine. A sample from $RuCl_3/Al_2O_3$ was washed with diluted ammonia solution after the hydrogen reduction to remove chlorine. As a result, the activity increased about four times. BET surface area was almost constant for these samples.

Effect of Hydrogen Treatment Temperature for $Ru_3(CO)_{12}/Al_2O_3$ and $RuCl_3/Al_2O_3$

Figure 1 shows the rates of ammonia synthesis at 673 K over $Ru_3(CO)_{12}/Al_2O_3$ and $RuCl_3/Al_2O_3$ catalysts as a function of hydrogen reduction temperature. In the case of $RuCl_3/Al_2O_3$, the activity increased with an increasing reduction temperature up to 923 K, probably due to chlorine removal from the catalyst. The activity increased from 8 to 32 μmol h^{-1} g^{-1}, which was almost the same value as that in the sample which was washed with diluted ammonia solution. The activity decreased with further heating at 973 K, probably due to sintering. The $Ru_3(CO)_{12}/Al_2O_3$ catalyst had higher activity than the $RuCl_3/Al_2O_3$ catalyst and kept almost the same activity when it was treated with hydrogen between 673 and 873 K. It maintained high dispersion under these conditions.

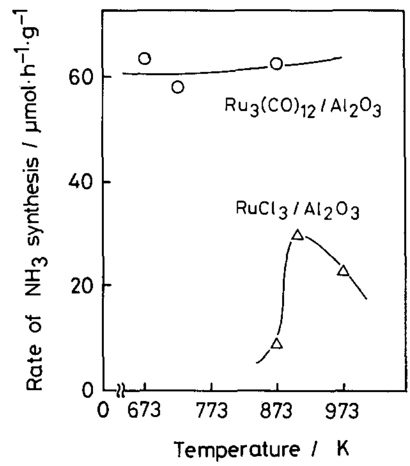

FIG. 1. Ammonia synthesis rate at 673 K under 101 kPa of $N_2 + 3H_2$ over 2 wt% Ru/Al_2O_3 with different precursors as a function of hydrogen treatment temperature.

Effect of Ru Loading for $Ru_3(CO)_{12}/Al_2O_3$

$Ru_3(CO)_{12}/Al_2O_3$ with various Ru loading was prepared. The rate of ammonia synthesis and hydrogen chemisorption data over these catalysts are shown in Table 1 and Fig. 2. The dispersion decreased with an increase in Ru loading (Table 1). The rate increased with the loading percentage; however, it had an S shape (Fig. 2). The rate was measured over two series of catalysts: one was reduced with hydrogen at 873 K and the other at 723 K. The TOF was low at high dispersion (H(*a*)/Ru = 0.65). A weak structure sensitivity was observed.

$Ru_3(CO)_{12}/Al_2O_3$ Promoted with Alkali Metal Nitrate

Ru/Al_2O_3 (2 wt%) prepared from $Ru_3(CO)_{12}$ was added with various kinds and amounts of alkali metal nitrate. The catalyst activities and adsorption data are shown in

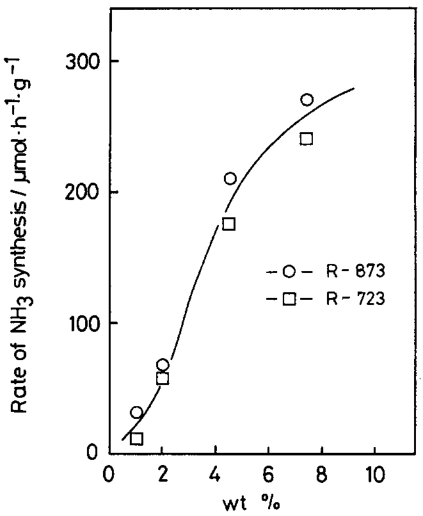

FIG. 2. Ammonia synthesis rate at 673 K under 101 kPa of N_2 + $3H_2$ over Ru/Al_2O_3 prepared from $Ru_3(CO)_{12}$ as a function of percentage of Ru loadings. The samples are reduced at 723 K (□) or 873 K (○).

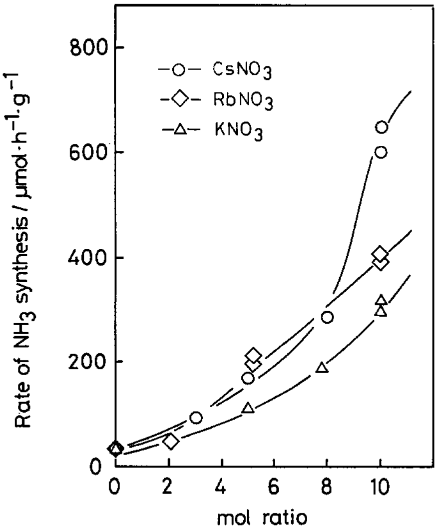

FIG. 3. Ammonia synthesis rate at 623 K under 101 kPa of N_2 + $3H_2$ over 2 wt% Ru/Al_2O_3 promoted with various alkali metal nitrates as a function of mol ratio of alkali metal against Ru; $Ru_3(CO)_{12}$ as a precursor; hydrogen treatment at 623 K for 4 h. Catalyst weight in the activity unit means the catalyst weight without promoter.

Figs. 3 and 4, respectively. The activity increased with an increase in promoter content; however, the curve was concave. At promoter (*M*)/Ru ratio of 10, the activity reached almost the maximum because alkali sometimes moved out from the catalyst layer. A surface of Al_2O_3, 180 $m^2\,g^{-1}$, could hold 2.63 mmol g^{-1} of Cs^+ ions (0.181 nm of ion radii) on the surface if Cs ions could be closely packed on the surface. Cs promoter with Cs/Ru = 10 corresponded to 2.0 mmol g^{-1}, close to the value 2.63 mmol g^{-1}, suggesting the saturation value of CsOH covered the Al_2O_3 surface with a monolayer. The promoter effect was similar among the three alkali elements at lower content; however, the heavier element was more effective at the high content region ($Cs^+ > Rb^+ > K^+$), probably due to the order of electronegativity of hydroxide (CsOH < RbOH < KOH).

Hydrogen chemisorption and BET area decreased gradually with an increase in Cs content on the $Ru{-}Cs^+/Al_2O_3$ catalyst (Fig. 4). The rate at 588 K and the chemisorption data are summarized in Table 2. The TOF increased with the alkali content.

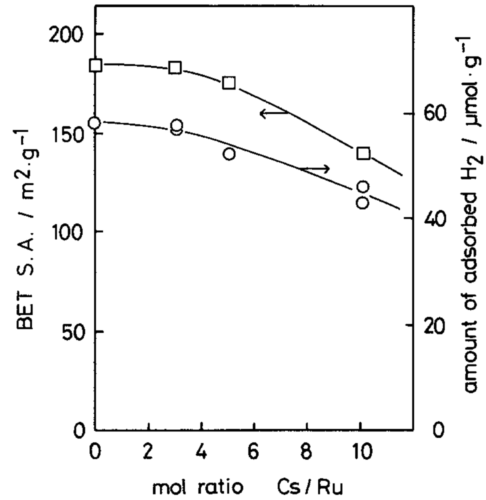

FIG. 4. Amount of adsorbed hydrogen and BET surface area of 2 wt% $Ru{-}Cs^+/Al_2O_3$ as a function of mol ratio of Cs against Ru; $Ru_3(CO)_{12}$ as a precursor; hydrogen treatment at 623 K. Catalyst weight in the adsorption unit means the catalyst weight without promoter.

TABLE 2

Summary of Ammonia Synthesis Rate and Hydrogen Chemisorption on 2 wt% Ru/Al_2O_3[a] Prepared from $Ru_3(CO)_{12}$ and Promoted with $CsNO_3$

Code No.:	9	10	11	12
Cs/Ru:[b]	0	3.0	5.1	10.1
Rate:[c]	13	29	46	214
H(*a*)/*M*:	0.59	0.59	0.53	0.45
TOF[d] × 10^4:	0.31	0.70	1.22	6.48
BET S.A.:[e]	184	183	174	141

[a] Promoted catalysts were treated with H_2 at 623 K for 4 h.
[b] Mol ratio.
[c] μmol h^{-1} g^{-1} at 588 K under 101 kPa of $N_2 + 3H_2$.
[d] NH_3/s/H(*a*) at 588 K.
[e] m^2 g^{-1}.

The rate at 588 K was measured over 2 wt% $Ru\text{-}Cs^+/Al_2O_3$ (Cs/Ru = 10), where the treatment temperature of the catalysts was changed. The results are shown in Fig. 5. The maximum rate was obtained when the catalyst was reduced with H_2 at 623 K. $CsNO_3$ was thought to be decomposed on the Ru surface most effectively at 623 K to give Cs_2O and/or CsOH (*4*). The reason the activity depends on the decomposition temperature is discussed later.

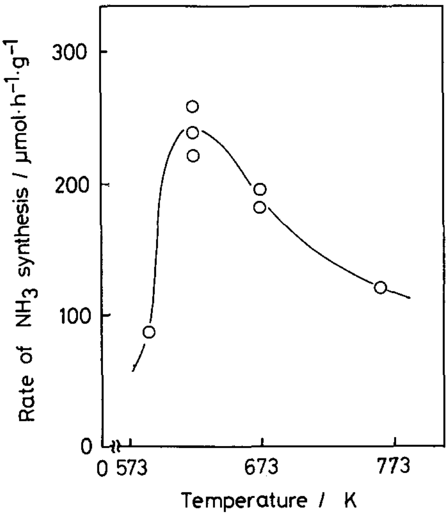

FIG. 5. Ammonia synthesis rate at 588 K under 101 kPa of $N_2 + 3H_2$ over 2 wt% $Ru\text{-}Cs^+/Al_2O_3$ as a function of hydrogen treatment temperature; $Ru_3(CO)_{12}$ as a precursor; Cs/Ru = 10 (mol/mol). Catalyst weight in the activity unit means the catalyst without promoter.

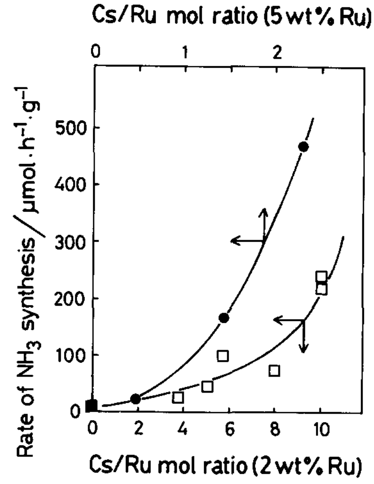

FIG. 6. Comparison of ammonia synthesis rates at 623 K under 101 kPa of $N_2 + 3H_2$ over 2 wt% $Ru\text{-}Cs^+/Al_2O_3$ and 5 wt% $Ru\text{-}Cs^+/Al_2O_3$. Activity is shown as a function of the amount of $CsNO_3$; $Ru_3(CO)_{12}$ as a precursor; hydrogen treatment at 623 K for 4 h. Catalyst weight in the activity unit means the catalyst weight without promoter. Upper and lower scales are related so as to have the same Cs content against Al_2O_3.

Since 5 wt% Ru/Al_2O_3 had the highest TOF among Ru/Al_2O_3 catalysts with any Ru weight percent, $CsNO_3$ was added to 5 wt% Ru/Al_2O_3 and the activity was measured. The results were compared with those for 2 wt% Ru/Al_2O_3 and are shown in Fig. 6. The tendency was similar—the curve was concave. The activity was almost proportional to Ru loading when total Cs amounts were the same.

XPS Measurements of Ru/Al_2O_3 Catalyst Prepared from $Ru_3(CO)_{12}$ Precursor

XPS data of Ru/Al_2O_3 catalyst and reference materials are shown in Table 3. $Ru_3(CO)_{12}/Al_2O_3$ evacuated at 623 K and stored in a dessicator gave a binding energy of Ru $3p_{3/2}$ at 463.4 eV, which showed that the surface ruthenium was oxidized (3+). Ruthenium was reduced to metal (462.1 ± 0.1 eV for Ru $3p_{3/2}$) after hydrogen treatment or disproportionation of $CsNO_3$. The value

TABLE 3

XPS Data of 2 wt% Ru/Al_2O_3 Prepared from $Ru_3(CO)_{12}$ Precursor

	Binding Energy (eV)			
	Ru $3p_{3/2}$	Al $2s$	O $1s$	Cs $3d_{5/2}$
Ru/Al_2O_3 before reduction[a]	463.4	119.2	531.9	—
Ru/Al_2O_3 after reduction[b]	462.1	119.2	531.8	—
Ru/Al_2O_3 with Cs/Ru = 3[b]	462.3	119.0	532.0	724.9
Ru/Al_2O_3 with Cs/Ru = 10[b]	462.2	119.0	532.0	725.1
Ru powder	462.0	—	—	—
$RuCl_3 \cdot 3H_2O$	463.3	—	—	—
Al metal	—	117.5[c]	—	—
Al_2O_3	—	119.5	532.0	—
$CsNO_3$	—	—	—	726.0
CsOH	—	—	—	725.5

[a] Stored in a dessicator after evacuation of $Ru_3(CO)_{12}/Al_2O_3$ at 723 K for 2 h.

[b] Treated with hydrogen at 623 K.

[c] From Ref. (*20*).

of binding energy for Cs $3d_{5/2}$ (725.0 ± 0.1 eV) of the sample after disproportionation of $CsNO_3$ was close to the value for CsOH. The value of Al 2*s* of Ru/Al_3O_3 was somehow lower than that of the reference alumina.

Although the binding energy was almost constant, the peak of oxygen was decreased by hydrogen treatment at high temperature, probably due to the desorption of H_2O and/or CO_2. The peak increased again after $CsNO_3$ addition, probably due to the oxygen content of CsOH.

DISCUSSION

In the first two sections, we discuss the effect of Ru precursors, and in the last two sections, we discuss the effect of promoters.

Dispersion of Ru/Al_2O_3 Prepared from Various Ru Precursors

Ru/Al_2O_3 prepared from $RuCl_3$ gives low dispersion (H/Ru), and the value depends on the reduction temperature. The values are 0.23 (this work) and 0.25 (*17*) for the samples reduced at 873 and 900 K, respectively. If the reduction temperature is not high (673 or 723 K) the value ranges from 0.05 to 0.20 (*4, 17, 18*). One reason may be due to residual chlorine; thus, the dispersion increases with hydrogen treatment at higher temperature (as in the case of $RuCl_3$/MgO) (*3*) or with addition of alkali metal nitrate (H/Ru from 0.20 to 0.60) (*4*).

$Ru(NO)(NO_3)_3/Al_2O_3$ catalyst gave better dispersion (0.35). Mieth and Schwarz have also reported that the same preparation method gave dispersion from 0.27 to 0.49 (*18*).

Many investigators have studied the state of $Ru_3(CO)_{12}$ adsorbed on Al_2O_3 (*8, 9, 11*). The ruthenium cluster reacts with surface OH and makes a bond between Ru and O. The anchored monoatomic complex, $-ORu(CO)_2O-$, can be a precursor of the well-dispersed Ru metal clusters. We also obtained high dispersion (H/Ru from 0.37 to 0.65 depending on loading), comparable to the value (0.65) reported by others (*9*). H/Ru of 2 wt% Ru/Al_2O_3 in Table 1 is 0.43, whereas that in Table 2 is 0.59. The reason for this is a difference in hydrogen reduction temperature. The former was reduced at 873 K; and the latter was reduced at 673 K. As a result, chlorine-free and highly dispersed Ru particles were obtained on Al_2O_3.

$Ru(acac)_3$ gave lower dispersion (0.28). K_2RuO_2 gave quite low dispersion (0.03). Ruthenium was assumed to be adsorbed as an anion (RuO_2^{2-}) in this case.

Structure Sensitivity of Ammonia Synthesis Reaction for Ru Catalyst

Generally the dissociation process of the N_2 molecule (ammonia synthesis) is considered to be a structure-sensitive reaction. The TOF of the reaction on small iron particles on the Fe/MgO catalyst is an order of magnitude lower than that on larger particles (*13*). Recent surface science works have also proved that nitrogen adsorption (*14*) and ammonia synthesis (*15*) are remarkably more active on the Fe(111) plane than on the other planes. Although an electronic factor is also important in the reaction on iron catalyst (K_2O promotion), the structural factor seems to be more important for iron.

For ruthenium catalysts, we have pointed out the importance of the electronic factor: promotion by basic compounds (*4, 5*) and inhibition by chlorine (*3*). In this study, we prepared chlorine-free and alkali-free Ru/Al_2O_3 catalysts. Thus, the structural factor can be discussed by comparing samples with different dispersions prepared from different precursors or with different loading (Table 1 code Nos. 2, 4–8; and Fig. 2). Nitrate can be removed almost completely from $Ru(NO)(NO_3)_3/Al_2O_3$ (*4, 7*). There is a trend that the TOF of larger particles is higher than that for smaller particles, except for the case of code No. 2. This trend seems to be reproducible if Fig. 2 is also taken into account. However, the effect was not remarkable when compared with the iron catalyst. The conclusion is that the reaction on Ru/Al_2O_3 has a small structure sensitivity. This effect is more remarkable in the case of CO hydrogenation on the Ru catalyst (*18*).

Mobility of Alkali Promoter over Ru/Al_2O_3

Below 873 K the rate on Ru/Al_2O_3 made from $Ru_3(CO)_{12}$ is independent from the reduction temperature (Fig. 1). The Ru particle seems to be rather stable after reduction. In the case of $RuCl_3/Al_2O_3$, the activity increases, probably due to chlorine removal, up to 923 K and decreases due to sintering of Ru particles above 923 K. On the other hand, the activity of promoted catalysts depends on the temperature of disproportionation of $CsNO_3$ over Ru. $CsNO_3$ is not decomposed by itself, at least below 673 K (*4*). The existence of the Ru particle is necessary for the disproportionation of $CsNO_3$ (*4*). It starts to decompose around 473 K:

$$CsNO_3 + 4H_2 \rightarrow 0.5Cs_2O + NH_3 + 2.5H_2O.$$

The decomposed products of Cs_2O are thought to become CsOH (*4*). XPS data of this work also suggest the presence of CsOH. SEM and EPMA study suggest that Cs_2O or CsOH is mobile over the catalyst (*6*). Thus, the Cs compound decomposed on the Ru surface is considered to move to the Al_2O_3 surface. H/Ru is not totally reduced to zero when Cs/Ru is increased to 10 (Fig. 4). Our model is that Cs_2O and CsOH partly cover the Ru surface or boundaries between Ru and Al_2O_3 and most of them move to the Al_2O_3 surface (first at acid site). The concave curves in Figs. 3 and 6 suggest that the Ru–CsOH interaction is weak when the Cs/Ru ratio is low. Because of the weak Ru–CsOH interaction, the high-temperature treatment may cause the separation of CsOH from Ru and may result in a decrease of activity as shown in Fig. 5. The most effective temperature is 623 K in hydrogen treatment. The morphologic action may be similar for 2 and 5 wt% Ru with respect to the interaction with Cs_2O and/or CsOH, because the activity depends on Ru loading, if the total number of Cs compounds are the same (Fig. 6).

Role of Alkali Promoter on Ru/Al_2O_3

In a previous paper, chlorine was an inhibitor of the reaction on Ru/MgO. KNO_3 removed chlorine from the Ru surface, which was also a function of the promoter.

Thus, it was uncertain whether the only role of alkali is to act as a scavenger of chlorine, because $RuCl_3$ is usually used as a precursor; the answer to this is no. Chlorine-free $Ru_3(CO)_{12}/Al_2O_3$ needed alkali for the promotion of the reaction. Although XPS results failed to prove the electron transfer to Ru, alkali is believed to affect the Ru surface, probably causing the change of electrostatic field, which might change the energy level of adsorbed N_2 (precursor state) on Ru (*21–23*). This alkali effect may be stronger in heavier alkali elements, which relates to the reactivity (CsOH > RbOH > KOH).

The TOF of $Ru–Cs^+/Al_2O_3$ at 588 K, which ranges from 1.9 to 20, has been reported (*4*). Unfortunately, we could not reproduce the abnormally high value of 20 [code No. S-6 in Ref. (*4*)] afterward, so the maximum TOF is considered to be 5.7 or 7. In this study we reproduced these maximum values for 2 wt% $Ru–Cs^+/Al_2O_3$ (Cs : Ru = 10) as shown in Table 2 (code No. 12, TOF = 6.5). The advantage of $Ru_3(CO)_{12}/Al_2O_3$ is to have high dispersion and to extend the high activity even at high loading. Thus, the gram base rate on 7.4 wt% Ru/Al_2O_3 was the highest among Ru/Al_2O_3 catalysts without a promoter (Table 1 and Fig. 2), and 5 wt% $Ru–Cs^+/Al_2O_3$ (Cs/Ru = 3.5) was the highest among the promoted Ru/Al_2O_3 (Fig. 6).

CONCLUSIONS

The chlorine-free Ru/Al_2O_3 catalyst can be prepared from $Ru_3(CO)_{12}$. This gives highly dispersed Ru particles on Al_2O_3. By using Cl-free catalyst, promoter actions are demonstrated clearly. The alkali promoter scavenges Cl ion on $RuCl_3/Al_2O_3$, but alkali promotes even Cl-free Ru surface. Alkali has a strong interaction with the Al_2O_3 surface in addition to the Ru surface. The Ru/Al_2O_3 catalyst most active with the $CsNO_3$ promoter can be prepared using the $Ru_3(CO)_{12}$ precursor.

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