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

2. A Lanthanide Oxide-Promoted Ru/Al_2O_3 Catalyst

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$La(NO_3)_3$, $Ce(NO_3)_3$, and $Sm(NO_3)_3$ were proved to be more effective promoters of ammonia synthesis than $CsNO_3$ when they were applied to a chlorine-free Ru/Al_2O_3 catalyst. Small amounts of lanthanide nitrates (M/Ru = 1) were as effective as a much greater amount of $CsNO_3$ (Cs/Ru = 10) for 2 wt% Ru/Al_2O_3. A chemisorption study disclosed that a smaller amount of lanthanide oxide could cover the Ru surface, whereas much more cesium oxide was necessary to cover the Ru surface. Lanthanide oxide was suggested to have a stronger interaction with the Ru surface than Cs_2O and/or CsOH, which are strongly basic and have a greater interaction with the Al_2O_3 surface. A model of promoter action is proposed. The apparent activation energies of this reaction were lower (11 to 15 kcal mol^{-1}) than those using a Cs^+ promoter (24 kcal mol^{-1}) under 101 kPa of $N_2 + 3H_2$. © 1992 Academic Press, Inc.

INTRODUCTION

When used in ammonia synthesis, ruthenium is known to be quite sensitive to the nature of the support and of the promoter (*1*). Compounds that have electron-donating or basic properties have been reported to be effective promoters. Alkali metals are the most effective, although they are deactivated by oxygen-containing compounds (*2*). Alkali nitrates have been reported to be decomposed to oxide and/or hydroxide over a Ru surface and to be stable and quite effective promoters (*3*). The effectiveness of a promoter or support is roughly related to the electronegativity of the compound (Cs > K > Na > CsOH > KOH > NaOH) (*4*). Thus, La_2O_3, Ce_2O_3, and Sm_2O_3 were not expected to be effective promoters, but in this study, such lanthanides were found to be quite effective promoters on Ru/Al_2O_3. The surface is characterized and the interaction of lanthanide oxides with Ru or Al_2O_3 is discussed.

EXPERIMENTAL

γ-Al_2O_3 (reference catalyst of the Catalysis Society of Japan, JRC-ALO-4; 200 m^2 g^{-1}), which had been baked in air at 773 K, was impregnated with $Ru_3(CO)_{12}$ (Aldrich) in tetrahydrofuran (THF). The Ru loaded was approximately 2 wt%. After evaporation and drying, a sample was heated *in vacuo* at 623 K for 2 h to remove CO and the weight corresponding to 1 g of reduced 2 wt% Ru/Al_2O_3 was transferred to an aqueous solution of the lanthanide nitrate. The sample was dried again and treated with hydrogen at 623 K for 4 h. Another series of 1.5 wt% Ru/Al_2O_3 catalysts was prepared from $RuCl_3 \cdot 3H_2O$ (Koso Chemical Co.), as described in a previous paper (*5*). This was also impregnated with lanthanide nitrate.

The rate of ammonia synthesis was measured below 673 K using a conventional flow system under 101 kPa (*6*). $N_2 + 3H_2$ gas (60

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ml min^{-1}), deoxidized by passing through Pd/Al_2O_3 and an active carbon trap at 195 K, was used for the ammonia synthesis. Hydrogen was passed through for reduction of the catalyst at a rate of 60 ml min^{-1}. During the addition of hydrogen, the temperature was increased to the programmed treatment temperature for $1\frac{1}{2}$ h and maintained for 4 h. The ammonia synthesis rate was determined by the decrease rate of the electron conductivity of a diluted sulfuric acid solution, which fixed the ammonia produced (*6, 7*).

After the catalyst was treated with hydrogen at 673 K for 2 h and evacuated at 673 K for 1 h, the hydrogen and CO chemisorption was measured at 273 K in a closed circulation system. The amount of adsorption was calculated by extrapolating the linear portion of an adsorption isotherm measured above 20 Torr to zero pressure. BET area was measured using nitrogen. The XPS (X-ray photoelectron spectroscopy) 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 the glass tubes connecting to the reactor were fused off. The sealed sample was opened in an argon atmosphere in the XPS chamber. Au $4f_{7/2}$ (83.8 eV) and impurities of C 1*s* (284.6 eV) were used as the standard values for determining binding energies.

RESULTS

Promoter Effect of Lanthanide Oxide on Ammonia Synthesis Using Ru/Al_2O_3

Rates of ammonia synthesis over various promoted 2 wt% Ru/Al_2O_3 catalysts prepared from $Ru_3(CO)_{12}$ were measured at 588 K under 101 kPa of $N_2 + 3H_2$ and are shown as a function of the promoter (*M*)/Ru mol ratio in Fig. 1. The activity was stable over 100 h. Cs was most effective at a mol ratio of 10 : 1. La, Ce, and Sm act as a promoter in a similar way but at smaller amounts. They are most effective at a 1 to 3 mol ratio (*M*/Ru). The activity of the catalyst with a 1 to 1 mol ratio of *M*/Ru is as high as that with a 10 to 1 mol ratio of Cs/Ru.

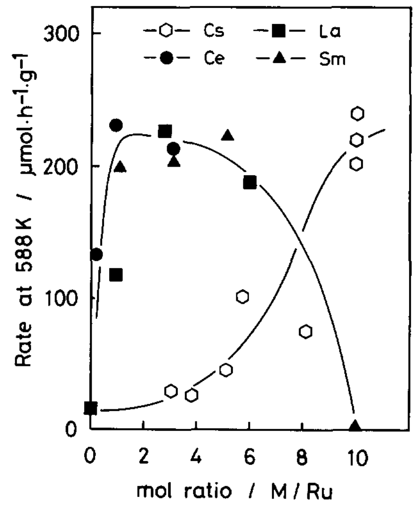

FIG. 1. Ammonia synthesis rate at 588 K under 101 kPa of $N_2 + 3H_2$ as a function of *M*/Ru mol ratio (*M* = lanthanide metal) in 2 wt% Ru–M_2O_3/Al_2O_3. $Ru_3(CO)_{12}$/Al_2O_3 was treated with H_2 at 623 K for 4 h.

The rate was measured with samarium-promoted Ru/Al_2O_3 prepared from $RuCl_3$ and is shown as a function of the amount of samarium in Fig. 2. The promotion effect

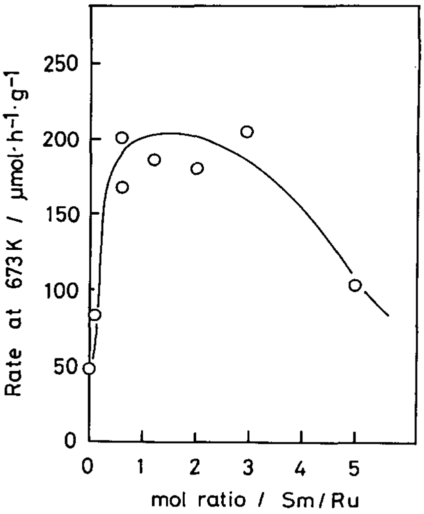

FIG. 2. Ammonia synthesis rate at 673 K under 101 kPa of $M_2 + 3H_2$ as a function of Sm/Ru ratio in 1.5 wt% Ru–Sm_2O_3/Al_2O_3. $RuCl_3$/Al_2O_3 was treated with H_2 at 773 K for 12 h.

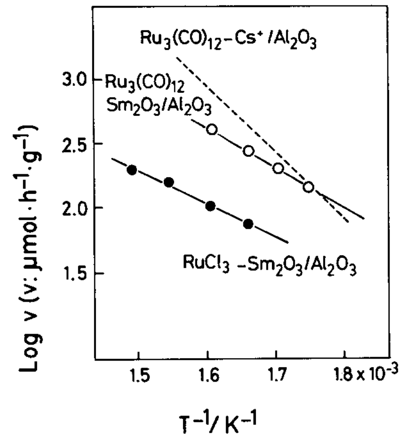

FIG. 3. Arrhenius plot of the rate of ammonia synthesis under 101 kPa of N_2 + $3H_2$ on 2 wt% Ru–Sm_2O_3/Al_2O_3 (Sm/Ru = 3.0, $Ru_3(CO)_{12}$ precursor, open circle), which was treated with H_2 at 623 K for 4 h; that on 1.5 wt% $RuCl_3$–Sm_2O_3/Al_2O_3 (Sm/Ru = 1.2, solid circle), which was treated at 773 K for 12 h; and that on 2 wt% Ru–Cs^+/Al_2O_3 (Cs/Ru = 10, $Ru_3(CO)_{12}$ precursor, dotted line), which was treated with H_2 at 623 K for 4 h.

seems to be similar to that depicted in Fig. 1. However, the activity is much lower than in the system prepared from $Ru_3(CO)_{12}$. The lanthanide promoter was found to be effective when chlorine-free Ru precursor was used. Catalyst activities were measured at various temperatures; the results for $Ru_3(CO)_{12}$–Sm_2O_3/Al_2O_3 (open circle), $RuCl_3$–Sm_2O_3/Al_2O_3 (solid circle), and $Ru_3(CO)_{12}$–CsOH/Al_2O_3 (dotted line) catalysts are shown in Fig. 3, and the activities and apparent activation energies are summarized in Table 1. Activation energies using the lanthanide promoter are all lower than those found using cesium.

In our previous study the decomposition of $CsNO_3$ to Cs_2O and/or CsOH over a Ru surface was discussed (*3*). Study of promoter decomposition disclosed that the Ru/Al_2O_3 catalyst was most effectively promoted when $CsNO_3$ was decomposed at 623 K. The activities of Ru–Sm_2O_3/Al_2O_3 catalysts prepared with various hydrogen-treatment temperatures were measured. For lanthanide nitrate, the rate of ammonia synthesis was affected in the same way as in the sample using an alkali promoter, as shown in Fig. 4. Synthesis was most effective when the sample was decomposed at 623 K. Such behavior suggests that lanthanide nitrate also decomposes over a Ru surface and that the product (oxide or hydroxide) mainly migrates to the support while some may stay on the Ru surface or the Ru–support boundary:

TABLE 1

Ammonia Synthesis Rate and Apparent Activation Energy over Promoted Ru/Al_2O_3 Catalysts[a]

Promoter (*M*)	Mol ratio *M*/Ru	Rate (μmol $h^{-1}g^{-1}$)		E_a(kcal mol^{-1})
		603 K	588 K	
La[b]	2.8	282	226	10.7
Ce[b]	3.1	239	216	11.5
Sm[b]	3.1	250	204	14.5
(Sm)[c]	1.2	72	58	11.1
(Sm)[c]	5.2	36	27	13.6
Cs[b]	3.0	48	29	24.2
Cs[b]	10.1	378	220	23.6
None[b]	0	19	13	15.0

[a] Promoted catalysts treated with H_2 at 623 K for 4 h; reaction condition: N_2 + $3H_2$ (60 ml min^{-1}) at 101 kPa.
[b] Base catalyst: $Ru_3(CO)_{12}$/Al_2O_3 (Ru 2 wt%).
[c] Base catalyst: $RuCl_3$/Al_2O_3 (Ru 1.5 wt%).

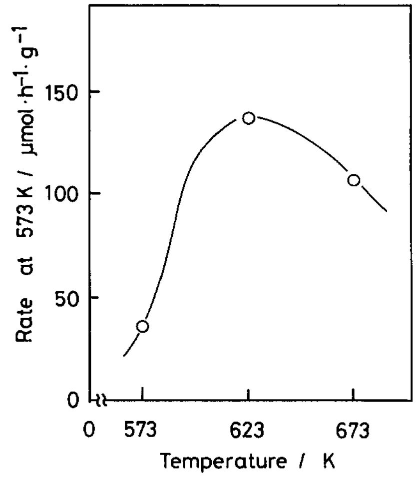

FIG. 4. Ammonia synthesis rate at 573 K under 101 kPa of N_2 + $3H_2$ over 2 wt% Ru–Sm_2O_3/Al_2O_3 as a function of H_2 treatment temperature; Sm/Ru = 3.0 (mol ratio).

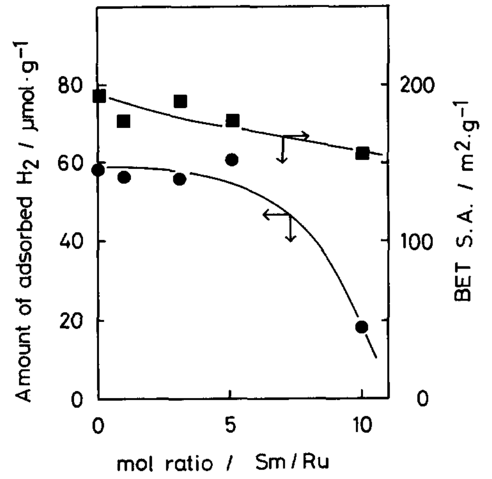

FIG. 5. H_2 adsorption and BET surface area (S.A.) as a function of Sm/Ru ratio in 2 wt% Ru–Sm_2O_3/Al_2O_3. $Ru_3(CO)_{12}$ is a precursor.

$$2M(NO_3)_3 + 24H_2 \xrightarrow{Ru} M_2O_3 + 6NH_3 + 15H_2O \quad (1)$$

(M = La, Ce, and Sm).

Adsorption Measurements

In order to characterize the surface of the catalyst, hydrogen and carbon monoxide adsorption were measured in addition to the BET surface area. The results are summarized in Fig. 5 and Table 2.

Our earlier studies concluded that the electronic effect of a support or a promoter was generally the most important for the activation of dinitrogen over a Ru surface, while a structural factor might be more important over the Fe surface. Since lanthanide oxide is not as strong a base as alkali metal oxides, the effectiveness of lanthanide oxide (or hydroxide) as a promoter was unexpected. The morphological aspect of the interaction between lanthanide and Ru should be clarified. An alumina surface of 180 $m^2 g^{-1}$ could hold 2.63 mmol of Cs^+ ions (0.181 nm of ion radius), 5.44 mmol of O^{2-} ions (0.126 nm), or 6.31 mmol of La^{3+} ions (0.117 nm) if every ion were closely packed on the surface. Promoter (M) with M/Ru = 10 corresponds to 2.0 mmol if 2 wt% (20 mg) of Ru was loaded. Thus, any promoter molecule with a M/Ru ratio lower than 10 could spread within the monolayer. However, the BET surface area decreased a little with the increase of the Sm/Ru mol ratio. Some part of the micropore may be blocked by the promoter because the BET area was changed. Lanthanide oxides seemed to aggregate.

Hydrogen adsorption is gradually decreased by an increase in the lanthanide. The hindrance of surface Ru by lanthanide accumulation was greater than that of cesium, as seen in Table 2. The amount of CO adsorption is greater than that of hydrogen, ranging from 1.4 to 1.9.

TABLE 2

Summary of Ammonia Synthesis Rate and Adsorption Experiments on 2 wt% Ru/Al_2O_3 Catalyst with Various Promoters[a]

Promoter (M):	None	Cs	Cs	La	Ce	Sm	Sm
M/Ru (mol ratio)	0	3.0	10.1	2.8	3.1	3.0	10.0
Rate at 588 K (μmol h^{-1} g^{-1})	13	29	214	226	216	204	19
H(a)/Ru	0.59	0.59	0.45	0.74	0.77	0.57	0.18
TOF × 10^4 at 588 K	0.31	0.70	6.48	4.19	3.86	5.09	1.47
CO(a)/Ru	1.08	—	—	1.23	1.09	0.83	0.34
CO(a)/H(a)	1.84	—	—	1.65	1.42	1.46	1.89
BET S.A. (m^2 g^{-1})	184	183	—	181	179	189	156

[a] All catalysts were treated with H_2 at 623 K for 4 h before the reaction. $Ru_3(CO)_{12}$ is a precursor.

TABLE 3

Binding Energies for Various Catalysts

Catalyst or reference material	Binding energy (eV)			
	Ru $3p_{3/2}$	Al 2*s*	O 1*s*	M $3d_{5/2}$[a]
2 wt% Ru/Al_2O_3 before reduction[b]	463.4	119.2	531.9	—
2 wt% Ru/Al_2O_3 after reduction[c]	462.1	119.2	531.8	—
Ru powder[c]	462.0	—	—	—
Al_2O_3	—	119.5	532.0	—
2 wt% Ru-La_2O_3/Al_2O_3[d]	462.6	119.3	531.6	835.8(3.2)[e]
La_2O_3	—	—	531.7	835.6(3.6)[e]
La_2O_3[f]	—	—	530.1	834.7(4.5)[e]
$La(OH)_3$[f]	—	—	532.1	835.9(3.7)[e]
Activated La_2O_3[g]	—	—	530.9	834.9(3.7)[e]
2 wt% Ru-Ce_2O_3/Al_2O_3[h]	462.6	119.2	531.9	886.4
$Ce(NO_3)_3$	—	—	—	886.2
CeO_2	—	—	530.0	882.8
2 wt% Ru-Sm_2O_3/Al_2O_3[i]	462.2	119.2	531.8	1084.6
$Sm(NO_3)_3$	—	—	—	1083.9
Sm_2O_3	—	—	531.5	1083.6

[a] M = La, Ce, or Sm.

[b] Prepared from $Ru_3(CO)_{12}$.

[c] Treated with H_2 at 623 K.

[d] After reaction, La/Ru = 2.8 (mol/mol).

[e] Satellite split.

[f] Data from Refs. (*8*, *9*).

[g] La_2O_3 converted to $La(OH)_3$, calcined at 623 K, and heated in H_2 at 573 K, [data from Ref. (*10*)].

[h] After reaction Ce/Ru = 3.1 (mol/mol).

[i] After reaction, Sm/Ru = 3.0 (mol/mol).

XPS Measurement

Both 2 wt% Ru/Al_2O_3 prepared from $Ru_3(CO)_{12}$ and samples promoted with lanthanide oxide were analyzed by XPS. The results are summarized in Table 3 together with reference material data (*8–10*). A part of the XPS spectra of the used catalysts and those of reference compounds are shown in Fig. 6. Since the Ru content was as small as 2 wt%, the peak at Ru $3d_{5/2}$ was concealed by the C 1*s* peak of contaminating carbon. A weak peak at Ru $3p_{3/2}$ suggests that ruthenium in Ru/Al_2O_3 (462.1 eV) and Ru–M_2O_3/Al_2O_3 (M = La, Ce, or Sm) (462.2 to 462.6 eV) is in the metallic state (462.0 eV); however, the ruthenium in $Ru_3(CO)_{12}$/Al_2O_3 that was evacuated at 723 K and stored in a dessicater was oxidized (3+, 463.4 eV).

The binding energies at Al 2*s* were all close to the value of Al_2O_3 (119.2 to 119.5 eV). The binding energy at O 1*s* of the promoted catalyst (531.6 to 531.9 eV) was a bit lower than that of Al_2O_3 (532.0 eV) or Ru/Al_2O_3 (531.8 to 531.9 eV). The lower value might be due to some contribution from the lower value for lanthanide oxides: La_2O_3 (531.7 eV) and Sm_2O_3 (531.5 eV).

The valence state of lanthanide is noteworthy, because the promoter nitrate decomposes over the Ru catalyst under hydrogen (a reducing atmosphere). XPS results show that La, Ce, and Sm were all in the 3+ state as can be seen in Fig. 6. The XPS spectra of cerium in cerium-promoted Ru/Al_2O_3 was the same as that of Ce_2O_3 and quite different from that of CeO_2.

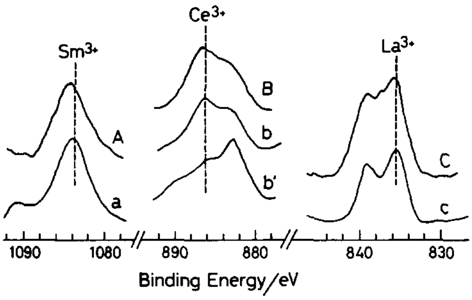

FIG. 6. XPS spectra of used catalysts (after reaction) and the reference compounds. (A) 2 wt% Ru–Sm_2O_3/Al_2O_3 (Sm/Ru = 3/1, mol/mol); (B) 2 wt% Ru–Ce_2O_3/Al_2O_3 (Ce/Ru = 3.1/1, mol/mol); (C) 2 wt% Ru–La_2O_3/Al_2O_3 (La/Ru = 2.8/1, mol/mol); (a) $Sm(NO_3)_3$; (b) $Ce(NO_3)_3$; (b') CeO_2; (c) La_2O_3. See also Table 3.

DISCUSSION

Chemical and Morphological State of Rare Earth Metal Promoters

Although we have no direct evidence, we assume that lanthanide nitrate is decomposed into oxide over a Ru surface (Eq. (1)). The fact that the rate of ammonia synthesis reaches a maximum for the treatment temperature of $Sm(NO_3)_3$ (Fig. 4) provides some indirect evidence. This is similar to the case of $CsNO_3$, which undergoes hydrogenolysis over a Ru surface (*3*). For $CsNO_3$, the final state was suggested to be hydroxide (CsOH) on Ru/Al_2O_3 (*3*).

In the case of lanthanide metal, however, the oxide is considered to be the final state, as suggested by the XPS results. $La(OH)_3$ is not stable and decomposes to La_2O_3 at 588 K. The oxides are quite stable. The melting points of La_2O_3, Ce_2O_3, and Sm_2O_3 are high (2588, 1965, and 2573 ± 50 K, respectively). As is seen in Fig. 1, a smaller amount of lanthanide oxide is enough for promotion compared to CsOH. Since CsOH has a low melting point (545 K), it spreads over the alumina support or reacts with the alumina. However, lanthanide oxide formed on the Ru surface or on the Ru–Al_2O_3 boundaries cannot spread easily to the support because of its low mobility (high melting point). Another reason is that an acidic site on the Al_2O_3 may react more easily with CsOH.

Hydrogen chemisorption decreases to one-third when the Sm/Ru mol ratio reaches 10, which suggests a strong interaction between Ru and lanthanide oxide (Fig. 5 and Table 2). This interaction seems to be much stronger than that between Ru and CsOH. Hydrogen chemisorption does not decrease when CsOH is added to the Ru surface [Fig. 4 in Ref. (*5*)]. The H/Ru ratio decreased to 0.18 at Sm/Ru = 10.0, while it was 0.45 at Cs/Ru = 10.1 (Table 2). It seems strange to find that the H/Ru is increased from 0.59 to 0.74 and 0.77 by the addition of La and Ce, respectively (Table 2). Two explanations are suggested: (1) La_2O_3 or Ce_2O_3 prevents sintering by anchoring small Ru particles on the support, or (2) hydrogen spills over to the La_2O_3 and Ce_2O_3. In order to discriminate between the two possible explanations, CO adsorption was measured also (Table 2). The Ru atom may absorb more than one CO molecule (*11*), while it adsorbs one H atom. However, a coordinatively unsaturated site on an oxide surface is believed to adsorb only one CO molecule or one H atom. Thus, if La_2O_3 or Ce_2O_3 have an active site for CO and H, the ratio CO(*a*)/H(*a*) might be decreased by addition of La_2O_3 or Ce_2O_3. This may be why the ratio decreased a little from 1.84 to 1.65, 1.42, and 1.46, but the number 1.89 for Sm/Ru = 10 is not reasonable.

Lanthanide oxides are more effective when applied on chlorine-free Ru/Al_2O_3 (Table 1). In the case of $CsNO_3$, the TOF (turnover frequency) on $Ru_3(CO)_{12}$–$CsNO_3$/Al_2O_3 and that on $RuCl_3$–$CsNO_3$/Al_2O_3 were almost the same. The Cs salt is considered to neutralize the Cl^- ion and to apply an electrostatic field to the Ru surface. $Sm(NO_3)_3$ could not neutralize Cl^- enough for $RuCl_3$/Al_2O_3, as seen by comparing Figs. 1 and 2 (and Table 1). Sm_2O_3 might not be mobile enough to scavenge all the Cl^- on the Ru catalyst. A morphological model of the lanthanide oxide promoter compared with the CsOH promoter is shown in Fig. 7. Our model suggests that Cs_2O and/or CsOH, which is produced on Ru by the hydrogeno-

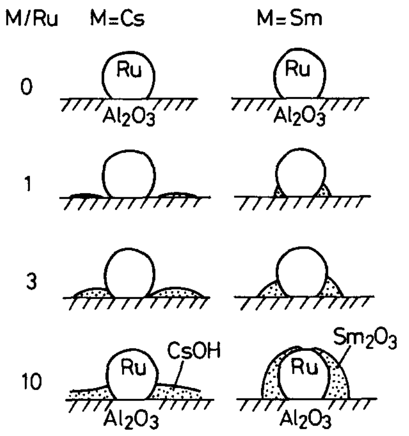

FIG. 7. Morphological models of Ru/Al_2O_3 catalysts promoted with $CsNO_3$ or with a lanthanide nitrate.

lysis of $CsNO_3$, move easily to the Al_2O_3 surface and that Cs_2O and/or CsOH reacts with the acidic center on Al_2O_3 (*5*). Thus, the interaction between Cs^+ and Ru is weak. However, lanthanides do not move but stay on the Ru surface or Ru–support boundaries.

Promoter Action of Lanthanide Oxide

Why are the lanthanide oxides such effective promoters, even though their basicities are not as high as those of alkali metal oxides or hydroxides? Lanthanides are known as SMSI (strong-metal support interaction) oxides (*12*). These oxides are considered to cover a precious metal surface if the surface is reduced to a lower valency. The temperature of our pretreatment is lower than the SMSI temperature (773 K). However, our lanthanide "promoter" is started from "nitrate," which is more reactive than "oxide" as a "support." Thus, during the disproportionation, low-valency lanthanide oxide might be produced partly on Ru surfaces. Direct bonding between Rh and oxide cation (Ta^{n+}) has been proposed in the SMSI state of the Rh/Ta_2O_5 catalyst, in which Ta_2O_5 is partly reduced to TaO_x (*13*). Such a state might be a good electron supplier to the Ru surface. Thus, a model is proposed as follows (M = La, Sm, Ce):

$$\text{Ru–Ru–Ru–}M \rightleftarrows \text{Ru}^-\text{–Ru}^-\text{–Ru}^-\text{–}M^{3+}. \quad (2)$$

Unfortunately, XPS results showed that most of the oxides have a high valency (3 +). However, we cannot disprove the existence of the reduced state of lanthanide, because the XPS data represent only an average value including data from the bulk phase.

Lanthanide ions have a large ionic radius in spite of their high valency (3+). Thus, they may coordinate extra oxygen molecules, producing O_2^- and O_2^{2-} (*14, 15*). Under the reducing conditions of this reaction, instead of gaining O_2^- from O_2, the Ru atom might be negatively charged through contact with lanthanide oxides. This might change the energy level of the molecular orbital of the adsorbed N_2 on the Ru surface (*16–18*).

Thus, lanthanide is understood to be an effective promoter both electronically and morphologically if a proper support is selected. Further study is needed to clarify the role of lanthanide promoters during ammonia synthesis. The difference in apparent activation energy between a lanthanide promoter and a CsOH promoter (Table 1, Fig. 3) suggests a difference in kinetics (*6*), which should also be studied in the future.

CONCLUSIONS

Lanthanide nitrates such as $La(NO_3)_3$, $Ce(NO_3)_3$, and $Sm(NO_3)_3$, were found to be effective promoters for ammonia synthesis on Ru/Al_2O_3 prepared from $Ru_3(CO)_{12}/Al_2O_3$. These promoters were only effective when the Ru catalyst did not contain the Cl ion. Such promoters are suggested to undergo disproportionation over the Ru surface to lanthanide oxides and to migrate to $Ru–Al_2O_3$ boundaries, whereas CsOH that is decomposed over Ru metal from $CsNO_3$ easily covers the acidic Al_2O_3 surface. The character of lanthanides may be similar to alkali earth metal oxides rather than alkali metal hydroxides (*19*). In addition, the ammonia synthesis with these catalyst systems has a very low apparent activation energy.

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