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NOTE

The Effect of Lanthanide Oxides as a Support for Ruthenium Catalysts in Ammonia Synthesis

Ruthenium is known to show significant activity for ammonia synthesis, particularly when promoted with alkali metal compounds, some showing greater activity than iron catalysts under atmospheric pressure (1, 2). In fact, ruthenium catalysts may be regarded as second-generation ammonia catalysts right alongside iron catalysts. Currently, a type of ruthenium catalyst is already being used in a commercial ammonia plant (3), proving its potential for promising applications in industry.

In this systematic study, lanthanide oxides were found to be effective *promoters* of the Ru catalyst (4). One of the roles of the lanthanide *promoter* is the release of hydrogen poisoning which subsequently retards the activation of dinitrogen (5). The three component "Ru-promoter/support" system refers to three distinct interactions: Ru-promoter, Ru-support, and promoter-support. A detailed study is necessary to clarify the role of the lanthanide *promoter*. However, lanthanide oxides used as the *support* in a two component system may provide a more comprehensive insight into the role of lanthana for Ru catalysis because of the simplicity. Another advantage is that lanthana pellets usually have higher catalyst density (e.g., 2.4 g ml^{-1} for 8–10 mesh CeO_2) than such conventional supports as active carbon (0.5 g ml^{-1} for 8–10 mesh sample). A *dense* catalyst packed in a smaller reactor is preferred in practical use.

Lanthanide oxide-supported Ru catalysts were prepared as follows: $La(NO_3)_3$, $Ce(NO_3)_3$, or $Sm(NO_3)_3$ (Kanto and Wako Pure Chemical Co.) in aqueous solution were mixed with a 5% aqueous ammonia solution having a pH of approximately 9. Deposited hydrate was filtered and then calcined in air at 873 K (1023 K in the case of Sm) for 4 h. The crystalline forms of each oxide were confirmed to be La_2O_3, CeO_2, and Sm_2O_3 by X-ray diffraction. The oxides were impregnated with $Ru_3(CO)_{12}$ (Tanaka Noble Metals Co.) in tetrahydrofuran (THF). $Ru_3(CO)_{12}$ is a better precursor than $RuCl_3$ because it is highly dispersed and is free of poisonous chlorine for ammonia synthesis (2, 4, 6). The amounts of Ru loading as reduced metal was approximately 0.5 wt% for La_2O_3, 1.0 wt% for CeO_2, and 0.4 wt% for Sm_2O_3, respectively. In the case of one-time impregnation these loading values almost reached the upper limit.

As a reference catalyst, 1.0 wt% Ru/MgO and 1.0 wt% Ru/TiO_2 were also prepared. MgO (Ube Co.) and TiO_2 (Nippon Aerosil Co.) baked in air at 773 K were impregnated with $Ru_3(CO)_{12}$ by the same method stated above.

These baked powders were compressed and broken down by a spatula into 8 to 10 mesh size. Ru carbonyl clusters were decomposed under N_2 gas flow or *in vacuo* at 773 K for 3 h. Before measuring the synthesis rate, a reduction treatment was carried out with $N_2 + 3H_2$ for 4 h at the given temperatures of 623 and 923 K, in which the temperatures were increased at a heating rate of 10 K min^{-1}. The ammonia synthesis rate was measured at 588 K under 0.1 MPa with a flow rate of 60 ml min^{-1} of $(N_2 + 3H_2)$ using a conventional flow system (4, 5) containing 1.0 g of the catalyst, unless otherwise stated.

Nitrogen and hydrogen adsorption were measured in a closed circulation system at 77 and 298 K, respectively. The surface area was calculated by measuring the nitrogen adsorption through the BET equation. Hydrogen consumption during the reduction treatment was also measured by the hydrogen pressure decrease in the closed system with a liquid nitrogen trap.

Lanthanide oxide has been reported to be an effective promoter of Ru/MgO (2). In the present study, the effects on ammonia activity has been quantitatively investigated and the lanthanide/Ru mole ratio of 1/1 was found to generate maximum activity. The maximum activity levels are shown in Fig. 1 as symbols c, s, and l (Ru–Ce^{3+}/MgO, Ru–Sm^{3+}/MgO, and Ru–La^{3+}/MgO), respectively. These activity levels are about twice as active as the non-promoted sample, *M* (Ru/MgO). However, these three lanthana are observed to have much higher activity when they are used as *supports*, shown in Fig. 1 as symbols C, S, and L (Ru/CeO_2, Ru/Sm_2O_3, and Ru/La_2O_3), respectively. The activity has been recalculated on the base of 1.0 wt% Ru although the Ru contents are different (0.5 wt% for La_2O_3 and 0.4 wt% for Sm_2O_3). The activity increases linearly with the Ru content up to 5.0 wt% (2). It should be noted that these samples have all been reduced at the same temperature of 773 K.

The promoter $CsNO_3$ decomposes into oxide due to the effects of the Ru metal powder (without support) at

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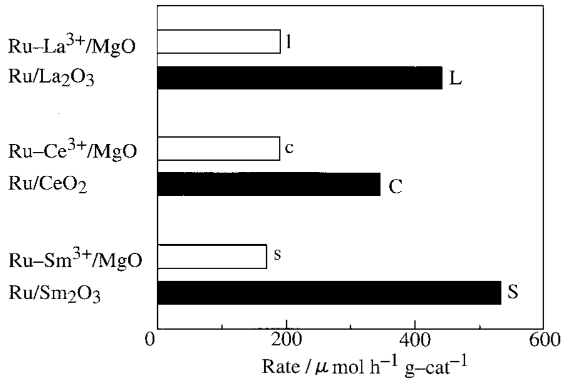

FIG. 1. Ammonia synthesis rate at 588 K on 1 g of supported catalyst with 1.0 wt% of Ru. Comparison of lanthanide promoter □ and support ■. All the samples were reduced at 773 K. Ru/lanthana (promoter) = 1/1 (mol/mol).

around 473 to 523 K and finally reacts with hydrogen to give hydroxide at below 573 K (7). $Ru_3(CO)_{12}$ is known to decompose almost completely at below 623 K to generate metal clusters on MgO (2). The addition of $CsNO_3$ as a promoter on Ru/MgO causes it to decompose at 373 to 423 K (2). The lanthanide nitrate promoter may also decompose to the corresponding oxide at below 673 K (2), then be stabilized. Heat treatment at a high temperature is, thus, necessary for the active phase to appear although excess heating may cause sintering. Suitable activation temperatures have been observed for each catalyst: 623 K for $Ru–Sm_2O_3/Al_2O_3$ (4), 673 K for Ru/MgO (2), 623 K for Ru–CsOH/MgO (2), and 573 K for Ru–BaO/MgO (2). Furthermore, past data show that heat treatment above 673 K causes an activity decrease.

However, for Ru/lanthana we observed a contrasting phenomena. Figure 2 shows the rate of ammonia synthesis at 588 K on various lanthana-supported Ru catalysts as a function of the reduction temperature. The activity of each catalyst increased when the reduction temperature was increased. The activity of Ru/La_2O_3 and Ru/Sm_2O_3 increased up to 873- and 923 K-reduction, respectively. However, in the case of Ru/CeO_2, maximum activity occurred at 773 K-reduction and then decreased at higher temperatures. For Ru/MgO, which was found to be the most effective oxide *support* until the present study, the activity increased only slightly while Ru/TiO_2 had no activity in any reduction temperature region (not shown in Fig. 2). Ru/La_2O_3 and Ru/Sm_2O_3 were both more active than Ru/CeO_2. Ru/La_2O_3 was found to be closest in activity levels to the most active catalyst ($Ru–Cs^+/MgO$) under atmospheric pressure (2).

Hydrogen adsorptions on Ru/CeO_2, Ru/Sm_2O_3, and Ru/MgO which were reduced at different temperatures were measured at 298 K and the corresponding dispersions (H/Ru) are shown in Fig. 3. It should be noted that hydrogen adsorption does not reach an equilibrium value due to spillover. Extrapolation of the linear adsorption time course back to zero was defined as the adsorption value. The amount of chemisorption on the Ru metal surface was calculated by extrapolation of the linear isotherm line back to zero pressure. The dispersion value for Ru/CeO_2 decreased to half (0.82 to 0.35) from a reduction temperature of 673 to 873 K. On the other hand, it remained the same or changed only slightly for Ru/MgO and Ru/Sm_2O_3. The values of CO adsorption (CO/Ru = 1.44, 1.21, 1.17 at 673, 773, 873 K reduction for Ru/CeO_2 and 1.10, 1.01, 0.95 at 673, 773, 873 K reduction for Ru/Sm_2O_3) were also measured at 273 K. Those values are about two times higher than for H/Ru. The twin adsorption model ($Ru(CO)_2$) can be proposed for these samples (8). These values (CO/Ru) also decreased when the hydrogen treatment temperature was increased and H/Ru was found to be more appropriate compared to CO/Ru.

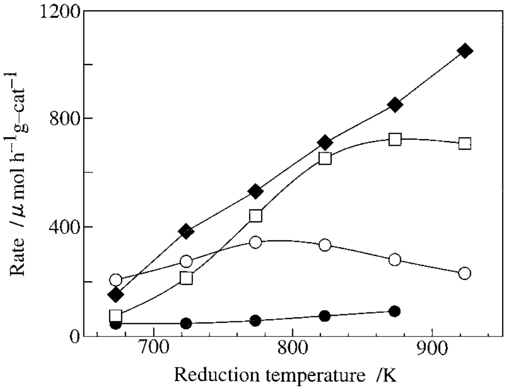

FIG. 2. Initial rates of ammonia synthesis at 588 K on supported (1.0 wt%) Ru catalysts as a function of H_2 reduction temperature. Rate on 1.0 wt% Ru/MgO (●), rate on 1.0 wt % Ru/CeO_2 (○), 2 × rate on 0.5 wt% Ru/La_2O_3 (□), 2.5 × rate on 0.4 wt% Ru/Sm_2O_3 (◆).

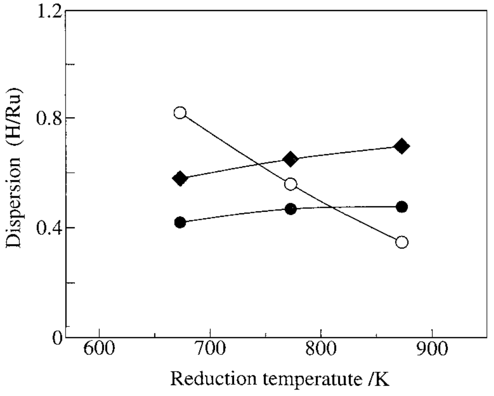

FIG. 3. Ru dispersion (H/Ru) of 1.0 wt% Ru/CeO_2 (○), 0.4 wt% Ru/Sm_2O_3 (◆), and 1.0 wt% Ru/MgO (●) as a function of H_2 reduction temperature.

The BET surface area of the catalysts was measured by nitrogen adsorption. A decrease in the surface area was observed when the reduction temperature was increased. Hydrogen treatment at temperatures from 673 to 873 K caused the surface area of Ru/CeO_2 to decrease from 54 to 38 m^2 g^{-1}. A structural change of the host oxide CeO_2 also occurred by high temperature reduction. For Ru/Sm_2O_3, it decreased from 29 to 24 m^2 g^{-1} at 673 and 873 K. Ru/MgO did not change in its dispersion (Fig. 3) and surface area (93 to 90 m^2 g^{-1} for 673 to 873 K) by the reduction. An unexpected and surprising finding was that the Ru dispersion on Sm_2O_3 (and MgO) did not change even after high temperature reduction of up to 873 K (Fig. 3). The activity increase with the reduction temperature can therefore be attributed to the change in the support (i.e., change in the metal support interaction). Turn over frequencies (TOFs) of ammonia synthesis on Ru/CeO_2, Ru/Sm_2O_3, and Ru/MgO are shown in Fig. 4 as a function of the reduction temperature. It can be seen that the TOFs on Ru/CeO_2 and Ru/Sm_2O_3 increase dramatically in correspondance with increases in the reduction temperature.

High temperature treatment in H_2 changes the state of the catalyst. Thus for Ru/CeO_2 and Ru/Sm_2O_3, hydrogen consumption during hydrogen treatment was measured and the results are shown in Fig. 5. We can see that a great deal of hydrogen has been consumed by both catalysts and the amount of hydrogen consumed increased with the hydrogen treatment temperature. Ruthenium carbonyl decomposes at below 623 K on Ru/MgO (2). During the evacuation treatment at 773 K we found that ruthenium carbonyl decomposes forming a small Ru metal cluster. Consequently, the amount of hydrogen consumption obtained can be attributed to the change of the support or the support surface. Three possibilities can be considered: (1) Part of the evolved CO may react with the lanthana forming an oxycarbide which may decompose by hydrogen treatment at high temperatures. (2) Part of the oxide in contact with the Ru particle is reduced (SMSI). (3) Hydrogen storage during reduction (9) and dissociative hydrogen adsorption on Ce_2O_3 should naturally be considered as factors in the extensive amount of hydrogen consumption. As can be seen in Fig. 5 the CeO_2 system consumes a much greater amount than the others. The right-hand scale shows the percentage of the oxygen removed from the oxide support. Among lanthanide oxides, only Ce_2O_3 is known as the reduced state of CeO_2 although it is not easily reduced to Ce_2O_3 unless it contains some metals on its surface. Rh or Ni supported on CeO_2 is known to accelerate the reduction of the host oxide and this has been confirmed with XPS and TPR techniques (10, 11). It can be assumed that Ru also acts as a catalyst for the reduction of CeO_2, and XPS data suggest the existence of Ce^{3+}. Thus, it can be reasonably concluded that the second hypothesis would be the most probable for the extensive hydrogen consumption.

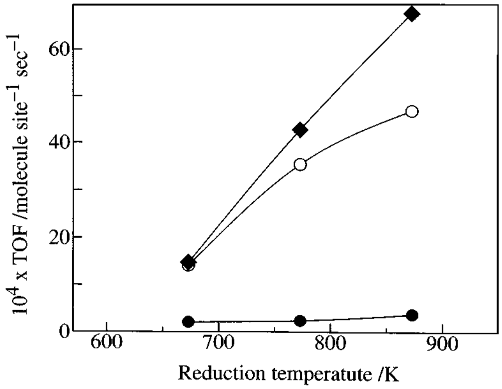

FIG. 4. Turn over frequencies of ammonia synthesis at 588 K on 1.0 wt% Ru/CeO_2 (○), 0.4 wt% Ru/Sm_2O_3 (◆), and 1.0 wt% Ru/MgO (●) as a function of H_2 reduction temperature.

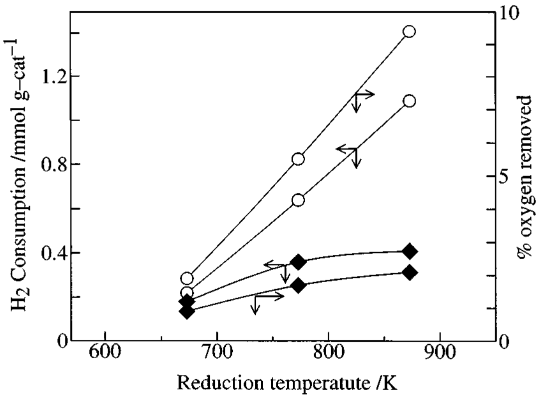

FIG. 5. H_2 consumption and percent oxygen removed from oxide (estimate) of 1.0 wt% Ru/CeO_2 (○) and 0.4 wt% Ru/Sm_2O_3 (◆) as a function of H_2 reduction temperature.

It should be noted that lanthanide oxides were found to be the most effective support with even better results than MgO. Basic supports or promoters have been found to be effective components of the Ru catalysts because these basic compounds provide electrons to the Ru surface atoms which activate the N–N bond. Sanderson's electronegativity of *compounds* was used as a measure of the electronic nature: 2.64 (TiO_2), 2.38 (CeO_2), 2.28 (Sm_2O_3), 2.20 (La_2O_3), and 2.05 (MgO) (2). It can be reasonably understood why Ru/MgO is active but Ru/TiO_2 is significantly less active. Then, why is lanthana so effective even though it has a higher value (than that of MgO)? The electronegativity of Ce_2O_3 (2.28), in a reduced state, is still higher than that of MgO (2.05). The electron-donating effect of metallic cerium has been reported in the Ce–Ru (0001) system (12). But ceria may not be reduced to the metallic state.

It can, therefore, be proposed that the partially reduced lanthanide oxide attached to a Ru particle undergoes an intimate interaction (SMSI). The Ru–lanthana interaction may be different (morphology effect) from that of Ru/MgO. In the highly reduced Ni/CeO_2 catalyst, the interaction between Ni and CeO_2 increases the Ni electron density (electronic effect) accompanied by a crystal-field effect (13).

As shown in Fig. 2, only the reaction rate on Ru/CeO_2 reached a maximum against the reduction temperature and Ru dispersion decreased (Fig. 3). This suggests that during the reduction process of CeO_2 to Ce_2O_3 a part of the reduced ceria covers the Ru surface (SMSI: decoration model). A decrease in the BET surface area also suggests the morphological change of the support. We have, therefore, concluded that the boundary site of Ru–lanthana is more active than the normal Ru surface. The high activity for CO, CO_2, and acetone hydrogenation has been explained as a result of the interaction between the metal and cerium cation (Ce^{3+}) or oxygen anion vacancy (10, 14) and these can be considered the active sites (15).

Similar discussions are possible with regard to the physical properties of lanthana. Partially reduced CeO_2 is known to be an *n*-type semiconductor (16). A mobile electron in CeO_2 reacts with Ru and can be explained in the following equation:

$$Ce^{4+}(O^{2-})_{2-x}(e^-)_{2x} + Ru \rightleftarrows Ce^{4+}(O^{2-})_{2-x} + Ru(e^-)_{2x}$$

However, a more detailed study of the oxidation state of Ce is still necessary for a complete understanding of the effect. As for La_2O_3 and Sm_2O_3, similar effects can be considered although no reducible state is known for either. Hydrogen consumption which is observed for Ru/Sm_2O_3 suggests the partially reduced states (SMSI): La_2O_{3-x} or Sm_2O_{3-x}. Such partially reduced lanthanide oxides tend to donate electrons to Ru as shown in the equation below or to modify the Ru surface morphologically. La_2O_3 is also known as an *n*-type semiconductor in the absence of oxygen gas (17).

$$La_2^{3+}(O^{2-})_{3-x}(e^-)_{2x} + Ru \rightleftarrows La_2^{3+}(O^{2-})_{3-x} + Ru(e^-)_{2x}$$

Unchanged H/Ru dispersion suggests that the reduced Sm_2O_3 does not move extensively up to the Ru surface.

The rates of ammonia synthesis on the Ru catalysts which were reduced at temperatures generating the maximum activity were measured for 12 h or more and are shown in Fig. 6. Although Ru/CeO_2 and Ru/MgO were stable beyond 22 or 12 h, respectively, Ru/La_2O_3 and Ru/Sm_2O_3 lost activity rapidly. However, the decrease in activity was recovered completely by the same reduction treatment for 1 h. One explanation can be that the reduced state of La_2O_{3-x} or Sm_2O_{3-x} may have different structures at different temperatures, while on the other hand, reduced CeO_2 remains in a stable phase (Ce_2O_3).

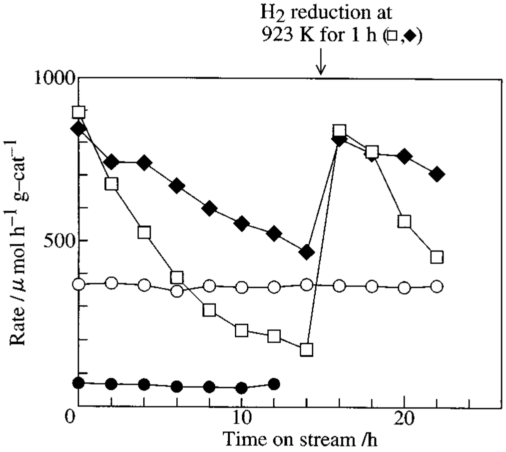

FIG. 6. Time course of ammonia synthesis rate at 588 K on Ru catalysts. Rate on 1.0 wt% Ru/CeO_2 (○, reduced at 773 K); 2 × rate on 0.5 wt% Ru/La_2O_3 (□, reduced at 923 K); 2.5 × rate on 0.4 wt% Ru/Sm_2O_3 (◆, reduced at 923 K); rate on 1.0 wt% Ru/MgO (●, reduced at 773 K and measured at 603 K).

For CO hydrogenation reaction, the loss in activity observed has been explained by the decrease in the active site covered by the reduced oxide (Ce_2O_3) or by reoxidation to CeO_2 through the H_2O produced. On the other hand, Lin *et al.* have reported that Rh/La_2O_3 and Rh/CeO_2 catalysts are active and durable for the hydrogenation of CO_2 to methanol (18). In this work, we have found that ammonia synthesis ($N_2 + 3H_2 = NH_3$) was also highly active over a long period of time on the Ru/CeO_2 catalyst as shown in Fig. 6.

In conclusion, we found that lanthanide oxides (CeO_2, Sm_2O_3, La_2O_3) were the most effective supports for ammonia synthesis. Furthermore, a significant increase in activity was observed by reduction at high temperatures. Among lanthanide oxides, Ru/Sm_2O_3 and Ru/La_2O_3 were found to be more active while only Ru/CeO_2 maintained stable activity for a long period of time. Our further studies will focus on the role hydrogen poisoning playing in these systems.

REFERENCES

1. Aika, K., Ohya, A., Ozaki, A., Inoue, Y., and Yasumori, I., *J. Catal.* **92**, 305 (1985).
2. Aika, K., Takano, T., and Murata, S., *J. Catal.* **136**, 126 (1992).
3. Report article, *Appl. Catal.* **67**, N18 (1991).
4. Murata, S., and Aika, K., *J. Catal.* **136**, 118 (1992).
5. Kadowaki, Y., and Aika, K., *J. Catal.* (1996), in press.
6. Moggi, P., Predieri, G., Albanesi, G., Papadopulos, S., and Sappa, E., *Appl. Catal.* **53** (1989).
7. Aika, K., Shiamazaki, K., Hattori, Y., Ohya, A., Ohshima, S., Shirota, K., and Ozaki, A., *J. Catal.* **92**, 296 (1985).
8. Solymosi, F., and Rasko, J., *J. Catal.* **15**, 197 (1989).
9. Zotin, F. M. Z., Tournayan, L., Varloud, J., Perrichon, V., and Frety, R., *Appl. Catal. A* **98**, 99 (1993).
10. Trovarelli, A., Dolcetti, G., Leitenburg, C., Kaspar, J., Finetti, P., and Santoni, A., *J. Chem. Soc. Faraday Trans. 9* **88**, 1311 (1992).

11. Barrault, J., Alouche, A., Paul-Boncour, V., Hilaire, L., and Percheron-Guegan, A., *Appl. Catal.* **46**, 269 (1989).
12. Walker, A. P., and Lambert, R. M., *J. Phys. Chem.* **96**, 2265 (1992).
13. Ramaroson, E., Tempere, J. F., Guilleux, M. F., Vergand, F., Roulet, H., and Dufour, G., *J. Chem. Soc. Faraday Trans. 8* **88**, 1211 (1992).
14. Mendelovici, L., and Steinberg, M., *J. Catal.* **93**, 353 (1985); **96**, 285 (1985).
15. Burch, R., and Flambard, A. R., *J. Catal.* **78**, 389 (1982).
16. Blumenthal, R. N., and Hofmaier, R. L., *J. Electrochem. Soc.* **121**, 126 (1974).
17. Vanbaelinghem, F., Pelloux, A., and Deportes, C., *J. Appl. Electrochem.* **6**, 67 (1976).
18. Fan, L., and Fujimoto, K., *J. Catal.* **150**, 217 (1994).

Yusuke Niwa
Ken-ichi Aika[1]

Department of Environmental Chemistry and Engineering
Interdisciplinary Graduate School of Science and Engineering
Tokyo Institute of Technology, 4259 Nagatsuta
Midori-ku, Yokohama 226, Japan

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[1] To whom correspondence should be addressed. E-mail: kenaika@ chemenv.titech.ac.jp.