A low-crystalline ruthenium nano-layer supported on praseodymium oxide as an active catalyst for ammonia synthesis†

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Ammonia is a crucial chemical feedstock for fertilizer production and is a potential energy carrier. However, the current method of synthesizing ammonia, the Haber–Bosch process, consumes a great deal of energy. To reduce energy consumption, a process and a substance that can catalyze ammonia synthesis under mild conditions (low temperature and low pressure) are strongly needed. Here we show that Ru/Pr₂O₃ without any dopant catalyzes ammonia synthesis under mild conditions at 18.1 times the rates reported with other highly active catalysts. Scanning transmission electron micrograph observations and energy dispersive X-ray analyses revealed the formation of low-crystalline nano-layers of ruthenium on the surface of Pr₂O₃. Furthermore, CO₂ temperature-programmed desorption revealed that the catalyst was strongly basic. These unique structural and electronic characteristics are considered to synergistically accelerate the rate-determining step of NH₃ synthesis, cleavage of the N≡N bond. We expect that the use of this catalyst will be a starting point for achieving efficient ammonia synthesis.

Introduction

Ammonia is one of the most important feedstocks in the modern chemical industry. Globally, >80% of ammonia produced is used to produce fertilizer, which is essential for growing crops. In addition, ammonia has recently attracted attention as a carrier of energy and hydrogen. Ammonia is produced by combining atmospheric N₂ with hydrogen produced by renewable energy. The ammonia is liquefied and transported to where it is used to generate power in engines or electricity in fuel cells. Ammonia is being considered as a carrier of energy and hydrogen because, (1) it has a high energy density (12.8 GJ m⁻³) and (2) a high hydrogen content (17.6 wt%), and (3) carbon dioxide is not released when hydrogen is produced by ammonia decomposition. If ammonia can be produced efficiently from renewable energy, it can contribute to the solution of global problems related to energy and food production.

Currently, most ammonia is synthesized via the Haber–Bosch process. This process is a major consumer of energy, accounting for about 1% of global energy consumption. In this process, about 60% of consumed energy is recovered and saved in ammonia as enthalpy. However, the remaining energy is lost, mainly during the production of hydrogen from natural gas, ammonia synthesis, and gas separation. Because ammonia synthesis is carried out at very high temperatures (>450 °C) and high pressures (>20 MPa), a major goal is the reduction of the high amount of energy used in this process. Curbing global energy consumption requires, inter alia, a catalyst that is able to produce ammonia at much lower temperatures and pressures than required for the iron-based catalysts used in the Haber–Bosch process.

Ruthenium is a possible catalyst for ammonia synthesis because of its higher activity at low pressure and temperature compared to that of iron-based catalysts. The rate-determining step in NH₃ synthesis is cleavage of the N≡N bond of N₂, because the bond energy is very high (945 kJ mol⁻¹). It has been reported that modification of the morphology of the Ru surface (“structural modification”) and of the Ru electronic states (“electronic modification”) are effective ways to accelerate the rate-determining step and thus enhance the ammonia-synthesis activity of the Ru catalyst. In the case of structural modification, the unusual unsaturated B₅-type site of Ru has been proven to be highly active. The B₅-type site consists of five Ru atoms: two at step edges and three on the lower terrace. The five Ru atoms are all associated with the transition state of adsorbed N₂, which results in weakening of the N≡N bond.
Adjusting the Ru particle size (e.g., to 5 nm when Ru particles are spherical) and changing the shape of Ru particles create an abundance of \( \text{B}_2 \)-type sites.\textsuperscript{16,28,21} In the case of electronic modification, the use of basic supports and the addition of a strong basic promoter to Ru catalysts has enhanced ammonia synthesis activity dramatically.\textsuperscript{15,26} The mechanism involves the transfer of electrons to the Ru metal from the basic components. Transfer of electrons from Ru to the antibonding \( \pi \)-orbitals of \( \text{N}_2 \) then results in weakening of the \( \text{N} \equiv \text{N} \) bond and promotion of \( \text{N} \equiv \text{N} \) cleavage.\textsuperscript{23} Weakening of the \( \text{N} \equiv \text{N} \) bond by doping with strong basic oxides has been confirmed by observation of the \( \text{N} \equiv \text{N} \) stretching frequency with infrared spectroscopy (IR); the most effective promoter has been reported to be \( \text{Cs}_2\text{O} \).\textsuperscript{23,24} In fact, most of the highly active Ru catalysts contain \( \text{Cs}_2\text{O} \) as a promoter.\textsuperscript{16,15,25,26} However, \( \text{CsOH} \), which may be produced in the presence of an \( \text{H}_2\text{O} \) impurity in the reactant, has a low melting point (272 °C) and may move on the surface of the catalyst particles or vaporize under the reaction conditions, the eventual result being degradation of the catalyst.\textsuperscript{27} On the other hand, \( \text{BaO} \) is also reported as an effective promoter and \( \text{Ba} \text{–Ru}/\text{activated carbon} \) (\( \text{Ba} \text{–Ru}/\text{AC} \)) has been used in commercial industrial processes.\textsuperscript{28} Recently, Horiuchi \textit{et al.} reported that \( \text{Ru}/\text{BaTiO}_3 \) and \( \text{Ba} \text{–Ru}/\text{MgO} \) show comparable high activity to \( \text{Cs} \text{–Ru}/\text{MgO} \).\textsuperscript{28} Notably, Ru-loaded electride \( [\text{Cs}_2\text{Al}\text{Li}_{24}\text{O}_{64}]^{1+} \) (e\textsuperscript{−})\(_4\) (Ru/C12A7:e\textsuperscript{−}), which is a new class of Ru catalyst supported on a non-oxide, shows high NH\(_3\)-synthesis activity without any dopant.\textsuperscript{10,29,30} This high activity has been attributed to the high electron-donating power of the electride.

We show here that a praseodymium oxide-supported Ru catalyst (Ru/Pr\(_2\text{O}_3\)) without any dopant exhibits unparalleled NH\(_3\) synthesis ability compared with highly active catalysts reported previously. The loading of Ru on the support was characterized by an unusual morphology of low-crystalline nanolayers, and the basicity of the catalyst was very high. We show that the combination of these features facilitated the activation of N\(_2\).

**Results and discussion**

**NH\(_3\)-synthesis activities of supported Ru-catalysts**

Fig. 1 compares the NH\(_3\)-synthesis activity of the Ru/Pr\(_2\text{O}_3\) catalyst with that of other supported Ru catalysts under the same reaction conditions. \( \text{Ba} \text{–Ru}/\text{activated carbon} \) (\( \text{Ba} \text{–Ru}/\text{AC} \)) has been used in industrial processes;\textsuperscript{28} \( \text{Cs} \text{–Ru}/\text{MgO} \) is one of the most active Ru catalysts in NH\(_3\) synthesis;\textsuperscript{25,11} and Ru/C12A7:e\textsuperscript{−} has attracted attention as a new active NH\(_3\)-synthesis catalyst.\textsuperscript{10,12} At 400 °C and 0.1 MPa (Fig. 1a), Ru/Pr\(_2\text{O}_3\) and Cs–Ru/MgO gave NH\(_3\) yields near the thermodynamic equilibrium (0.88%). Both the yields and NH\(_3\) production rates were higher than those achieved with the Ru/C12A7:e\textsuperscript{−} and \( \text{Ba} \text{–Ru}/\text{AC} \) catalysts. In the industrial process, it is important to obtain high one-pass NH\(_3\) yields to avoid the high energy usage required for gas separation. Furthermore, from the standpoint of thermodynamic regulation, NH\(_3\) synthesis is favored if the reaction is carried out under high pressure.\textsuperscript{9} We therefore measured the NH\(_3\)-synthesis activity at 1.0 MPa (Fig. 1b), where the NH\(_3\) yield at the thermodynamic equilibrium increases to 7.9%. Note that 1.0 MPa is still much lower than the reaction pressure used for the Haber–Bosch process. With the increase in reaction pressure, the differences in the activities of the catalysts were more pronounced: the NH\(_3\) yield reached 4.8% and the rate of formation obtained over Ru/Pr\(_2\text{O}_3\) reached 19 000 \( \mu \text{mol g}^{-1} \text{h}^{-1} \), 1.8 times the values associated with other catalysts.

To understand why the rates of NH\(_3\) synthesis are so high when catalyzed by Ru/Pr\(_2\text{O}_3\), we compared the characteristics of Ru/Pr\(_2\text{O}_3\) with those of Ru/MgO and Ru/CeO\(_2\). All of the catalysts were loaded with 5 wt% Ru. Among the dopant-free simple oxide-supported Ru catalysts, Ru/MgO and Ru/CeO\(_2\) have shown relatively high NH\(_3\)-synthesis activity,\textsuperscript{12} and CeO\(_2\) is a rare-earth oxide like Pr\(_2\text{O}_3\). Fig. S2\textsuperscript{†} shows \textit{in-situ} X-ray diffraction patterns of the catalysts after activation in pure H\(_2\) at 400 °C. In the cases of Ru/MgO and Ru/CeO\(_2\), only diffraction patterns assigned to cubic-type MgO and CeO\(_2\) were obtained. In the case of Ru/Pr\(_2\text{O}_3\), the diffraction peaks were attributed to rare earth C-type Pr\(_2\text{O}_3\).\textsuperscript{13} On the other hand, the fact that no diffraction peaks of the Ru species were apparent in the patterns of the
catalyst samples suggests that the crystallite size of the loaded Ru was too small to be detected. NH₃-synthesis activities of the Ru catalysts were then measured at 0.9 MPa after reduction at 400 °C. Ru/Pr₂O₃ catalyzed NH₃ synthesis at a much higher rate than that of Ru/MgO and Ru/CeO₂ at all temperatures from 310 to 390 °C (Fig. 2). At 390 °C in particular, the NH₃ synthesis rate of Ru/Pr₂O₃ was 15 200 μmol g⁻¹ h⁻¹, much higher than that of Ru/CeO₂ (7 400 μmol g⁻¹ h⁻¹) and Ru/MgO (1 500 μmol g⁻¹ h⁻¹). Furthermore, the long-term stability of the Ru/Pr₂O₃ catalyst at 390 °C under 0.9 MPa was evidenced by the fact that the rate of NH₃ synthesis was stable for 50 h (Fig. S3†).

Specific surface areas of Ru/Pr₂O₃, Ru/CeO₂, and Ru/MgO were 20.4, 33.5, and 46.4 m² g⁻¹, respectively (Table 1). There was no clear correlation between specific surface area and catalytic activity. Interestingly, the H/Ru ratio, a measure of Ru dispersion, was very low for Ru/Pr₂O₃ compared with that of the other catalysts. As a result, the turnover frequency of Ru/Pr₂O₃ was >3.5 times that of Ru/CeO₂ and Ru/MgO. These results suggest that the high turnover frequency of Ru/Pr₂O₃ makes the excellent rate of synthesis of NH₃ (activity per weight of catalyst) possible.

**Structural properties of Ru/Pr₂O₃**

As the NH₃-synthesis ability of a supported Ru catalyst is related to the morphology of the loaded Ru and the basicity of the support material, we used scanning transmission electron micrograph (STEM) observations and energy dispersive X-ray (EDX) analysis to investigate the morphology. Fig. 3 and S4† show high-angle annular dark-field (HAADF) images and EDX maps of Ru/Pr₂O₃ following treatment of the catalyst with H₂ at 400 °C. Fig. S5 and S6† show analogous images and maps of Ru/CeO₂ and Ru/MgO, respectively. A number of particles identified as Ru species by EDX were supported on MgO and CeO₂, but were seldom observed over Pr₂O₃. However, the EDX map showed that Ru was dispersed over the entire Pr₂O₃ surface. In the reconstructed overlapping EDX images, the greenish edges of the catalyst particles indicated that the surfaces of the catalyst particles were covered by the Ru species. These results suggest that the state of Ru is completely different when it is loaded over Pr₂O₃ versus MgO and CeO₂. To further investigate the surface morphology, we made high-resolution STEM (HR-STEM) observations (Fig. 4, and see Fig. S7–S9†). On Ru/MgO and Ru/CeO₂, the lattice fringes of the Ru species and the supports were clearly apparent. The d space of the Ru species was 0.21 nm, which is consistent with that of the (101) plane of metallic Ru. Mean diameters of the Ru particles were 1.8 ± 0.7 nm on Ru/MgO and 2.5 ± 0.8 nm on Ru/CeO₂. In addition, the surface of the supports of these catalysts was smooth, and changes in the lattice fringe were clearly observed on the boundaries between Ru particles and supports (Fig. 4b and c, S8 and S9†). In contrast, on Ru/Pr₂O₃, the surface of Pr₂O₃ was covered by layers of Ru rather than by particles. The fact that the lattice fringes of most parts of the Ru layers were not apparent indicated that the crystallinity of the Ru layers was low. The thickness of the Ru layers was 0.5–3 nm, and Ru particles were sometimes included in the layers. Thus, we considered that the surface of Pr₂O₃ was covered mainly with low-crystalline Ru nano-layers.

To explain why the Ru on the Pr₂O₃ support possessed such a unique morphology, we analysed the X-ray diffraction patterns of the catalyst precursors of Ru/Pr₂O₃. As shown in Fig. S10, the bare support [before impregnation with Ru₃(CO)₁₂] showed the structure of fluorite-type Pr₆O₁₁. However, after impregnation with Ru₃(CO)₁₂ in tetrahydrofuran (THF) and drying, the peaks assigned to Pr₆O₁₁ became smaller, and peaks attributed to Pr(OH)₃ and PrOOH appeared. Furthermore, after heat treatment under a stream of Ar at 350 °C, only peaks corresponding to PrOOH were observed. At this point, the HAADF STEM and overlay of the EDX maps of Ru/Pr₂O₃ demonstrated that the surfaces of the catalyst particles were covered by Ru species (Fig. S11†). These results indicate that Ru₃(CO)₁₂ reacted with the O⁻² in Pr₆O₁₁ and Pr⁴⁺ was reduced to Pr³⁺, with the formation of CO₂. The support then reacted with the H₂O impurity in the THF, and after heat treatment in the Ar stream, Ru and PrOOH were formed. In brief, the results reveal that the high reactivity between Ru₃(CO)₁₂ and Pr₆O₁₁ prevented aggregation of Ru₃(CO)₁₂ with Ru₃(CO)₁₂ and contributed to the formation of the unique structure of the loaded Ru. The rough surface of the Pr₂O₃ and the fuzziness of the boundary between Ru and Pr₂O₃ in the HR-STEM image in Fig. 4a and S7† was probably due to the reaction between Ru₃(CO)₁₂ and Pr₆O₁₁. Furthermore, during H₂ treatment, PrOOH was converted to Pr₂O₃ (Fig. S2†). During this process, part of the Ru included in the Ru layers was crystallized to form Ru particles, and thus Ru particles were sometimes observed in the Ru layers in the HR-STEM images (Fig. S7†). As shown in the HR-STEM images, the Ru species over Pr₂O₃ were arranged in a low-crystalline, nano-layered structure. In such a structure, unsaturated Ru atoms were not precisely arranged and formed step-and-terrace sites similar to a B₅-type site. The unique surface morphology of Ru in Ru/Pr₂O₃ would promote N₂ adsorption and subsequent cleavage of the N≡N bond.
In addition, we carried out STEM-EDX observations of Ru/Pr$_2$O$_3$ after the long-term stability test shown in Fig. S3. As shown in Fig. S12 and S13, Pr$_2$O$_3$ was still covered with low-crystalline Ru nano-layers, as it was before reaction, and distinct changes of the structure were not observable. These results demonstrate the high durability of the unique surface structure of Ru/Pr$_2$O$_3$ under the conditions used for NH$_3$ synthesis.

### Basic properties of Ru/Pr$_2$O$_3$

We used CO$_2$ temperature-programmed desorption (CO$_2$-TPD) measurements of the catalysts (Fig. 5) to evaluate another crucial determinant of NH$_3$-synthesis ability, the basicity of the support. To remove the contribution of the CO$_2$ that remained on the surface even after H$_2$ reduction, we subtracted the CO$_2$-TPD profile without CO$_2$ adsorption from that after CO$_2$ adsorption (see Fig. S14† for original figures). CO$_2$ desorption was observed at 50–680 °C on Ru/Pr$_2$O$_3$, 50–600 °C on Ru/CeO$_2$, and 50–500 °C on Ru/MgO. CO$_2$ desorption observed in the high temperature region (≥300 °C) was greatest on Ru/Pr$_2$O$_3$, intermediate on Ru/CeO$_2$, and least on Ru/MgO. These results indicate that the basic sites on Ru/Pr$_2$O$_3$ are the strongest, and those on Ru/MgO are the weakest. We used the total amount of CO$_2$ desorbed as a metric of basic density over the catalysts. Ru/Pr$_2$O$_3$ had the highest basic density, 4.4 μmol m$^{-2}$, almost twice that of Ru/CeO$_2$, 2.3 μmol m$^{-2}$, and Ru/MgO, 2.2 μmol m$^{-2}$. These results reveal that the surface basicity of Ru/Pr$_2$O$_3$ was much stronger than that of Ru/MgO and Ru/CeO$_2$. This strong surface basicity results in the most effective electron donation to Ru and promotes N$_2$ adsorption and subsequent cleavage of the N≡N bond. Furthermore, we can say that Pr$_2$O$_3$ is covered by islands of Ru nano-layers, which allow large amounts of CO$_2$ to adsorb on the surface of uncovered Pr$_2$O$_3$. Note also that the CO$_2$ desorption temperature and the total density of the basic sites were higher on Ru/CeO$_2$ than on Ru/MgO. This difference accounts for the higher NH$_3$-synthesis activity of Ru/CeO$_2$ than that of Ru/MgO.

### Activation of N$_2$ over Ru/Pr$_2$O$_3$

Finally, to understand the activation of N$_2$ molecules over the Ru/Pr$_2$O$_3$ catalyst, we examined the states of the adsorbed N$_2$ with FT-IR techniques. The IR spectra after the addition of N$_2$ to Ru/MgO, Ru/CeO$_2$, and Ru/Pr$_2$O$_3$ at room temperature are shown in Fig. 6. The IR spectrum of each catalyst shows a broad peak around 2350 to 2100 cm$^{-1}$; such peaks are assignable to the stretching vibration mode of the N$_2$ adsorbed with an end-on orientation on the Ru surface.$^{21,22,23}$ Note that the peak absorbance of N$_2$ adsorbed on Ru/Pr$_2$O$_3$ occurred at a lower frequency (2178 cm$^{-1}$) than the corresponding peak absorbances on Ru/MgO (2210 cm$^{-1}$) and Ru/CeO$_2$ (2189 cm$^{-1}$). In the spectrum of $^{15}$N$_2$ adsorbed on Ru/Pr$_2$O$_3$, the peak absorbance was shifted to a lower frequency (2106 cm$^{-1}$) compared to

### Table 1 Physicochemical properties of supported Ru catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Specific surface area (m$^2$ g$^{-1}$)</th>
<th>H/Ru$^a$</th>
<th>Turnover frequency$^b$ (s$^{-1}$)</th>
<th>Density of base sites$^c$ (μmol m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/Pr$_2$O$_3$</td>
<td>20.4</td>
<td>0.17</td>
<td>0.050</td>
<td>4.4</td>
</tr>
<tr>
<td>Ru/CeO$_2$</td>
<td>33.5</td>
<td>0.29</td>
<td>0.014</td>
<td>2.3</td>
</tr>
<tr>
<td>Ru/MgO</td>
<td>46.4</td>
<td>0.3</td>
<td>0.003</td>
<td>2.2</td>
</tr>
</tbody>
</table>

$^a$ Estimated by using H$_2$ chemisorption capacity. $^b$ Calculated by using H/Ru value and NH$_3$ yield at 390 °C under 0.9 MPa. $^c$ Estimated by using CO$_2$-TPD.
The curves show the di
frequencies of the peak absorbances of N2 adsorbed on Ru/
(14/15)1/2
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| 679 This journal is © The Royal Society of Chemistry 2017

Conclusions

In summary, we demonstrated that Ru/Pr2O3 without any
dopant catalyzed a high rate of NH3 synthesis under mild
reaction conditions (0.1–1.0 MPa). Characteristics of Ru/Pr2O3
include low-crystalline Ru nano-layers formed by the reaction
between Ru3(CO)12 and Pr6O11 and strong basicity of Pr2O3.
These characteristics are considered to synergistically accele-
rate the rate-determining step of ammonia synthesis: cleavage
of the N≡N bond of N2. In addition, substitution of some of the
praseodymium with another element without degrading its activity for 
NH3 synthesis is currently in progress, because Pr is
an expensive element. The outcome of the research will appear
in a coming contribution. We believe that our catalyst will
facilitate the development of an effective method for synthe-
sizing ammonia from renewable energy under environmentally
benign conditions. Such a method can be expected to
contribute to the solution of food and energy crises globally.

Acknowledgements

This work was supported by CREST, Japan Agency of Science
and Technology (JST). STEM/TEM observations were performed
as part of a program conducted by the Advanced Characteriza-
tion Nanotechnology Platform Japan, sponsored by the Ministry
of Education, Culture, Sports, Science and Technology (MEXT),
Japan. K. Sato thanks the Program for the Elements Strategy
Initiative for Catalysts & Batteries (ESICB) commissioned by
MEXT. T. Toriyama (Kyushu University) is acknowledged for
assistance with STEM/TEM observations. The authors thank Mr
Y. Wada, Ms. M. K. Nakao, and Mr T. Terasawa (Oita University)
for assistance with sample preparation, catalytic activity tests,
and characterization techniques. We acknowledge Prof. K.
Shimizu (Hokkaido University) for fruitful discussions con-
cerning IR analysis.

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