

CrossMark
click for updatesCite this: *Chem. Sci.*, 2017, 8, 674

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

Katsutoshi Sato,^{*ab} Kazuya Imamura,^{‡b} Yukiko Kawano,^b Shin-ichiro Miyahara,^a Tomokazu Yamamoto,^c Syo Matsumura^c and Katsutoshi Nagaoka^{*b}

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 1.8 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.

Received 30th May 2016
Accepted 30th August 2016

DOI: 10.1039/c6sc02382g

www.rsc.org/chemicalscience

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.¹ In addition, ammonia has recently attracted attention as a carrier of energy and hydrogen.^{2–5} 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.² 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.^{6–8} 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.⁹ 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.^{10–12}

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}).^{13,14} 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.^{15,16} In the case of structural modification, the unusual unsaturated B₅-type site of Ru has been proven to be highly active.^{17–19} 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.¹⁷

^aElements Strategy Initiative for Catalysts and Batteries, Kyoto University, 1-30 Goryo-Ohara, Nishikyo-ku, Kyoto 615-8245, Japan

^bDepartment of Applied Chemistry, Faculty of Engineering, Oita University, 700 Dannoharu, Oita 870-1192, Japan. E-mail: nagaoka@oita-u.ac.jp

^cDepartment of Applied Quantum Physics and Nuclear Engineering, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan

† Electronic supplementary information (ESI) available: Detailed procedures for each method, catalytic performance, STEM-EDX images, detailed characterization. See DOI: 10.1039/c6sc02382g

‡ Present address: Research Laboratory of Hydrothermal Chemistry, Faculty of Science, Kochi University, 2-5-1 Akebono-cho, Kochi 780-8520, Japan.



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 B₅-type sites.^{18,20,21} In the case of electronic modification, the use of basic supports and the addition of a strong basic promoter to Ru catalysts have enhanced ammonia synthesis activity dramatically.^{15,16} The mechanism involves the transfer of electrons to the Ru metal from the basic components. Transfer of electrons from Ru to the antibonding π -orbitals of N₂ then results in weakening of the N≡N bond and promotion of N≡N cleavage.²² Weakening of the N≡N bond by doping with strong basic oxides has been confirmed by observation of the N≡N stretching frequency with infrared spectroscopy (IR); the most effective promoter has been reported to be Cs₂O.^{23,24} In fact, most of the highly active Ru catalysts contain Cs₂O as a promoter.^{10,15,25,26} However, CsOH, which may be produced in the presence of an H₂O 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.²⁷ On the other hand, BaO is also reported as an effective promoter and Ba–Ru/activated carbon (Ba–Ru/AC) has been used in commercial industrial processes.²⁸ Recently, Horiuchi *et al.* reported that Ru/BaTiO₃ and Ba–Ru/MgO show comparable high activity to Cs–Ru/MgO.²⁶ Notably, Ru-loaded electride [Ca₂₄Al₂₈O₆₄]⁴⁺(e[−])₄ (Ru/C12A7:e[−]), which is a new class of Ru catalyst supported on a non-oxide, shows high NH₃-synthesis activity without any dopant.^{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/Pr₂O₃) without any dopant exhibits unparalleled NH₃ 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 N₂.

Results and discussion

NH₃-synthesis activities of supported Ru-catalysts

Fig. 1 compares the NH₃-synthesis activity of the Ru/Pr₂O₃ catalyst with that of other supported Ru catalysts under the same reaction conditions. Ba–Ru/activated carbon (Ba–Ru/AC) has been used in industrial processes;²⁸ Cs–Ru/MgO is one of the most active Ru catalysts in NH₃ synthesis;^{25,31} and Ru/C12A7:e[−] has attracted attention as a new active NH₃-synthesis catalyst.^{10–12} At 400 °C and 0.1 MPa (Fig. 1a), Ru/Pr₂O₃ and Cs–Ru/MgO gave NH₃ yields near the thermodynamic equilibrium (0.88%). Both the yields and NH₃ production rates were higher than those achieved with the Ru/C12A7:e[−] and Ba–Ru/AC catalysts. In the industrial process, it is important to obtain high one-pass NH₃ yields to avoid the high energy usage required for gas separation. Furthermore, from the standpoint of thermodynamic regulation, NH₃ synthesis is favored if the reaction is carried out under high pressure.⁹ We therefore measured the NH₃-synthesis activity at 1.0 MPa (Fig. 1b), where the NH₃ yield at the thermodynamic equilibrium increases to

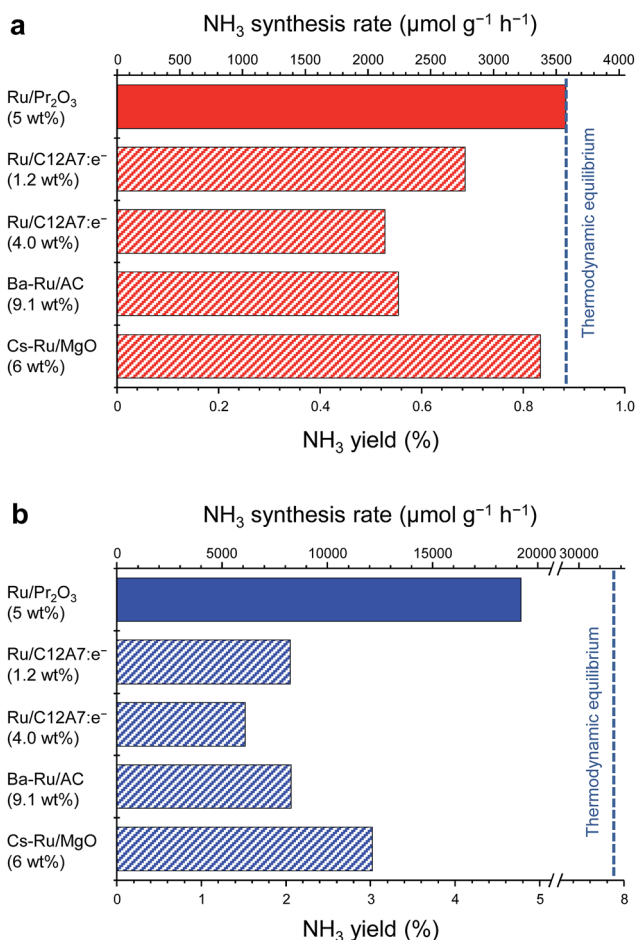


Fig. 1 Catalytic performance of supported Ru catalysts for NH₃ synthesis at (a) 0.1 MPa and (b) 1 MPa. Reaction conditions: catalyst, 0.2 g; reactant gas, H₂/N₂ = 3 with a flow rate of 60 mL min^{−1}; reaction temperature, 400 °C. With the exception of Ru/Pr₂O₃, NH₃ synthesis rates are reproduced from ref. 10.

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 NH₃ yield reached 4.8% and the rate of formation obtained over Ru/Pr₂O₃ reached 19 000 μmol g^{−1} h^{−1}, >1.8 times the values associated with other catalysts.

To understand why the rates of NH₃ synthesis are so high when catalyzed by Ru/Pr₂O₃, we compared the characteristics of Ru/Pr₂O₃ with those of Ru/MgO and Ru/CeO₂. All of the catalysts were loaded with 5 wt% Ru. Among the dopant-free simple oxide-supported Ru catalysts, Ru/MgO and Ru/CeO₂ have shown relatively high NH₃-synthesis activity,³² and CeO₂ is a rare-earth oxide like Pr₂O₃. Fig. S2† shows *in-situ* X-ray diffraction patterns of the catalysts after activation in pure H₂ at 400 °C. In the cases of Ru/MgO and Ru/CeO₂, only diffraction patterns assigned to cubic-type MgO and CeO₂ were obtained. In the case of Ru/Pr₂O₃, the diffraction peaks were attributed to rare earth C-type Pr₂O₃.³³ 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. NH_3 -synthesis activities of the Ru catalysts were then measured at 0.9 MPa after reduction at 400 °C. Ru/ Pr_2O_3 catalyzed NH_3 synthesis at a much higher rate than that of Ru/MgO and Ru/ CeO_2 at all temperatures from 310 to 390 °C (Fig. 2). At 390 °C in particular, the NH_3 synthesis rate of Ru/ Pr_2O_3 was 15 200 $\mu\text{mol g}^{-1} \text{h}^{-1}$, much higher than that of Ru/ CeO_2 (7400 $\mu\text{mol g}^{-1} \text{h}^{-1}$) and Ru/MgO (1500 $\mu\text{mol g}^{-1} \text{h}^{-1}$). Furthermore, the long-term stability of the Ru/ Pr_2O_3 catalyst at 390 °C under 0.9 MPa was evidenced by the fact that the rate of NH_3 synthesis was stable for 50 h (Fig. S3†).

Specific surface areas of Ru/ Pr_2O_3 , Ru/ CeO_2 , and Ru/MgO were 20.4, 33.5, and 46.4 $\text{m}^2 \text{g}^{-1}$, 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/ Pr_2O_3 compared with that of the other catalysts. As a result, the turnover frequency of Ru/ Pr_2O_3 was >3.5 times that of Ru/ CeO_2 and Ru/MgO. These results suggest that the high turnover frequency of Ru/ Pr_2O_3 makes the excellent rate of synthesis of NH_3 (activity per weight of catalyst) possible.

Structural properties of Ru/ Pr_2O_3

As the NH_3 -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/ Pr_2O_3 following treatment of the catalyst with H_2 at 400 °C. Fig. S5 and S6† show analogous images and maps of Ru/ CeO_2 and Ru/MgO, respectively. A number of particles identified as Ru species by EDX were supported on MgO and CeO_2 , but were seldom observed over Pr_2O_3 . However, the EDX map showed that Ru was dispersed over the entire Pr_2O_3 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 Pr_2O_3 versus MgO and CeO_2 . 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/ CeO_2 , 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/ CeO_2 . 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/ Pr_2O_3 , the surface of Pr_2O_3 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 Pr_2O_3 was covered mainly with low-crystalline Ru nano-layers.

To explain why the Ru on the Pr_2O_3 support possessed such a unique morphology, we analysed the X-ray diffraction patterns of the catalyst precursors of Ru/ Pr_2O_3 . As shown in Fig. S10,† the bare support [before impregnation with $\text{Ru}_3(\text{CO})_{12}$] showed the structure of fluorite-type Pr_6O_{11} . However, after impregnation with $\text{Ru}_3(\text{CO})_{12}$ in tetrahydrofuran (THF) and drying, the peaks assigned to Pr_6O_{11} became smaller, and peaks attributed to $\text{Pr}(\text{OH})_3$ 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/ Pr_2O_3 demonstrated that the surfaces of the catalyst particles were covered by Ru species (Fig. S11†). These results indicate that $\text{Ru}_3(\text{CO})_{12}$ reacted with the O^{2-} in Pr_6O_{11} and Pr^{4+} was reduced to Pr^{3+} , with the formation of CO_2 . The support then reacted with the H_2O 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 $\text{Ru}_3(\text{CO})_{12}$ and Pr_6O_{11} prevented aggregation of $\text{Ru}_3(\text{CO})_{12}$ with $\text{Ru}_3(\text{CO})_{12}$ and contributed to the formation of the unique structure of the loaded Ru. The rough surface of the Pr_2O_3 and the fuzziness of the boundary between Ru and Pr_2O_3 in the HR-STEM image in Fig. 4a and S7† was probably due to the reaction between $\text{Ru}_3(\text{CO})_{12}$ and Pr_6O_{11} . Furthermore, during H_2 treatment, PrOOH was converted to Pr_2O_3 (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 Pr_2O_3 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 B_5 -type site. The unique surface morphology of Ru in Ru/ Pr_2O_3 would promote N_2 adsorption and subsequent cleavage of the $\text{N}\equiv\text{N}$ bond.

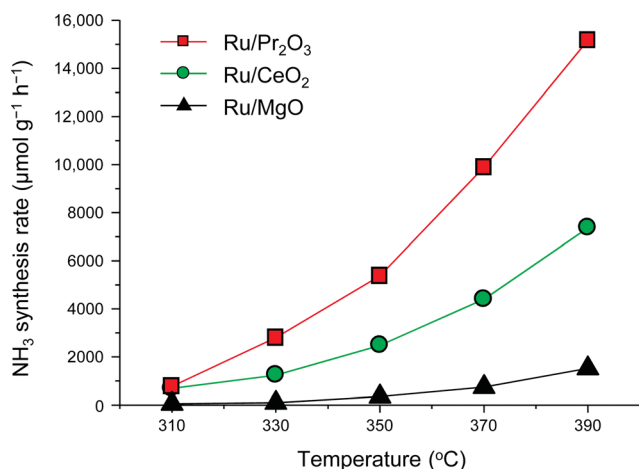


Fig. 2 Rate of NH_3 synthesis over supported Ru catalysts. Reaction conditions: catalyst, 0.2 g; reactant gas, $\text{H}_2/\text{N}_2 = 3$ with a flow rate of 60 mL min^{-1} ; pressure, 0.9 MPa.



Table 1 Physicochemical properties of supported Ru catalysts

Catalyst	Specific surface area ($\text{m}^2 \text{g}^{-1}$)	H/Ru ^a	Turnover frequency ^b (s^{-1})	Density of base sites ^c ($\mu\text{mol m}^{-2}$)
Ru/Pr ₂ O ₃	20.4	0.17	0.050	4.4
Ru/CeO ₂	33.5	0.29	0.014	2.3
Ru/MgO	46.4	0.3	0.003	2.2

^a Estimated by using H₂ chemisorption capacity. ^b Calculated by using H/Ru value and NH₃ yield at 390 °C under 0.9 MPa. ^c Estimated by using CO₂-TPD.

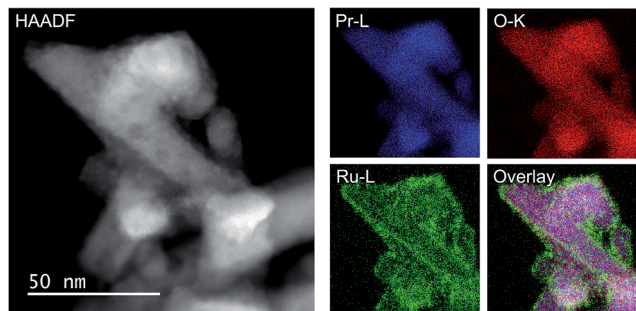


Fig. 3 HAADF-STEM image, Pr-L, O-K, and Ru-L STEM-EDX maps, and reconstructed overlay image of Pr, O, and Ru for Ru/Pr₂O₃ after H₂ reduction.

In addition, we carried out STEM-EDX observations of Ru/Pr₂O₃ after the long-term stability test shown in Fig. S3.† As shown in Fig. S12 and S13,† Pr₂O₃ 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/Pr₂O₃ under the conditions used for NH₃ synthesis.

Basic properties of Ru/Pr₂O₃

We used CO₂ temperature-programmed desorption (CO₂-TPD) measurements of the catalysts (Fig. 5) to evaluate another crucial determinant of NH₃-synthesis ability, the basicity of the support. To remove the contribution of the CO₂ that remained on the surface even after H₂ reduction, we subtracted the CO₂-TPD profile without CO₂ adsorption from that after CO₂ adsorption (see Fig. S14† for original figures). CO₂ desorption was observed at 50–680 °C on Ru/Pr₂O₃, 50–600 °C on Ru/CeO₂, and 50–500 °C on Ru/MgO. CO₂ desorption observed in the high

temperature region (≥ 300 °C) was greatest on Ru/Pr₂O₃, intermediate on Ru/CeO₂, and least on Ru/MgO. These results indicate that the basic sites on Ru/Pr₂O₃ are the strongest, and those on Ru/MgO are the weakest. We used the total amount of CO₂ desorbed as a metric of basic density over the catalysts. Ru/Pr₂O₃ had the highest basic density, 4.4 $\mu\text{mol m}^{-2}$, almost twice that of Ru/CeO₂, 2.3 $\mu\text{mol m}^{-2}$, and Ru/MgO, 2.2 $\mu\text{mol m}^{-2}$. These results reveal that the surface basicity of Ru/Pr₂O₃ was much stronger than that of Ru/MgO and Ru/CeO₂. This strong surface basicity results in the most effective electron donation to Ru and promotes N₂ adsorption and subsequent cleavage of the N≡N bond. Furthermore, we can say that Pr₂O₃ is covered by islands of Ru nano-layers, which allow large amounts of CO₂ to adsorb on the surface of uncovered Pr₂O₃. Note also that the CO₂ desorption temperature and the total density of the basic sites were higher on Ru/CeO₂ than on Ru/MgO. This difference accounts for the higher NH₃-synthesis activity of Ru/CeO₂ than that of Ru/MgO.

Activation of N₂ over Ru/Pr₂O₃

Finally, to understand the activation of N₂ molecules over the Ru/Pr₂O₃ catalyst, we examined the states of the adsorbed N₂ with FT-IR techniques. The IR spectra after the addition of N₂ to Ru/MgO, Ru/CeO₂, and Ru/Pr₂O₃ 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 N₂ adsorbed with an end-on orientation on the Ru surface.^{21,23,24} Note that the peak absorbance of N₂ adsorbed on Ru/Pr₂O₃ occurred at a lower frequency (2178 cm^{-1}) than the corresponding peak absorbances on Ru/MgO (2210 cm^{-1}) and Ru/CeO₂ (2189 cm^{-1}). In the spectrum of ¹⁵N₂ adsorbed on Ru/Pr₂O₃, the peak absorbance was shifted to a lower frequency (2106 cm^{-1}) compared to

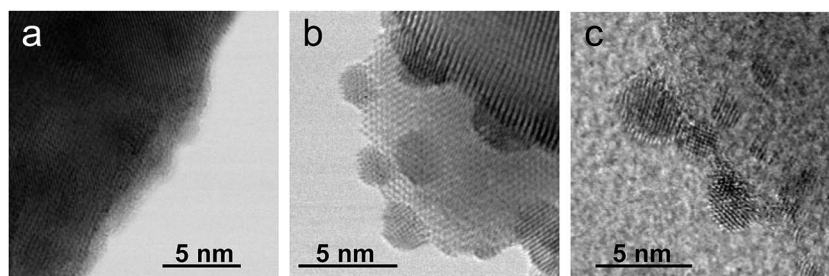


Fig. 4 HR-STEM images of (a) Ru/Pr₂O₃, (b) Ru/CeO₂, and (c) Ru/MgO, after H₂ reduction.



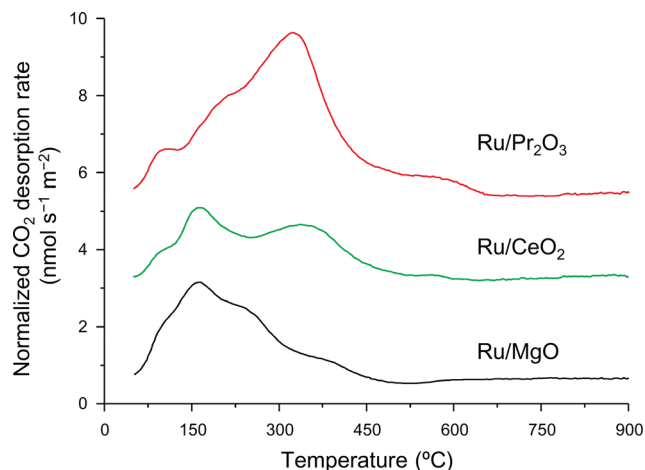


Fig. 5 CO₂-TPD profiles of supported Ru catalysts. Following H₂ reduction at 400 °C, CO₂ adsorption was carried out at 50 °C. These curves show the difference between the curves shown in Fig. S14† to remove the contribution of CO₂ that remained on the surface of the catalysts even after H₂ pre-treatment.

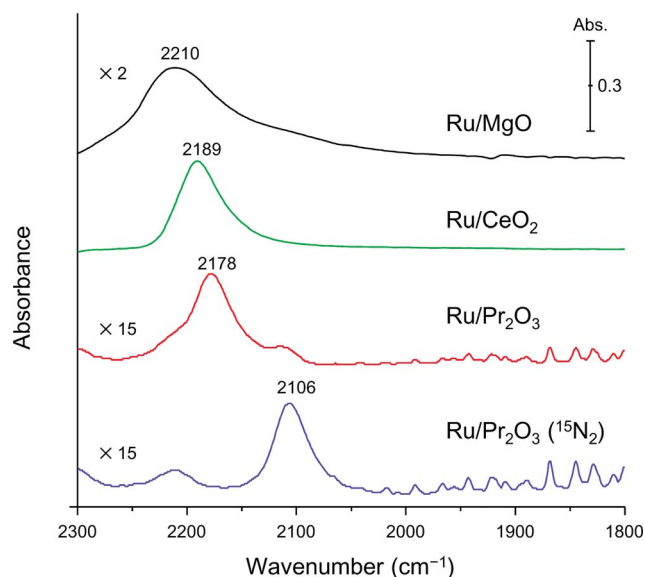


Fig. 6 Difference infrared spectra of N₂ molecules (before and after N₂ adsorption) on supported Ru catalysts. Spectra were collected under 6 kPa of N₂ (¹⁵N₂ for Ru/Pr₂O₃) at 25 °C.

that on Ru/Pr₂O₃ (2178 cm⁻¹), which is in good agreement with the frequency estimated from the isotope effect (2178 cm⁻¹ × (14/15)^{1/2} = 2104 cm⁻¹).^{23,24} These results suggest that these peaks are associated with the N₂ on the Ru surfaces. The lower frequencies of the peak absorbances of N₂ adsorbed on Ru/Pr₂O₃ compared to those of Ru/MgO and Ru/CeO₂ indicate that the N≡N bond of N₂ was further weakened over the low-crystalline Ru nano-layers on Pr₂O₃ relative to Ru nanoparticles on the other supports. We surmise that the morphology of the Ru surface and the basicity of the catalyst contributed synergistically to the weakening of the N≡N bond and enhanced the catalytic activity for NH₃ synthesis.

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 accelerate 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 synthesizing 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 Characterization 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 concerning IR analysis.

Notes and references

- 1 J. W. Erisman, M. A. Sutton, J. Galloway, Z. Klimont and W. Winiwarter, *Nat. Geosci.*, 2008, **1**, 636–639.
- 2 A. Klerke, C. H. Christensen, J. K. Nørskov and T. Vegge, *J. Mater. Chem.*, 2008, **18**, 2304–2310.
- 3 R. Schlögl, *ChemSusChem*, 2010, **3**, 209–222.
- 4 F. Schüth, R. Palkovits, R. Schlögl and D. S. Su, *Energy Environ. Sci.*, 2012, **5**, 6278–6289.
- 5 J. W. Makepeace, T. J. Wood, H. M. A. Hunter, M. O. Jones and W. I. F. David, *Chem. Sci.*, 2015, **6**, 3805–3815.
- 6 H. Bielawa, O. Hinrichsen, A. Birkner and M. Muhler, *Angew. Chem., Int. Ed.*, 2001, **40**, 1061–1063.
- 7 T. Kandemir, M. E. Schuster, A. Senyshyn, M. Behrens and R. Schlögl, *Angew. Chem., Int. Ed.*, 2013, **52**, 12723–12726.
- 8 S. Perathoner and G. Centi, *ChemSusChem*, 2014, **7**, 1274–1282.
- 9 C. W. Hooper, *Ammonia Synthesis: Commercial Practice*, in *Catalytic Ammonia Synthesis, Fundamentals and Practice*, ed. J. R. Jennings, Springer, US, 1991, pp. 253–283.

- 10 M. Kitano, Y. Inoue, Y. Yamazaki, F. Hayashi, S. Kanbara, S. Matsuishi, T. Yokoyama, S. W. Kim, M. Hara and H. Hosono, *Nat. Chem.*, 2012, **4**, 934–940.
- 11 F. Hayashi, M. Kitano, T. Yokoyama, M. Hara and H. Hosono, *ChemCatChem*, 2014, **6**, 1317–1323.
- 12 Y. Inoue, M. Kitano, S.-W. Kim, T. Yokoyama, M. Hara and H. Hosono, *ACS Catal.*, 2014, **4**, 674–680.
- 13 S. Gambarotta and J. Scott, *Angew. Chem., Int. Ed.*, 2004, **43**, 5298–5308.
- 14 H. K. Chae, D. Y. Siberio-Perez, J. Kim, Y. Go, M. Eddaoudi, A. J. Matzger, M. O'Keeffe and O. M. Yaghi, *Nature*, 2004, **427**, 523–527.
- 15 K. Aika, H. Hori and A. Ozaki, *J. Catal.*, 1972, **27**, 424–431.
- 16 K. Aika, M. Kumasaka, T. Oma, O. Kato, H. Matsuda, N. Watanabe, K. Yamazaki, A. Ozaki and T. Onishi, *Appl. Catal.*, 1986, **28**, 57–68.
- 17 S. Dahl, A. Logadottir, R. C. Egeberg, J. H. Larsen, I. Chorkendorff, E. Törnqvist and J. K. Nørskov, *Phys. Rev. Lett.*, 1999, **83**, 1814–1817.
- 18 C. J. H. Jacobsen, S. Dahl, P. L. Hansen, E. Törnqvist, L. Jensen, H. Topsøe, D. V. Prip, P. B. Møenshaug and I. Chorkendorff, *J. Mol. Catal. A: Chem.*, 2000, **163**, 19–26.
- 19 S. Dahl, E. Törnqvist and I. Chorkendorff, *J. Catal.*, 2000, **192**, 381–390.
- 20 Z. Song, T. Cai, J. C. Hanson, J. A. Rodriguez and J. Hrbek, *J. Am. Chem. Soc.*, 2004, **126**, 8576–8584.
- 21 Z. You, K. Inazu, K. Aika and T. Baba, *J. Catal.*, 2007, **251**, 321–331.
- 22 K. Aika, A. Ohya, A. Ozaki, Y. Inoue and I. Yasumori, *J. Catal.*, 1985, **92**, 305–311.
- 23 J. Kubota and K. Aika, *J. Chem. Soc., Chem. Commun.*, 1991, 1544.
- 24 J. Kubota and K. Aika, *J. Phys. Chem.*, 1994, **98**, 11293–11300.
- 25 K. Aika, T. Takano and S. Murata, *J. Catal.*, 1992, **136**, 126–140.
- 26 Y. Horiuchi, G. Kamei, M. Saito and M. Matsuoka, *Chem. Lett.*, 2013, **42**, 1282–1284.
- 27 J. G. van Ommen, W. J. Bolink, J. Prasad and P. Mars, *J. Catal.*, 1975, **38**, 120–127.
- 28 D. E. Brown, T. Edmonds, R. W. Joyner, J. J. McCarroll and S. R. Tennison, *Catal. Lett.*, 2014, **144**, 545–552.
- 29 M. Kitano, Y. Inoue, H. Ishikawa, K. Yamagata, T. Nakao, T. Tada, S. Matsuishi, T. Yokoyama, M. Hara and H. Hosono, *Chem. Sci.*, 2016, **7**, 4036–4043.
- 30 Y. Lu, J. Li, T. Tada, Y. Toda, S. Ueda, T. Yokoyama, M. Kitano and H. Hosono, *J. Am. Chem. Soc.*, 2016, **138**, 3970–3973.
- 31 F. Rosowski, A. Hornung, O. Hinrichsen, D. Herein, M. Muhler and G. Ertl, *Appl. Catal., A*, 1997, **151**, 443–460.
- 32 Y. Niwa and K.-i. Aika, *Chem. Lett.*, 1996, **25**, 3–4.
- 33 G. Adachi and N. Imanaka, *Chem. Rev.*, 1998, **98**, 1479–1514.

