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Explorative Study of a Ru/CeO₂ Catalyst for NH₃ Synthesis from Renewable Hydrogen and Demonstration of NH₃ Synthesis under a Range of Reaction Conditions

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The potential of Ru/CeO₂ catalysts to catalyze the synthesis of ammonia from renewable hydrogen was explored under ambient and high-pressure conditions. Different types of Ru precursors, CeO₂, and their combinations strongly influenced NH₃ synthesis activity. The catalytic activities of Ru(acac)₃ and Ru(NO)(NO₃)₃ were relatively high at ambient pressure. The activity of 1 wt% Ru/CeO₂ with Ru(NO)(NO₃)₃ as a Ru precursor was studied at high pressure. The dependence of NH₃ synthesis activities on temperature, pressure, space velocity, and H₂/N₂ ratio were investigated. The parameter dependences differed somewhat between different types of CeO₂. Use of CeO₂ with high surface area resulted in relatively high NH₃ synthesis rates and good low-pressure activity. Demonstration of NH₃ synthesis using the optimized Ru/CeO₂ catalyst was performed with a bench-scale plant with the recirculation of unreacted gases. NH₃ synthesis activity was measured using more than 130 combinations of temperature, pressure, space velocity, and H₂/N₂ ratio. NH₃ concentrations in the product gases were close to equilibrium value for the reaction conditions around 400 °C. The effects of operation load on the response of NH₃ production was acceptable. Ru/CeO₂ catalysts are good candidates for industrial NH₃ synthesis from renewable hydrogen.

Keywords

Ammonia, Variable hydrogen, Ruthenium, Cerium oxide, Demonstration

1. Introduction

Reduction of emissions of greenhouse gases is one of the most important challenges for the establishment of a sustainable energy society. CO₂ is the most important greenhouse gas, so consideration must be given to decreasing or storing CO₂ emissions. Hydrogen as a fuel is a promising way to reduce reliance on fossil fuels. Hydrogen emits only H₂O on combustion and can be produced *via* electrolysis of water using electricity derived from renewable energy. Storage of renewable energy as hydrogen is an effective way to make use

of renewable energy, but high-density storage of hydrogen is desirable for large-scale transportation of hydrogen, especially over global distances. Ammonia is a possible hydrogen storage material, which contains 17.6 wt% hydrogen and can store approximately 10.7 kg-H₂/100 L at 1 MPa and 25 °C¹⁾.

The Haber-Bosch process has been used to synthesize ammonia for more than 100 years²⁾. Many potentially important techniques have been developed to produce ammonia with very high efficiency. One of the important requirements for efficient operation is a constant feed supply. This requirement is common to any chemical process. However, the supply of hydrogen derived from renewable energy is frequently variable, because the output of electricity generated from a renewable energy source, such as photovoltaic or wind

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turbines, varies with time and meteorological conditions. The rate of production of hydrogen *via* alkaline water electrolysis using renewable electricity frequently changes because of the variable input of electricity³⁾. Ammonia synthesis from renewable hydrogen must therefore be able to accommodate fluctuating hydrogen feed conditions.

Battery storage and the hydrogen buffer tank are effective ways to stabilize fluctuations in the hydrogen supply, so operation with constant feed gas supply should be possible. However, such facilities would increase the cost and size of a plant, so a more effective approach is to use a reactor that can accommodate a variable hydrogen supply. In other words, change in the reaction condition is possible according to the situation of the hydrogen supply. Therefore, development of a noble catalyst and associated process is necessary for ammonia production with a variable hydrogen supply. Under these circumstances, the ammonia synthesis catalyst should function under a range of conditions dependent on the input of renewable electricity. Low-temperature operation results in low energy consumption, but low-pressure operation is unnecessary for ammonia production and plant size. Appropriate conditions along with a source of hydrogen should be selected, and the plant should be operated according to such conditions.

An ammonia synthesis catalyst that can be used with a variable supply of hydrogen must meet activity requirements under a range of reaction conditions. High activity at low temperature, and high activity at NH_3 concentration close to the equilibrium concentration at high temperature are both important. Research into NH_3 -synthesis catalysts has focused on improving low-temperature activity at ambient pressure. Aika *et al.* have studied the reaction mechanisms on Fe catalysts^{4),5)}. They found that Ru catalysts supported on basic oxides with alkaline metal additives (*e.g.*, Ru/Cs/MgO) exhibited good activity at around 300–350 °C^{6),7)}. During the last decade, several discoveries have been made concerning the support materials for supported Ru and Co catalysts. Electrides such as C_{12}A_7 ^{8),9)} were identified as support materials, and CaNH_2 could serve as the support material for Ru and Co catalysts^{10),11)}. Several lanthanide oxides were identified as support materials for Ru^{12)–15)}. However, there is less information on the effect of the H_2/N_2 ratio and space velocity (SV) on the catalytic activity, especially at high pressure. The pressure dependence of the ammonia synthesis activity for Ru/Cs/MgO and Ru/CeO₂ shows the activity of Ru/Cs/MgO decreases with higher pressure, and the activity of Ru/CeO₂ increases monotonically with higher pressure up to 5 MPa¹⁶⁾.

In this study, we focused on the catalytic activity of Ru/CeO₂ which has NH_3 synthesis activity at 5 MPa. NH_3 synthesis catalyzed by Ru/CeO₂^{17),18)} is known, but

the activity of Ru/CeO₂ under various reaction conditions is less understood, especially the dependence of activity on pressure. Effects of the CeO₂ and Ru precursors on the catalytic activity have been studied only at ambient pressure. To evaluate the catalytic activity of Ru/CeO₂, we investigated low temperature and maximum activity, and the ratio of NH_3 concentration to the equilibrium concentration. Synthesis of NH_3 from renewable hydrogen does not require outstanding catalytic activity under ideal conditions. Instead, satisfactory activity over a wide range of conditions is preferable. The selected Ru/CeO₂ catalysts were tested under various combinations of H_2/N_2 ratios and space velocities, as well as at high pressure. A candidate Ru/CeO₂ catalyst was selected and manufactured based on the results of these tests, and the catalyst was then installed in an ammonia synthesis plant demonstration facility. The plant was used to study ammonia synthesis as a function of reaction parameters. This report includes the results of the demonstration experiments with Ru/CeO₂.

2. Experimental

2.1. Catalyst Preparation

The catalyst used in the laboratory test, 1 wt% Ru/CeO₂, was prepared by the impregnation method. The Ru precursors and solvents used were $\text{Ru}_3(\text{CO})_{12}$ in tetrahydrofuran, $\text{Ru}(\text{acac})_3$ in acetone, $\text{Ru}(\text{dpm})_3$ in acetone, $[\text{Ru}(\text{OH})(\text{NO})(\text{NH}_3)_4](\text{NO}_3)_2$ in distilled water (DW), $\text{Ru}(\text{NO}_3)_3$ in DW, $\text{Ru}(\text{NO})(\text{NO}_3)_3$ in DW, RuCl_3 in DW, $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ in DW, and Na_2RuO_4 in DW. The CeO₂ precursors used were CeO₂(A) (Daiichi Kigenso Kagaku Kogyo Co., Ltd.; 167 m²/g), CeO₂(B) (Daiichi Kigenso Kagaku Kogyo Co., Ltd.; 133 m²/g), and CeO₂(C) ($\text{Ce}(\text{NO}_3)_3$ calcined at 900 °C for 4 h, 10 m²/g). After Ru loading, the samples were calcined in a flow of 10 % H_2/N_2 at 300 °C for 1 h.

The catalyst used in the demonstration test was a Ru/CeO₂ catalyst prepared by the optimum preparation procedure, then pelletized in a cylinder with a diameter of ~3 mm and height of ~3 mm.

2.2. Activity Tests in the Laboratory

Activity tests were performed in fixed-bed flow reactors under ambient and high-pressure conditions. For the test under ambient conditions, catalyst (0.2 g) was placed in a quartz reactor with an inner diameter of 8 mm. The feed gas was 75 % H_2 and 25 % N_2 with a total flow rate of 80 mL min⁻¹. Purities of feed gases was 99.9999 %. The catalyst was pretreated in the feed gas at 600 °C for 30 min, and then the activity measurement was carried out at temperatures ranging from 300 to 600 °C in steps of 50 °C. Product gases were analyzed using a Fourier transform IR spectrometer (Thermo Fisher, iS50) equipped with a multi-reflection gas cell (optical path length, 2.4 m).

Fig. 1 Exterior Appearance and Process Flow Diagram of the Demonstration Facility for NH_3 Synthesis

For high-pressure tests, catalyst (1 mL) was set in a tubular reactor with an inner diameter of 12 mm. Catalyst pretreatment was carried out exactly as described above. Reaction condition variables were temperature, pressure, H_2/N_2 ratio, and space velocity in the ranges of 300–450 $^\circ\text{C}$, 0–10 MPaG, 1–4, and 3000–12,000 h^{-1} , respectively. Product gases were analyzed with a Fourier-transform IR spectrometer (Perkin Elmer, Frontier) equipped with a multi-reflection gas cell (optical path length, 2 m).

2. 3. Demonstration Test

Figure 1 shows the exterior appearance of the demonstration facility and the process flow diagram. Feed gases were fed from commercial cylinders. Purities of feed gases were 99.99 %. The demonstration plant included the feed gas purification systems, a thermal oil heating system, a gas-recirculating system, and a cryogenic separation system. Contamination in the feed gases was thought to be so low that the inhibition effect of contamination on the catalytic activity was negligible. The reactor was a single-bed tubular reactor with an inner volume of ~ 3 L and an inner diameter of 49.5 mm; a double-pipe structure was adopted. The catalyst was set in the inner tube, and heat-exchange oil flowed between the inner and outer tubes to supply and remove heat. The demonstration plant had a capacity of 20 kg/day of liquid ammonia.

3. Results and Discussion

3. 1. Catalytic Activities at Lab Scale

3. 1. 1. Activity Test at Ambient Pressure

We investigated NH_3 synthesis activity as a function of various precursors of 1 wt% Ru/CeO_2 . Figure 2 shows the effects of the Ru precursors and CeO_2 on NH_3 synthesis activity. We used nine types of Ru precursors. We evaluated NH_3 synthesis activity on the basis of three metrics: NH_3 concentrations in the prod-

(a) Activity at 325 $^\circ\text{C}$, (b) maximum NH_3 formation rate, and (c) ratio of NH_3 concentration to equilibrium concentration at 500 $^\circ\text{C}$. Colors indicate forms of CeO_2 as follows: khaki, calcined CeO_2 (A); blue, CeO_2 (B); and green, CeO_2 (C).

Fig. 2 Effects of the Types of Ru Precursors and CeO_2 on NH_3 Synthesis Activity of 1 wt% Ru/CeO_2

uct gas at 325 °C as a metric of low-temperature activity, maximum concentration as a metric of maximum capacity, and ratio of NH_3 concentration to the equilibrium concentration at 500 °C as a metric of the influence of the thermodynamic equilibrium constraint.

The low-temperature activities were in the order $\text{Ru}(\text{acac})_3\text{-CeO}_2(\text{B}) > \text{Ru}_3(\text{CO})_{12}\text{-CeO}_2(\text{B}) > \text{Ru}(\text{NO})(\text{NO}_3)_3\text{-CeO}_2(\text{A}) > \text{RuCl}_3\text{-CeO}_2(\text{B}) > \text{Ru}_3(\text{CO})_{12}\text{-CeO}_2(\text{C})$. These results indicated that CeO_2 with high surface area was not required to obtain high activity. Interestingly, although a chloride-containing precursor is known to be undesirable because of Cl inhibition¹⁹, RuCl_3 exhibited relatively high low-temperature activity. $\text{Ru}_3(\text{CO})_{12}$ also showed high activity at low temperature.

The maximum capacities were in the order $\text{Na}_2\text{RuO}_4\text{-CeO}_2(\text{A}) > \text{Ru}(\text{acac})_3\text{-CeO}_2(\text{A}) > \text{Ru}(\text{acac})_3\text{-CeO}_2(\text{B}) > \text{Ru}(\text{NO})(\text{NO}_3)_3\text{-CeO}_2(\text{A}) > \text{Ru}(\text{NO})(\text{NO}_3)_3\text{-CeO}_2(\text{B})$. Na_2RuO_4 exhibited the highest activity, but all CeO_2 catalysts had low activity at low temperature. NH_3 synthesis capacities of $\text{Ru}(\text{acac})_3$ and $\text{Ru}(\text{NO})(\text{NO}_3)_3$ were high on $\text{CeO}_2(\text{A})$ and $\text{CeO}_2(\text{B})$.

The ratios of NH_3 concentration at equilibrium were in the order $\text{Ru}(\text{acac})_3\text{-CeO}_2(\text{B}) > \text{Ru}(\text{NO})(\text{NO}_3)_3\text{-CeO}_2(\text{B}) > \text{Ru}(\text{acac})_3\text{-CeO}_2(\text{A}) > \text{Ru}(\text{dpm})_3\text{-CeO}_2(\text{A}) > \text{Ru}_3(\text{CO})_{12}\text{-CeO}_2(\text{B})$. NH_3 concentrations exceeded 80 % of the equilibrium concentration in all of these cases, suggesting that the thermodynamic equilibrium constraint was not very significant.

$\text{Ru}(\text{acac})_3\text{-CeO}_2(\text{B})$ and $\text{Ru}(\text{NO})(\text{NO}_3)_3\text{-CeO}_2(\text{A})$ showed high activities at 300–600 °C. For $\text{Ru}_3(\text{CO})_{12}\text{-CeO}_2(\text{B})$ was a slightly better support than other CeO_2 types, although the effect of different types of CeO_2 was small. The worst combination was $\text{Ru}(\text{dpm})_3\text{-CeO}_2(\text{C})$, which had very low activity at all temperatures. The lower activity of $\text{Ru}(\text{dpm})_3$ compared to $\text{Ru}(\text{acac})_3$ might have been due to the large size of the dipivaloyl-methanate ligand. Comparison of the activities of $\text{Ru}(\text{NO})(\text{NO}_3)_3$ and $\text{Ru}(\text{NO}_3)_3$ revealed that the nitrosyl ligand influenced the magnitude of NH_3 synthesis activity. The activities of Ru precursors that contained chloride were low at low temperatures, and maximum capacities, except for $\text{RuCl}_3\text{-CeO}_2(\text{B})$, were also low, although the NH_3 concentration was relatively close to its equilibrium value at 500 °C for catalysts with $\text{CeO}_2(\text{A})$ and $\text{CeO}_2(\text{B})$. The implication is that the specific combination of a Ru precursor and CeO_2 greatly influenced the catalytic activity.

To confirm whether the differences in NH_3 synthesis activity associated with different types of CeO_2 were due to differences in the specific surface areas of CeO_2 or not, $\text{CeO}_2(\text{A})$ was calcined at 600 °C and 1000 °C before Ru loading. These catalysts were designated A6 and A10, and had specific surface areas of 109 m^2/g and 18 m^2/g , respectively. The surface areas of A6 and A10 were similar to those of $\text{CeO}_2(\text{B})$ and $\text{CeO}_2(\text{C})$ in

(a) Activity at 325 °C, (b) maximum NH_3 formation, and (c) ratio of NH_3 concentration to equilibrium concentration at 500 °C. Colors indicate forms of CeO_2 as follows: khaki, no calcination; blue, 600 °C; and green, 1000 °C.

Fig. 3 Effects of the Types of Ru Precursors and Calcination Temperature of $\text{CeO}_2(\text{A})$ on NH_3 Synthesis Activity of 1 wt% Ru/CeO_2

Fig. 2. For $\text{Ru}_3(\text{CO})_3$, the low-temperature activity of A6 was slightly lower than those of non-calcined $\text{CeO}_2(\text{A})$ and A10 (**Fig. 3**). The dependence of the activity on the surface area was different from that shown in **Fig. 2**. Six types of Ru precursors excluding $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}(\text{NO}_3)_3$, and Na_2RuO_4 exhibited high low-temperature activity for A6. The low-temperature activities for A6 compared to those for $\text{CeO}_2(\text{B})$ in **Fig. 2** were higher except for $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}(\text{NO}_3)_3$, and CuCl_3 . Moreover, the low-temperature activities for A10 were much higher than for $\text{CeO}_2(\text{C})$. These results suggest that the surface area was not a dominant parameter for the low-temperature activity. The chemical state of CeO_2 and the combination with Ru precursor were suspected to strongly affect the low-temperature activity. Maximum capacity for $\text{Ru}(\text{NO}_3)_3$, $\text{Ru}(\text{NO})(\text{NO}_3)_3$, and Na_2RuO_4 showed different depen-

$H_2/N_2 = 3$ and SV $12,000\text{ h}^{-1}$. Symbols indicate temperatures as follows: (●) 440 °C, (■) 400 °C, (▲) 360 °C, and (◆) 320 °C.

Fig. 4 Pressure Dependence of the Catalytic Activities of (a) 1 wt% Ru/CeO₂(A) and (b) 1 wt% Ru/CeO₂(B)

dences on the surface area. The maximum capacity was dramatically increased by calcination of CeO₂(A), especially in the case of Ru(NO₃)₃. The dependences of all activity indices on the surface area differed from that shown in Fig. 2 for [Ru(OH)(NO)(NH₃)₄](NO₃)₂, Ru(NH₃)₆Cl₃, and Ru(dpm)₃, but were similar to that shown in Fig. 2 for Ru(acac)₃ and RuCl₃. The dependences of the ratio to equilibrium on the surface areas of the three Ru precursors were similar to that in Fig. 2. Based on these results, we suspected that NH₃ synthesis activity mainly depended on the chemical state rather than the area of the CeO₂ surface.

Active Ru/CeO₂ exhibited high dispersion of Ru particles²⁰. We suspected that Ru dispersion affects the NH₃ synthesis activity. Moreover, we confirmed that reduction pretreatment was important to obtain the appropriate surface. Use of various pretreatment temperatures showed that the required pretreatment time for obtaining similar activity increased at lower pretreatment temperature. Surface oxygen vacancy of CeO₂ is one of important characteristics related to catalytic activity²¹. Therefore, low temperature formation of oxygen vacancy of CeO₂ might be important, and short pretreatment time is favorable for more efficient plant operation.

3.1.2. Activity Test under High-pressure Conditions

Based on these results, we prepared 1 wt% Ru/CeO₂ using Ru(NO)(NO₃)₃ and CeO₂(A) calcined at 600 °C, a combination that had performed well in terms of all three indices. We then investigated high-pressure re-

actions over 1 wt% Ru/CeO₂, and for comparison, 1 wt% Ru/CeO₂ similarly prepared using CeO₂(B). Figure 4 shows the pressure dependence of the activity of these catalysts. NH₃ concentrations in the product gases of both catalysts were similar if the reaction conditions were comparable. For Ru/CeO₂(A), NH₃ concentrations in the product gas increased with higher pressure and almost reached a plateau above 5 MPaG and 4 MPaG at 440 °C and 400 °C, respectively. In contrast, the NH₃ concentration decreased with higher pressure above 5 MPaG and 3 MPaG at 360 °C and 320 °C, respectively. Reduced activity of Ru/Cs/MgO under high pressure condition was suspected to be due to hydrogen poisoning¹⁶. For Ru/CeO₂(B), the NH₃ concentration increased with higher pressure, continuously at 440 °C but reached a plateau at 360 °C. Surface NH_x species may be important in the reaction mechanism over Ru/CeO₂²². The difference in pressure dependence trends between Ru/CeO₂(A) and Ru/CeO₂(B) might be affected by the varying contribution of NH_x species. NH₃ formation rates were higher for Ru/CeO₂(A) than for Ru/CeO₂(B) because the apparent density was higher for Ru/CeO₂(B) (2.3 g/mL) than for Ru/CeO₂(A) (1.5 g/mL).

Figure 5 shows the dependence of the NH₃ synthesis activity on the SV and the H₂/N₂ ratio at 400 °C and 5 MPaG. NH₃ concentration in the product gas decreased and the rate of NH₃ formation increased with higher SV (Fig. 5(a)). NH₃ formation rate increased almost linearly with SV for both catalysts, but the increase was greater for Ru/CeO₂(A) than for Ru/

Reaction conditions were 400 °C, 5 MPaG, H₂/N₂ = 3 for (a) and SV 12,000 h⁻¹ for (b). Meaning of symbols as follows: (●, ○) 1 wt% Ru/CeO₂(A) and (■, □) 1 wt% Ru/CeO₂(B).

Fig. 5 Dependence of NH₃ Synthesis Activity on (a) Space Velocity and (b) H₂/N₂ Ratio

CeO₂(B). NH₃ formation was highest for both catalysts at an H₂/N₂ ratio of 1, and then decreased as the H₂/N₂ ratio increased further (Fig. 5(b)). Ammonia formation rates over Ru catalysts are known to reach a maximum at an H₂/N₂ ratio of less than 3^{23,24}). Hydrogen poisoning was a possible reason, so that the maximum activity was obtained at H₂/N₂ ratio lower than 3.

Consequently, NH₃ production was highest for 1 wt% Ru/CeO₂(A), and the optimum pressure region was below 5 MPaG. The chemical and/or physical properties of CeO₂ affected NH₃ production under high-pressure conditions. Based on these findings, we adjusted the conditions for preparing Ru/CeO₂ and loading Ru from an economic perspective. A prototype Ru/CeO₂ catalyst exhibited continuous increase in NH₃ formation even at 400 °C as the pressure increased up to 10 MPaG²²).

3. 2. Demonstration Test

The improved Ru/CeO₂ catalyst for the demonstration test was installed in the reactor of the demonstration plant shown in Fig. 1. This test monitored the steady-state activity under more than 130 combinations of various reaction conditions of temperature, pressure, SV, and H₂/N₂ ratio. The experiments at the plant were conducted from Monday through Friday each week. The plant was shut down on weekends, so required weekly start up and shutdown operation. This phase of the studies confirmed the response of NH₃ productivity to the changes of reaction conditions.

Figure 6 shows the temperature dependence of NH₃ production at the demonstration plant. Temperature control was achieved by regulating the temperature at the reactor inlet. The catalyst bed showed a distribution of temperatures. Reaction conditions were 8 MPaG, SV of 6000 h⁻¹, H₂/N₂ ratio of 1, and recircu-

Reaction condition was 8 MPaG, SV 6000 h⁻¹, and H₂/N₂ ratio 1 with recirculation of unreacted gases. Meaning of symbols as follows: (●) NH₃ concentration and (○) ratio of NH₃ concentration to equilibrium concentration.

Fig. 6 Dependence of NH₃ Production in the Demonstration Plant on the Inlet Temperature

lation of the unreacted gases. Ammonia formation was observed at 300 °C, and the rate of NH₃ formation increased with higher inlet temperature. Ammonia concentrations above 380 °C and 400 °C exceeded 12 %. NH₃ concentration reached 90 % of the equilibrium value at 400 °C.

Figure 7 shows the pressure dependence of NH₃ production with inlet temperature of 400 °C, SV of 6000 h⁻¹, and H₂/N₂ ratio 1. Ammonia concentrations in the product gas increased with higher pressure. NH₃ concentrations at each pressure were close to the equilibrium value, suggesting that very close to maximum production was achieved at 400 °C.

Figure 8 shows the effect of H₂/N₂ ratio on NH₃

Reaction condition was 400 °C at reactor inlet, SV 6000 h⁻¹, and H₂/N₂ ratio 1 with recirculation of unreacted gases. Meaning of symbols as follows: (●) NH₃ concentration and (----) equilibrium concentration.

Fig. 7 Pressure Dependence of NH₃ Production in the Demonstration Plant

production. NH₃ concentration in the product gas increased with higher H₂/N₂ ratio and reached the maximum at H₂/N₂ ratios of about 1.8 and 2 at pressures of 8 MPaG and 5 MPaG, respectively. Comparing with the results in Fig. 5, hydrogen poisoning was reduced for the demonstration catalyst. The reason for better resistance against hydrogen poisoning is under investigation. Operation of the Ru/CeO₂ catalyst is desirable at a relatively low H₂/N₂ ratio at 8 MPa. In contrast, the variation in activity in the range of measured temperature was small at 5 MPaG. Therefore, operation at 5 MPaG pressure close to the H₂/N₂ ratio of 3 was favored.

We confirmed the response of NH₃ production to changes in the operation load by varying the flow rate of feed gas without changing the H₂/N₂ ratio as shown in Fig. 9. Increase of the load from medium to high and from low to high caused the NH₃ concentration to fall and then stabilize within 3 h. Decrease of the load from high to medium caused NH₃ formation to stabilize within 1 h. Decrease of the load from high to low caused NH₃ formation to initially stabilize within 1 h and then stabilize again 2 h later. The flow rates of H₂ and N₂ stabilized within 1 h, so the response of NH₃ production to changes of load was satisfactory.

Figure 10 shows change in the relative activity with time on stream. The relative activity gradually increased with longer time on stream, finally reaching 1.1. This trend could be explained by conversion to the highly reduced state of CeO₂ as the reaction proceeded. As described above, formation of the vacancy site of lattice oxygen was related to the catalytic activity.

Reaction condition was 400 °C at the reactor inlet and SV 6000 h⁻¹ with recirculation of unreacted gases. Meaning of symbols as follows: (●) 8 MPaG and (■) 5 MPaG.

Fig. 8 Effect of H₂/N₂ Ratio on NH₃ Production in the Demonstration Plant

Reaction condition was 400 °C, 8 MPaG, and H₂/N₂ ratio = 3 with recirculation of unreacted gases. Meaning of colors as follows: (red) NH₃ concentration, (blue) H₂ flow rate, and (black) N₂ flow rate.

Fig. 9 Time Course of Load-change Test with the Demonstration Plant

The results of the demonstration tests indicated that the activity exhibited by Ru/CeO₂ was sufficient for NH₃ synthesis under various reaction conditions, especially at ~400 °C, and the response of NH₃ synthesis to changes in the operation load was satisfactory. We concluded that Ru/CeO₂ was suitable for use in operation with a H₂ supply that varied in response to the supply of renewable electricity.

In addition, we filled the H₂ cylinder with renewable hydrogen produced by a polymer electrolyte membrane electrolyzer connected to a photovoltaic cell. Purity of the H₂ used was more than 99.99 %. We then attempted to synthesize green ammonia²⁾. We confirmed no change in NH₃ production after changing from com-

Reaction condition was 400 °C, 5 MPaG, and $H_2/N_2 = 1$, and SV 6000 h^{-1} .

Fig. 10 Time Course of Relative Activity

mercial hydrogen to renewable hydrogen. The green ammonia was used as a fuel in the ammonia gas turbine power generator system. Electricity was then recovered from the green ammonia. We therefore succeeded in establishing the entire value chain from renewable energy to electricity *via* ammonia storage.

4. Conclusions

The present study investigated the potential of Ru/CeO₂ catalysts for the synthesis of ammonia from renewable hydrogen. Catalytic activity was evaluated under ambient and high-pressure conditions. The explorative study at ambient pressure investigated the effects of different types of Ru precursors and CeO₂. The combination of Ru and CeO₂ precursors strongly influenced the NH₃ synthesis activity. The activities of Ru(acac)₃-CeO₂(B) and Ru(NO)(NO₃)₃-CeO₂(A) catalysts were high over a wide range of temperatures. However, the different types of CeO₂ had only small effects on the activity of Ru₃(CO)₁₂, so various forms of CeO₂ could be used. The calcination temperature of CeO₂(A) and the chemical properties of the CeO₂ also influenced the NH₃ synthesis activity, but the surface area of the CeO₂ did not have particularly sensitive effects.

High-pressure activity measurements were carried out for 1 wt% Ru/CeO₂ using Ru(NO)(NO₃)₃ as a Ru precursor. The dependences of NH₃ synthesis activities on temperature, pressure, SV, and the H_2/N_2 ratio were investigated. The rate of NH₃ formation using CeO₂(A) was relatively high, even at low pressure. Similar trends of catalytic activity with different SV and H_2/N_2 ratio were obtained for Ru/CeO₂(A) and Ru/CeO₂(B).

Demonstration tests of NH₃ synthesis on Ru/CeO₂ were performed with a bench-scale plant with recirculation of unreacted gases. Ru/CeO₂ catalyst was manufactured with the optimal conditions with respect to Ru loading and other preparation conditions. Renewable electricity is likely to generate variable hydrogen supply, so NH₃ synthesis activity was studied with more than 130 combinations of temperature, pressure, SV, and H_2/N_2 ratio. Ammonia concentrations in the product gases were close to the equilibrium value for the reaction conditions at ~400 °C. The response of NH₃ production to changes in the operation load was satisfactory. Evaluation of the catalyst durability found that the relative activity increased with longer time on stream up to 350 h. We conclude that Ru/CeO₂ catalysts are suitable for NH₃ synthesis using renewable hydrogen.

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要 旨

再生可能エネルギー由来水素アンモニア合成のための Ru/CeO₂触媒開発と 種々の反応条件でのアンモニア合成実証試験

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再生可能エネルギー由来の変動性を有する水素供給を可能としたアンモニア合成プロセス構築のため, Ru/CeO₂を触媒として探索研究を行った。触媒活性評価は, 常圧および高圧反応条件で行った。Ru 前駆体と CeO₂種ならびにその組み合わせによって NH₃ 合成活性は大きく影響された。Ru(acac)₃と Ru(NO)(NO₃)₃は常圧での活性試験において, 比較的高い NH₃ 合成活性が得られることが分かった。高圧活性試験では, Ru(NO)(NO₃)₃を前駆体として用いた 1 wt% Ru/CeO₂で評価した。温度, 圧力, 空間速度, H₂/N₂比に対する NH₃ 合成活性の影響を検討した。これらのパラメーター変化に対する傾向は CeO₂ 種の影響を受け, 高比表面積 CeO₂ を用いることで比較的低圧での NH₃ 合成

活性が高まることが分かった。最適化された Ru/CeO₂ による NH₃ 合成実証試験は, 未反応ガスをリサイクルしたベンチスケール試験装置で行った。温度, 圧力, 空間速度, H₂/N₂比を変化させ, 130 条件におよぶ条件での NH₃ 製造試験を行った。生成物ガス中の NH₃ 濃度は 400 °C 付近の条件ではほぼ平衡濃度に達していた。H₂ 供給量変化に応じた NH₃ 製造量変更時における NH₃ 生成が条件変化に追従するかを確認したところ, 条件には依存するものの長くとも 3 時間以内で定常状態に達することが確認された。Ru/CeO₂ 触媒は, 再生可能エネルギー由来水素を原料にした NH₃ 合成に適する触媒であると結論づけた。