1. Introduction

Reactive nitrogen (Nr) species, such as NO, NO₂, NO₃⁻, and NO₂⁻, are harmful chemicals that cause environmental pollution (photochemical smog and acid rain) and have deleterious effects on human health. The environmental capacity for these Nr species has been estimated to be already overflowed in the world¹. Therefore, it is urgent issue to optimize and control the nitrogen circulation in the nature.

Nitrogen oxides (NOₓ) are mainly emitted by vehicles and the thermal power plant using fossil fuels like coal, petroleum, natural gas². Methods for reducing NOₓ emissions include NOₓ storage/reduction, lean NOₓ traps, and selective catalytic reduction; and the literature on these methods is vast³–⁸. A major deNOₓ technic is by NH₃, whereby NOₓ is reduced to N₂ by NH₃:

\[
4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}
\]  

(1)

The standard heat of formation of NO is −90 kJ mol⁻¹, and the standard heat of combustion of NH₃ is 383 kJ mol⁻¹. The excess energy compensates for the internal energy of NO. NO (bond energy, 632 kJ mol⁻¹) has much higher reactivity than N₂ (945 kJ mol⁻¹) and can therefore be easily converted to other nitrogen-containing compounds. However, because NH₃ is not only a useful raw material for the synthesis of various kinds of chemicals but also an energy carrier⁹,¹⁰, we have been studying catalysts for NO conversion to NH₃. We recently proposed a concept, designated recNOₓ, for recovery of NOₓ as the energy carrier¹¹. If NOₓ can
be converted to useful substances such as NH₃, then a higher concentration of NO is in combustion exhaust gases is actually preferable; and combustors can be operated under the most efficient conditions without the need to be concerned about NO suppression. Therefore, implementation of recNOₓ systems can be expected to considerably decrease CO₂ emissions.

There are two ways to generate NH₃ from NOₓ: the NO-H₂ reaction (2NO + 5H₂ → 2NH₃ + 2H₂O) and the NO-CO-H₂O reaction (2NO + 5CO + 6H₂O → 2NH₃ + 3CO₂)²⁻¹²⁻¹⁶⁻¹. Although the NO-H₂ reaction proceeds at temperatures as low as 100 °C, forming NH₃ with high selectivity is difficult under stoichiometric conditions¹⁶⁻¹⁷⁻¹, and high NH₃ selectivity is necessary for efficient recovery of NOₓ. We previously reported that a Pt/TiO₂-catalyzed NO-CO-H₂O reaction shows high NH₃ selectivity in the temperature range from 100 to 300 °C¹¹⁻¹²⁻¹³⁻¹⁶⁻¹⁸⁻¹. We investigated the effects of the crystal structure of the TiO₂ support on the catalyst activity, and we estimated the kinetic parameters of the reaction¹¹⁻¹²⁻¹⁶⁻¹. The specific surface area of anatase TiO₂ is larger than that of rutile TiO₂ because the rutile phase is generated at higher temperatures and therefore has relatively large crystallites¹⁵⁻¹⁻⁻²¹⁻²¹. In our previous study, we evaluated the effects of the crystal structure of TiO₂ supports with different surface areas¹¹⁻¹, but to more accurately determine crystal structure effects, samples with similar specific surface areas must be evaluated.

In this study, we evaluated the activities of Pt catalysts supported on anatase and rutile TiO₂ with relatively high and low specific surface area. We determined the physical and chemical properties of the Pt/TiO₂ catalysts, and we discuss the mechanism of the NO-CO-H₂O reaction over these catalysts.

2. Experimental

2.1. Catalyst Preparation

TiO₂-supported platinum catalysts were prepared by means of an incipient wetness method. Four different TiO₂ supports were used: TiO₂(A)H (SSP-M, Sakai Chemical Industry Co.; A = anatase, H = high specific surface area), TiO₂(A)L (Wako Pure Chem. Ind., Ltd.; L = low specific surface area), TiO₂(R)H (STR-100N, Sakai Chemical Industry Co.; R = rutile), and TiO₂(R)L, which was prepared by calcination of TiO₂(R)H at 900 °C for 6 h. H₂PtCl₆ (Wako Pure Chem. Ind., Ltd.) was used as a Pt precursor and was diluted to the desired concentration with deionized water. The powdered TiO₂ supports were immersed in the aqueous Pt solution, and the resulting suspensions were allowed to stand for 30 min and then dried at 100 °C overnight in a drier. The dried samples were calcined at 500 °C for 4 h in air and then reduced with 10 vol% H₂ in N₂ as a balance gas at 400 °C for 1 h. This procedure yielded 1 wt% Pt/TiO₂ catalysts, which were sieved to 250-150 µm for activity testing and characterization.

2.2. Activity Test

Activity tests were performed in a fixed-bed flow reactor. Catalyst (150 mg) was placed in a quartz reactor with an outer diameter of 10 mm, and quartz glass wool was placed in the middle of the reactor. The reaction conditions for the activity tests are shown in Table 1; the total gas flow rate was set at 250 mL min⁻¹. Product gases were analyzed by means of Fourier transform IR spectroscopy in a multireflection gas cell (optical path length, 2.4 m) and by gas chromatography (3000 Micro GC, INFICON). NO conversion, CO conversion, and NO conversion to NH₃ were calculated by means of the following equations:

\[ \text{NO conversion} \text{%} = \frac{(\text{NO}_\text{in} - \text{NO}_\text{out})}{\text{NO}_\text{in}} \times 100 \quad (2) \]

\[ \text{CO conversion} \text{%} = \frac{(\text{CO}_\text{in} - \text{CO}_\text{out})}{\text{CO}_\text{in}} \times 100 \quad (3) \]

\[ \text{CO conversion to NH}_3 \text{%} = \frac{\text{NH}_3_\text{out}}{(\text{NH}_3_\text{tot} + 2\text{N}_2_\text{out} + 2\text{N}_2\text{O}_\text{out})} \quad (4) \]

Reaction orders were calculated by means of a power-law rate equation:

\[ r = kP_{\text{NO}}^{m}P_{\text{CO}}^{n}P_{\text{H}_2\text{O}}^{p} \quad (5) \]

where \( r \) is rate of the NH₃ synthesis reaction (in mol g⁻¹ h⁻¹); \( k \) is the rate constant; and \( l, m, n \) are the reaction orders with respect to NO, CO, and H₂O, respectively. Additional details regarding experimental conditions are described in a previous paper¹¹⁻¹³⁻¹.

2.3. Characterizations

The crystal structures of the catalysts and supports were determined by X-ray diffraction analysis (SmartLab, Rigaku Corp.) under the following conditions: scan speed, 0.2°; scan step, 1°; and 2\( \theta \) range, 20-60°). The crystallite sizes of the TiO₂ supports were estimated by means of the Scherrer equation. N₂ adsorption-desorption isotherms were measured at −196 °C (BELSORP-mini II, MicrotracBEL Corp.). Specific surface areas and pore size distributions were calculated by means of the Brunauer-Emmett-Teller equation and the Barrett-Joyner-Halenda method, respectively.

Platinum dispersions were calculated by means of

| Reaction          | Balance gas | NO [%] | CO [%] | H₂O [%] | CO₂ [%] |
|-------------------|-------------|--------|--------|---------|---------|
| NO-CO-H₂O         | Ar          | 0.1    | 0.3    | 1       | -       |
| CO-H₂O            | Ar          | -      | 0.3    | 1       | -       |
| NO-CO-H₂O-CO₂     | Ar          | 0.1    | 0.3    | 1       | 1       |
CO pulse adsorption (BEL-METAL-3, MicrotracBEL Corp.). Catalyst samples were oxidized with O₂ (99.9999 %) at 400 °C for 20 min and then reduced with H₂ (99.9999 %) at 400 °C for 20 min. The distributions of Pt particle sizes were estimated by transmission electron microscopy (TEM) analysis (JEM-2100F, JEOL Ltd.); the sizes were estimated to be in the range between 0 nm and 3.2 nm.

Temperature-programmed reduction by hydrogen (H₂-TPR) was carried out as follows. Each catalyst sample (150 mg) was placed in a quartz tube, and measurements were performed with a Cyrocat (MicrotracBEL Corp.). The samples were pretreated by oxidation at 500 °C for 1 h, cooled to −70 °C, and then treated with H₂ (1 vol% in helium, 50 mL min⁻¹) at −70 °C. The effluent gas was analyzed by time of flight mass spectrometry (JMS-MT3010HRGA, JEOL Ltd.). After the signal for H₂ at \( m/z \) stabilized, the samples were heated to 800 °C (10 °C min⁻¹).

Temperature-programmed desorption of CO₂ (CO₂-TPD) was carried out in a flow reactor system equipped with a quadrupole mass spectrometer (Microvision, Spectra Co.). Each sample (150 mg) was placed in the quartz reactor used for the activity tests and reduced at 400 °C for 30 min with H₂ (10 vol% in helium). Next, the sample was purged with helium gas at 400 °C for 30 min and cooled to room temperature. The sample was then treated with a flow of CO₂ (10 vol% in helium) until saturation of the mass signal for CO₂ at \( m/z \) 44. Finally, the sample was purged with helium for 30 min and then heated to 500 °C (at 10 °C min⁻¹) while the signal at \( m/z \) 44 was monitored.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurement was carried out with an iS50 spectrometer (Thermo Fisher Scientific K. K.) equipped with a DRIFT cell. Each catalyst was placed in the cell of Heat Chamber Type-1000 °C (S. T. Japan Inc.) and reduced under H₂ at 400 °C for 30 min, cooled to room temperature, and then exposed to a flow of 0.3 % CO and 0.5 % H₂O (bubbling at 10 °C) with and without 0.1 % NO in He. Total gas flow was 30 mL min⁻¹. Background was measured under He in the presence of 0.5 % H₂O. The spectra of Pt/TiO₂(A)H and Pt/TiO₂(R)H were measured at 150 °C and 200 °C.

Temperature-programmed desorption of NH₃ (NH₃-TPD) was carried out in a flow reactor system equipped with a quadrupole mass spectrometer (Microvision, Spectra Co.). Each sample (100 mg) was placed in the quartz reactor used for the activity tests and reduced at 400 °C for 30 min with H₂ (10 vol% in argon). Next, the sample was purged with argon gas at 400 °C for 30 min and cooled to room temperature. The sample was then treated with a flow of NH₃ (0.5 vol% in argon) until saturation of the mass signal for NH₃ at \( m/z \) 17. Finally, the sample was purged with argon for 1 h and then heated to 600 °C (at 10 °C min⁻¹) while the signal at \( m/z \) 17 was monitored.

### 2.4. Catalytic Activities

#### 2.4.1. Activity Test

The activities of the Pt/TiO₂ catalysts for the NOₐ COₐ H₂O reaction were measured, and the results are shown in Fig. 1. The NO conversions at 110 °C for Pt/TiO₂(A)H and Pt/TiO₂(R)H were 33 % and 21 %, respectively, and the temperatures at which NO conversion reached 90 % were 200 °C and 180 °C (Fig. 1a). That is, at low temperature, Pt/TiO₂(A)H exhibited higher NO conversion than Pt/TiO₂(R)H, but almost complete NO conversion was achieved at a lower temperature with Pt/TiO₂(A)H than with Pt/TiO₂(R)H. Over Pt/TiO₂(A)L and Pt/TiO₂(R)L, NO conversion was complete at temperatures above 325 °C and 225 °C, respectively, and the temperatures at which NO conversion reached 10 % were 225 °C and 125 °C (Fig. 1a). The trends for NO conversion to NH₃ were similar to those for NO conversion for all the catalysts except Pt/ TiO₂(A)L (Fig. 1b); over this catalyst, the maximum
NO conversion to NH₃ was 90 %, whereas NO conversion reached almost 100 %. These results suggest that high NH₃ selectivity was due mainly to high surface area, and that the effects of the crystal structure of the support were negligible. The trends in CO conversion for the catalysts were similar to those for NO conversion (Fig. 1c), because the CO concentration in the feed was slightly higher than the stoichiometric concentration.

The activities of Pt/TiO₂ catalysts for the NO-CO reaction and CO-H₂O reaction were performed. NH₃ formation were not confirmed during NO-CO reaction for all catalysts. The results of CO-H₂O reaction were shown in Fig. 2. CO conversion of Pt/TiO₂(A)L and Pt/TiO₂(R)L were lower than that for the NO-CO-H₂O reaction. Previously, we supposed that the CO-H₂O reaction could an origin of hydrogen supply for NH₃ formation11). For high-surface-area catalysts, CO conversion increased with increasing temperature, and then decreased along with the equilibrium line. CO conversion for Pt/TiO₂(R)H was lower than that of the NO-CO-H₂O reaction as well as the low-surface area catalysts. On the contrary, Pt/TiO₂(A)H exhibited higher CO conversion that of the NO-CO-H₂O reaction at around 200 °C. It is noted that for Pt/TiO₂(A)H and Pt/TiO₂(R)H, CO conversion of that NO-CO-H₂O reaction exceeded the equilibrium of CO conversion. This behavior may be due to consumption of H₂ formed from the CO-H₂O reaction by the reaction to form NH₃. From these results, Pt/TiO₂(A)H showed different behavior of hydrogen supply from the CO-H₂O reaction.

2. 4. 2. Kinetic Measurements

The reaction orders for the NO-CO-H₂O reaction are listed in Table 2 for the four Pt/TiO₂ catalysts. In all cases, the order with respect to NO was positive. For Pt/TiO₂(A)H and Pt/TiO₂(R)H the orders with respect to CO were close to zero, whereas for Pt/TiO₂(A)L and Pt/TiO₂(R)L, the orders were −0.47 and −0.54, respectively. These results suggest CO poisoning of the low-surface-area catalysts occurred regardless of the crystal structure of the support. The reaction orders with respect to H₂O for Pt/TiO₂(A)H and Pt/TiO₂(A)H were positive, and those for Pt/TiO₂(A)L and Pt/TiO₂(R)L were close to zero. Previously, we reported that the reaction orders with respect to CO and H₂O for Pt/TiO₂(A) differed from the corresponding values for Pt/TiO₂(R)L11). These results suggest that the differences between the reaction orders were due not to differences in crystal structure but to differences in surface area. In our previous report, we speculated that H₂O adsorption on TiO₂ and subsequent reaction are an important source of hydrogen to form NH₃. If this is in fact the case, surface area would be the most important factor controlling the rate of H₂O activation. That is, the number and/or the density of H₂O-activation sites on the TiO₂ surface would strongly influence the rate of NO-CO-H₂O reaction, independent of the crystal structure.

2. 5. Characterization of Physical Properties

2. 5. 1. X-ray Diffraction and N₂ Adsorption

To investigate the difference in activity, we attempted to elucidate differences in the physical properties of the Pt/TiO₂ catalysts. The X-ray diffraction (XRD) patterns of the catalysts and supports are shown in Fig. 3. All the peaks in the patterns of Pt/TiO₂(A)H, TiO₂(A)H, Pt/TiO₂(R)H, and TiO₂(R)H were broader than the peaks in the Pt/TiO₂(A)L, TiO₂(A)L, Pt/TiO₂(R)L, and TiO₂(R)L patterns, suggesting that the samples with high specific surface area consisted of TiO₂ with a small crystallite size. The TiO₂ crystallite sizes, as calculated by means of the Scherrer equation, are listed in Table 3. The Pt/TiO₂(A)H and Pt/TiO₂(R)H crystallite sizes were almost the same. The diffraction peak at 39.8°, which was assigned to metallic Pt, was ob-

| Catalyst   | Temp. [°C] | l   | m   | n   | Report     |
|------------|------------|-----|-----|-----|------------|
| Pt/TiO₂(A)H| 125        | 0.34| −0.06| 0.39| Ref. 11    |
| Pt/TiO₂(A)L| 200        | 0.27| −0.46| 0.06| this report|
| Pt/TiO₂(R)H| 100        | 0.32| −0.06| 0.20| this report|
| Pt/TiO₂(R)L| 150        | 0.60| −0.54| 0.01| this report|
served only for Pt/TiO$_2$(A)L; Pt/TiO$_2$(R)L did not show a peak for Pt diffraction. Taken together with the results of the activity measurements, these results indicate that NH$_3$ selectivity in the NO-CO-H$_2$O reaction increased with decreasing crystallite size for both anatase and rutile TiO$_2$.

Nitrogen adsorption-desorption isotherms are shown in Fig. 4a. Pt/TiO$_2$(A)H and Pt/TiO$_2$(R)H exhibited a hysteresis loop. The specific surface areas ($S_{BET}$) of the catalysts, as calculated by means of the Brunauer-Emmett-Teller equation, are listed in Table 3. The values decreased in the order Pt/TiO$_2$(A)H $>$ Pt/TiO$_2$(R)H $>$ Pt/TiO$_2$(R)L $>$ Pt/TiO$_2$(A)L. Pt/TiO$_2$(A)H and Pt/TiO$_2$(R)H had much larger surface areas than Pt/TiO$_2$(R)L and Pt/TiO$_2$(A)L. Pore size distributions were determined by means of the Barrett-Joyner-Halenda method and are shown in Fig. 4b. The mean pore diameters for Pt/TiO$_2$(A)H and Pt/TiO$_2$(R)H were 4.7 nm and 19 nm, respectively.

Measurements of the activity of the catalysts in the NO-CO-H$_2$O reaction revealed that gradual decline was appeared at temperatures at which NO and CO conversions exceeded 95%, especially in the case of the Pt/TiO$_2$(A)H catalyst. Taken together with the XRD and N$_2$ adsorption results, these results indicate that similar crystallite sizes and the surface area of Pt/TiO$_2$(A)H had 1.8 times than that of Pt/TiO$_2$(R)H. Next, we investigated how the chemical aspects of the catalyst

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**Table 3** Physical Properties of Pt Catalysts

| Catalyst       | Crystallite size$^a$ [nm] | $S_{BET}$ [m$^2$ g$^{-1}$] | $d_{BET}$$^b$ [nm] | CO/Pt | Mean Pt particle size [nm] |
|----------------|---------------------------|----------------------------|-------------------|-------|---------------------------|
| Pt/TiO$_2$(A)H | 19 (18)                   | 93                         | 4.7               | 0.32  | 3.5                       |
| Pt/TiO$_2$(A)L | 43 (42)                   | 7.9                        | -                 | 0.04  | 28                        |
| Pt/TiO$_2$(R)H | 22 (22)                   | 53                         | 19                | 0.26  | 4.4                       |
| Pt/TiO$_2$(R)L | 42 (41)                   | 12                         | -                 | 0.34  | 3.4                       |

$^a$ Calculated by means of the Scherrer equation using the half-widths of the anatase TiO$_2$ (101) and rutile TiO$_2$ (110) peaks, respectively. Numbers in parentheses are the crystallite sizes of the supports.

$^b$ Mean pore diameter.
surface related with the activity.

2.5.2. CO Pulse Adsorption and Transmission Electron Microscopy Measurement

To determine the morphology of the Pt particles, we carried out CO pulse adsorption experiments; the CO/Pt molar adsorption ratios and estimated mean particle sizes are listed in Table 3. Comparison of the CO/Pt ratios for the four catalysts suggests that Pt dispersion on anatase TiO₂ depended on specific surface area, whereas that on rutile TiO₂ did not. The mean particle sizes estimated on the basis of CO adsorption were 3.5, 28, 4.4, and 3.4 nm for Pt/TiO₂(A)H, Pt/TiO₂(A)L, Pt/TiO₂(R)H, and Pt/TiO₂(R)L, respectively. To obtain additional information about Pt particle size, we also obtained TEM images (Fig. 5) and used them to calculate particle size distributions (Table 3). Comparison of the mean particle sizes calculated on the basis of CO adsorption and TEM revealed that the two values for Pt/TiO₂(A)H and Pt/TiO₂(R)H were comparable, suggesting that the dispersion of Pt particles observed in Fig. 5a were representative of the entire surface. For Pt/TiO₂(A)L and Pt/TiO₂(R)L, the values determined by CO adsorption were higher than the TEM values. The particle size distributions for these two catalysts indicate that there were some relatively large Pt particles, which would have increased the mean particle size as measured by CO adsorption. For Pt/TiO₂(A)L, the mean particle size based on CO adsorption was much larger than that based on TEM. As shown in Fig. 5b, there were in fact some large Pt particles in this catalyst. Although the TEM image of Pt/TiO₂(A)L showed small Pt particles, Pt particles would be mainly consisted of the large agglomeration. Consideration of the size and morphology of the Pt particles on TiO₂(A)H and TiO₂(R)H indicated that there was no correlation between activity and Pt morphology. This result suggests that the physical properties of Pt were the critical determinant of activity. Therefore, we focused on the differences in chemical properties.

2.6. Characterization of Chemical Properties

2.6.1. Temperature Programmed Reduction by Hydrogen Measurement

The H₂-TPR profile of Pt/TiO₂(A)H (Fig. 6a) showed reduction peaks at 126 °C and 200-560 °C, which were attributed to reduction of PtOₓ species and surface oxygen of TiO₂, respectively. In the profile for TiO₂(A)H, the peaks at 370-715 °C were attributed to surface oxygen of TiO₂. The fact that the TiO₂ reduction peak for Pt/TiO₂(A)H appeared at a much lower temperature than that for TiO₂(A)H suggests a strong interaction between Pt and TiO₂. For Pt/TiO₂(R)H (Fig. 6b), reduction peaks were observed at 126, 379, and 635 °C and were attributed to PtOₓ species, surface oxygen of TiO₂, and some of the bulk TiO₂, respectively. The reduction peaks for TiO₂(R)H appeared at 16 °C and 430-730 °C. These results suggest that the interaction between Pt and rutile TiO₂ was also strong. In our previous study, we observed a small reduction peak at 50 °C for rutile TiO₂ (5 m² g⁻¹), and there was no peak shift due to Pt loading. Comparison of these previous results suggests that when the TiO₂ support has a high specific surface area (small crystallite size), Pt and TiO₂ interact strongly, regardless of the crystal structure. The temperature for the PtOₓ reduction peak was the same for both Pt/TiO₂(A)H and Pt/TiO₂(R)H, suggesting that Pt particles on these
supports had similar reducibilities. These results indicate that the chemical properties of Pt, such as reducibility and Pt-TiO₂ interactions, were similar, despite that fact that the reducibilities of anatase and rutile TiO₂ differed, and their surface chemical properties can be expected to differ.

2.6.2. Temperature Programmed Desorption by Carbon Dioxide

To evaluate the differences in their surface chemical properties, we investigated the desorption behavior of the CO₂ product gas by means of CO₂-TPD: profiles for Pt/TiO₂(A)H and Pt/TiO₂(R)H are shown in Fig. 7. The profile for Pt/TiO₂(A)H had one desorption peak (at 66 °C), whereas the profile for Pt/TiO₂(R)H had three peaks (at 67, 135 [shoulder], and 288 °C). The amount of CO₂ desorbed from Pt/TiO₂(R) was larger than the amount desorbed from Pt/TiO₂(A), indicating that Pt/TiO₂(R)H adsorbed CO₂ more strongly than Pt/TiO₂(A)H did. Because declining CO conversion was observed on Pt/TiO₂(A)H, we suspect that the interaction between CO₂ and the rutile TiO₂ surface was less related to the activity. To clarify the effect of the CO₂ generated during the NO-CO-H₂O reaction, we carried out NO-CO-H₂O-CO₂ reactions over Pt/TiO₂(A)H and Pt/TiO₂(R)H (Fig. 8). For both catalysts, the temperature dependence of NO conversion during the NO-CO-H₂O-CO₂ reaction was almost identical to that during the NO-CO-H₂O reaction (Fig. 8a), and the same was true for the temperature dependence of NO conversion to NH₃ (Fig. 8b). These results suggest that the CO₂ produced during the NO-CO-H₂O reaction did not influence activity.

2.6.3. Diffuse Reflectance Infrared Fourier Transform Spectroscopy and Temperature Programmed Desorption by Ammonia

DRIFTS measurement was carried out to confirm intermediates during the NO-CO-H₂O reaction on Pt/TiO₂(A)H and Pt/TiO₂(R)H at 150 °C and 200 °C, and the results are shown in Fig. 9. In the spectra of Pt/TiO₂(A)H during the NO-CO-H₂O reaction at 150 °C and 200 °C was confirmed negative peak at 3650-3500 cm⁻¹ and positive peak at 3500-3100 cm⁻¹ in Fig. 9a (i, iii), and these peaks were attributed to surface OH groups on TiO₂ and NH₃ species. Negative peak means that OH groups were consumed in the reaction. Similarly, negative peak at 3800-3550 cm⁻¹ and 3500-3100 cm⁻¹ was confirmed on Pt/TiO₂(R)H. The peaks at 1590 cm⁻¹ and 1220 cm⁻¹ were attributed to nitrate species. The peaks at 1428 cm⁻¹ and 1180 cm⁻¹ were attributed to v(ending) symmetry of NH₃. All peaks became smaller with increasing temperature. It is noted that the peaks attributed to formate species on Pt/TiO₂(A)H were almost disappeared at 200 °C. Taking into account of lower CO conversion at around 200 °C in the NO-CO-H₂O reaction than that in the CO-H₂O reaction, decrease in peak intensity for formate
species is suspected to relate with the decline of CO conversion. NH$_3$ formation at around 200 °C in the NO-CO-H$_2$O reaction responded to suppressed CO conversion. Since the CO-H$_2$O reaction could supply hydrogen to form NH$_3$, the formate species was likely to be a supply source of hydrogen to form NH$_3$ in the NO-CO-H$_2$O reaction.

We carried out NH$_3$-TPD to investigate the effect of formed NH$_3$ adsorption on the activity of the NO-CO-H$_2$O reaction. The NH$_3$ evolution profiles for Pt/TiO$_2$(A)H and Pt/TiO$_2$(R)H are shown in Fig. 10. For Pt/TiO$_2$(A)H, NH$_3$ evolution peaks appeared at 104 °C and 262 °C; for Pt/TiO$_2$(R)H, there were peaks at 108 °C and 287 °C. These results suggest that strength of acid sites was similar. The area of NH$_3$ desorption profile for Pt/TiO$_2$(A)H was larger than that for Pt/TiO$_2$(R)H, though the desorption amounts of NH$_3$ per unit surface area for Pt/TiO$_2$(A)H and Pt/TiO$_2$(R)H were 1.4 intensity/m$^2$ and 1.3 intensity/m$^2$, respectively. These results suggest that the acidic properties of the high-surface-area TiO$_2$ supported Pt catalysts were similar. So, effect of the acidic property of TiO$_2$ surface on the catalytic activity was excluded.

3. Conclusions

We investigated the NO-CO-H$_2$O reaction and CO-H$_2$O reaction over Pt supported on rutile and anatase

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**Fig. 8** Temperature Dependence of (a) NO Conversion and (b) NO Conversion to NH$_3$ for Pt/TiO$_2$(A)H (●) and Pt/TiO$_2$(R)H (■) for a Reaction Mixture Consisting of 0.1 % NO, 0.3 % CO, 1 % H$_2$O, and 1 % CO$_2$ with Argon as the Balance Gas; and Pt/TiO$_2$(A)H (○) and Pt/TiO$_2$(R)H (□) for a Reaction Mixture Consisting of 0.1 % NO, 0.3 % CO, and 1 % H$_2$O with Argon as the Balance Gas.

**Fig. 9** Diffuse Reflectance Infrared Fourier Transform Spectra of Pt/TiO$_2$(A)H (i, iii) and Pt/TiO$_2$(R)H (ii, iv).

Reaction mixture: 0.1 % NO, 0.3 % CO and 0.5 % H$_2$O in helium. Reaction temperature was 150 °C (i, ii) and 200 °C (iii, iv).
TiO₂ with high and low specific surface areas. Catalytic activity tests of NO-CO-H₂O reaction revealed that at around 100 °C, Pt/TiO₂(A)H, which has a high specific surface area, showed higher activity than the other three tested catalysts; although Pt/TiO₂(R)H, which also has high specific surface area, showed 100% NO conversion to NH₃ at a lower temperature than Pt/TiO₂(A)H. The catalytic activity test of CO-H₂O reaction showed difference in activity of CO conversion on Pt/TiO₂(A)H compared to Pt/TiO₂(R)H. The two Pt/TiO₂ catalysts with low specific surface areas exhibited lower activity for NO-CO-H₂O reaction than the two catalysts with high specific surface areas. Measurements of the kinetic parameters revealed that the reaction orders with respect to CO and H₂O depended not on the crystal structure of the TiO₂ but on its surface area. The TiO₂ crystal structure was found to influence the activity. XRD analysis, pore size distributions calculated by means of N₂ adsorption experiments, and Pt dispersions calculated by means of CO pulse adsorption experiments and TEM showed no clear relationship between these results and catalytic activity. CO₂-TPD and tests of the catalyst activities in the NO-CO-H₂O-CO₂ reaction revealed that the CO₂ produced by the NO-CO-H₂O reaction did not affect to activity. DRIFTS measurements of these catalysts suggested that the behavior of formate species against temperature was different at 200 °C between anatase and rutile TiO₂ support. Adsorbed NH₃ observed by DRIFTS was no related to difference in activity. We suspect that behavior of formate species formation on the catalyst surfaces was related to NH₃ formation. Therefore, we concluded that difference of crystalline structure of TiO₂ influenced on the surface formate species formation, and then catalytic activity of NH₃ formation in the NO-CO-H₂O reaction was affected on the surface species.

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要  旨

酸化チタン担持白金触媒上での水存在下の一酸化窒素の一酸化炭素による還元における担体表面特性に対する活性への影響

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燃焼プロセスから放出される反応性窒素種を有用な化合物の合成の原料として利用する方法を開発することを目標に、Pt/TiO2触媒上での NO-CO-H2O 反応を利用して、NO から NH3 への選択的変換を検討した。触媒活性試験により、250 ℃未満では高比表面積担体を用いた触媒の活性が担体の結晶構造に依存することが明らかになった。NH3 生成に必要な水素の供給反応の一つと考えられる CHO-H2O と NO-CO-H2O 反応の CO 転化率を比較した。ルチル型 TiO2 担持白金触媒は NO-CO-H2O 反応の CO 転化率が CO-H2O 反応の CO 転化率よりも高くなったのに対して、アナターゼ型 TiO2 担持白金触媒では 200 ℃付近で CO-H2O 反応の CO2 転化率の方が高くなり、TiO2 結晶構造の違いによって反応性に差が生じることが分かった。触媒表面の化学的および物理的特性が活性に与える影響を明らかにするために種々のキャラクタリゼーションを行った。CO2-TPD 測定により、NO-CO-H2O 反応中に形成された CO2 が活性に影響がないことが明らかになった。DRIFTS 測定によって、NO-CO-H2O 反応下で触媒に吸着した formate 種およびアンモニア種を確認した。特に formate 種はアナターゼ上でのみ 200 ℃で消失することを確認し、formate 種の生成と NH3 生成には関連があることが示唆された。以上の結果から、TiO2 表面で形成される formate 種の生成が NO-CO-H2O 反応における NH3 生成に影響を及ぼすと考えた。