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Effect of Chemical and Physical Properties of Titanium Oxide Support Surface during Nitrogen Monoxide Reduction by Carbon Monoxide in Presence Water over Titanium Oxide Supported Platinum Catalyst

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With the goal of developing a method for utilizing reactive nitrogen species emitted from combustion processes as raw materials for the synthesis of useful compounds, we investigated the selective conversion of NO_x to NH₃ by means of the NO-CO-H₂O reaction over Pt/TiO₂ catalysts. High NH₃ selectivity was obtained for high-specific-surface-area catalysts. Catalytic activity tests revealed that the activities of catalysts depended on the crystal structure of the support. Comparing CO conversion between NO-CO-H₂O reaction and CO-H₂O reaction, which could play a role of H-supply reaction, Pt/TiO₂ exhibited higher CO conversion for the NO-CO-H₂O reaction than that for CO-H₂O reaction except for high-surface-area anatase TiO₂-supported catalyst around 200 °C. We focused on how the chemical and physical properties of the catalyst surface. Specifically, we carried out temperature-programmed desorption of CO₂, which revealed that the CO₂ formed during the NO-CO-H₂O reaction had no effect on the difference in activity. Carbonaceous surface species and NH_x species were observed on the surface of Pt/TiO₂ catalyst during NO-CO-H₂O reaction by diffused reflectance infrared Fourier transform spectroscopy, and difference in formate formation on anatase-TiO₂ supported Pt catalyst was confirmed compared to rutile-TiO₂ supported Pt catalyst. We supposed that the difference in activity between anatase and rutile TiO₂ was caused by behavior of formate formation.

Keywords

Platinum catalyst, Titanium oxide support, Nitrogen oxide, Ammonia

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 arguent issue to optimize and control the nitrogen circulation in the nature.

Nitrogen oxides (NO_x) are mainly emitted by vehicles and the thermal power plant using fossil fuels like coal, petroleum, natural gas²⁾. Methods for reducing NO_x emissions include NO_x storage/reduction, lean NO_x

traps, and selective catalytic reduction; and the literature on these methods is vast^{3)~8)}. A major deNO_x technic is by NH₃, whereby NO_x is reduced to N₂ by NH₃:

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 carrier^{9),10)}, we have been studying catalysts for NO conversion to NH₃. We recently proposed a concept, designated recNO_x, for recovery of NO_x as the energy carrier¹¹⁾. If NO_x can

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Table 1 Activity Test Conditions

Reaction	Balance gas	NO [%]	CO [%]	H ₂ O [%]	CO ₂ [%]
NO-CO-H ₂ O	Ar	0.1	0.3	1	-
CO-H ₂ O	Ar	-	0.3	1	-
NO-CO-H ₂ O-CO ₂	Ar	0.1	0.3	1	1

be converted to useful substances such as NH₃, then a higher concentration of NO_x 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 recNO_x systems can be expected to considerably decrease CO₂ emissions.

There are two ways to generate NH₃ from NO_x: the NO-H₂ reaction ($2\text{NO} + 5\text{H}_2 \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O}$) and the NO-CO-H₂O reaction ($2\text{NO} + 5\text{CO} + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_3 + 5\text{CO}_2$)^{12)~16)}. Although the NO-H₂ reaction proceeds at temperatures as low as 100 °C, forming NH₃ with high selectivity is difficult under stoichiometric conditions^{16),17)}, and high NH₃ selectivity is necessary for efficient recovery of NO_x. We previously reported that a Pt/TiO₂-catalyzed NO-CO-H₂O reaction shows high NH₃ selectivity in the temperature range from 100 to 300 °C^{11),18)}. 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⁾. 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 crystallites^{19)~21)}. In our previous study, we evaluated the effects of the crystal structure of TiO₂ supports with different surface areas¹¹⁾, 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 pow-

dered 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:

$$\text{NO conversion (\%)} = (\text{NO}_{\text{in}} - \text{NO}_{\text{out}}) / \text{NO}_{\text{in}} \times 100 \quad (2)$$

$$\text{CO conversion (\%)} = (\text{CO}_{\text{in}} - \text{CO}_{\text{out}}) / \text{CO}_{\text{in}} \times 100 \quad (3)$$

$$\text{CO conversion to NH}_3 (\%) = \frac{\text{NH}_{3\text{out}}}{(\text{NH}_{3\text{out}} + 2\text{N}_{2\text{out}} + 2\text{N}_2\text{O}_{\text{out}})} \quad (4)$$

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

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

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

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, 1.0°; and 2θ 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 mixture: 0.1 % NO, 0.3 % CO, 1 % H₂O in argon as the balance gas.

Fig. 1 Temperature Dependence of (a) NO Conversion, (b) NO Conversion to NH₃, and (c) CO Conversion for Pt/TiO₂(A)H (●), Pt/TiO₂(A)L (○), Pt/TiO₂(R)H (■), and Pt/TiO₂(R)L (□)

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* 2 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 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 NO-CO-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(R)H than with Pt/TiO₂(A)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 NH_3 was 90 %, whereas NO conversion reached almost 100 %. These results suggest that high NH_3 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. NH_3 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 NH_3 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 than 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 reac-

tion 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 NH_3 . 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 that 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 NH_3 ¹¹⁾. 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-

Reaction mixture: 0.3 % CO, 1 % H₂O in argon as the balance gas.

Fig. 2 Temperature Dependence of CO Conversion for Pt/TiO₂(A)H (●), Pt/TiO₂(A)L (○), Pt/TiO₂(R)H (■), Pt/TiO₂(R)L (□) and Equilibrium Conversion (dashed line)

Table 2 Reaction Orders with Respect to NO (*l*), CO (*m*) and H₂O (*n*) for the NO-CO-H₂O Reaction

Catalyst	Temp. [°C]	<i>l</i>	<i>m</i>	<i>n</i>	Report
Pt/TiO ₂ (A)H	125	0.34	-0.06	0.39	Ref. 11)
Pt/TiO ₂ (A)L	200	0.27	-0.46	0.06	this report
Pt/TiO ₂ (R)H	100	0.32	-0.06	0.20	this report
Pt/TiO ₂ (R)L	150	0.60	-0.54	0.01	this report

served only for Pt/TiO₂(A)L; Pt/TiO₂(R)L did not show a peak for Pt diffraction. Taken together with the results of the activity measurements, these results indicate that NH₃ selectivity in the NO-CO-H₂O reaction in-

Fig. 3 X-ray Diffraction Patterns of Pt/TiO₂ Catalysts and TiO₂ Supports

creased with decreasing crystallite size for both anatase and rutile TiO₂.

Nitrogen adsorption-desorption isotherms are shown in **Fig. 4a**. Pt/TiO₂(A)H and Pt/TiO₂(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/TiO₂(A)H $\gg$ Pt/TiO₂(R)H $\gg$ Pt/TiO₂(R)L $>$ Pt/TiO₂(A)L. Pt/TiO₂(A)H and Pt/TiO₂(R)H had much larger surface areas than Pt/TiO₂(R)L and Pt/TiO₂(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/TiO₂(A)H and Pt/TiO₂(R)H were 4.7 nm and 19 nm, respectively.

Measurements of the activity of the catalysts in the NO-CO-H₂O reaction revealed that gradual decline was appeared at temperatures at which NO and CO conversions exceeded 95 %, especially in the case of the Pt/TiO₂(A)H catalyst. Taken together with the XRD and N₂ adsorption results, these results indicate that similar crystallite sizes and the surface area of Pt/TiO₂(A)H had 1.8 times than that of Pt/TiO₂(R)H. Next, we investigated how the chemical aspects of the catalyst

Fig. 4 (a) Nitrogen Adsorption-desorption Isotherms and (b) Pore Size Distributions for Pt/TiO₂(A)H (●), Pt/TiO₂(A)L (○), Pt/TiO₂(R)H (■), and Pt/TiO₂(R)L (□)

Table 3 Physical Properties of Pt Catalysts

Catalyst	Crystallite size ^{a)} [nm]	S_{BET} [m ² g ⁻¹]	d_{BJH} ^{b)} [nm]	CO/Pt	Mean Pt particle size [nm]	
					CO pulse	TEM
Pt/TiO ₂ (A)H	19 (18)	93	4.7	0.32	3.5	1.3
Pt/TiO ₂ (A)L	43 (42)	7.9	-	0.04	28	1.6
Pt/TiO ₂ (R)H	22 (22)	53	19	0.26	4.4	1.1
Pt/TiO ₂ (R)L	42 (41)	12	-	0.34	3.4	1.7

a) Calculated by means of the Scherrer equation using the half-widths of the anatase TiO₂ (101) and rutile TiO₂ (110) peaks, respectively. Numbers in parentheses are the crystallite sizes of the supports.

b) Mean pore diameter.

Fig. 5 Transmission Electron Microscopy Images (a1-d1) and Pt Particle Size Distributions of Pt/TiO₂ Catalysts (a2-d2): (a) (A)H, (b) (A)L, (c) (R)H, and (d) (R)L

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 PtO_x species and surface oxygen of TiO₂, respectively²². 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 TiO₂²³. For Pt/TiO₂(R)H (**Fig. 6b**), reduction peaks were observed at 126, 379, and 635 °C and were attributed to PtO_x species, surface oxygen of TiO₂, and some of the bulk TiO₂, respectively^{22,24}. 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 loading¹¹. 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 PtO_x 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)H, indicating that Pt/TiO₂(R)H adsorbed CO₂ more strongly than Pt/TiO₂(A)H did. Because decline 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 to activity.

Fig. 6 H₂-Temperature-programmed Reduction Profiles of Pt/TiO₂(A)H (a, black), TiO₂(A)H (a, gray), Pt/TiO₂(R)H (b, black), and TiO₂(R)H (b, gray)

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 NH_x 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 spectra at 1590, 1530, 1428, 1379, 1367, 1220 and 1180 cm⁻¹ were observed on Pt/TiO₂(A)H in Fig. 9b-i. The peaks at 1590 cm⁻¹ and 1220 cm⁻¹ were attributed to nitrate species²⁵. The peaks at 1428 cm⁻¹ and 1180 cm⁻¹ were attributed to vending symmetry of NH₃^{26,27}. The peaks at 1530, 1379 and 1367 cm⁻¹ were attributed to formate species^{28,29}. For Pt/TiO₂(R)H, the peaks at 1600, 1545, 1435, 1381, 1362, 1350, 1224 and 1181 cm⁻¹ were observed (Fig. 9b-ii). The peaks at 1600 cm⁻¹ and 1224 cm⁻¹ were attributed to nitrate species²⁵. The peaks at 1428 cm⁻¹ and 1181 cm⁻¹ were attributed to vending symmetry of NH₃^{26,27}. The peaks at 1545, 1381, 1362 and 1350 cm⁻¹ was attributed to formate species^{28,29}. 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

Fig. 7 CO₂-Temperature-programmed Desorption Profiles of Pt/TiO₂(A)H (solid line) and Pt/TiO₂(R)H (dashed line)

Fig. 8 Temperature Dependence of (a) NO Conversion and (b) NO Conversion to NH_3 for $\text{Pt/TiO}_2(\text{A})\text{H}$ (●) and $\text{Pt/TiO}_2(\text{R})\text{H}$ (■) for a Reaction Mixture Consisting of 0.1 % NO, 0.3 % CO, 1 % H_2O , and 1 % CO_2 with Argon as the Balance Gas; and $\text{Pt/TiO}_2(\text{A})\text{H}$ (○) and $\text{Pt/TiO}_2(\text{R})\text{H}$ (□) for a Reaction Mixture Consisting of 0.1 % NO, 0.3 % CO, and 1 % H_2O with Argon as the Balance Gas

Reaction mixture: 0.1 % NO, 0.3 % CO and 0.5 % H_2O in helium. Reaction temperature was 150 °C (i, ii) and 200 °C (iii, iv).

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

species is suspected to relate with the decline of CO conversion. NH_3 formation at around 200 °C in the NO-CO- H_2O reaction responded to suppressed CO conversion. Since the CO- H_2O 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_2O reaction.

We carried out NH_3 -TPD to investigate the effect of formed NH_3 adsorption on the activity of the NO-CO- H_2O reaction. The NH_3 evolution profiles for $\text{Pt/TiO}_2(\text{A})\text{H}$ and $\text{Pt/TiO}_2(\text{R})\text{H}$ are shown in **Fig. 10**. For $\text{Pt/TiO}_2(\text{A})\text{H}$, NH_3 evolution peaks appeared at 104 °C and 262 °C; for $\text{Pt/TiO}_2(\text{R})\text{H}$, 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 $\text{Pt/TiO}_2(\text{A})\text{H}$ was larger than that for $\text{Pt/TiO}_2(\text{R})\text{H}$, though the desorption amounts of NH_3 per unit surface area for $\text{Pt/TiO}_2(\text{A})\text{H}$ and $\text{Pt/TiO}_2(\text{R})\text{H}$ 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_2O reaction and CO- H_2O reaction over Pt supported on rutile and anatase

Fig. 10 NH_3 -Temperature-programmed Desorption Profiles of Pt/TiO₂(A)H (solid line) and Pt/TiO₂(R)H (dashed line)

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 affected 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 spec-

cies.

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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 CO-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表面上で形成される 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察した。