

[Regular Paper]

Characterization and Reactivity Analysis of Hydrogen Adspecies on Platinum Nano-particles Supported on Alumina

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The dispersion state of Pt nano-particles supported on Al₂O₃ was investigated by gas chemisorption. The amount of H₂ chemisorption was larger than that of CO over the entire range of Pt dispersion. Pt dispersion beyond 100 % was estimated for Pt/Al₂O₃ with nano-sized Pt particles by H₂ chemisorption. FT-IR measurements of hydrogen species adsorbed on Pt/Al₂O₃ with different Pt dispersions revealed that hydrogen species dissociatively adsorbed on Pt nano-particles and spilled over onto Al₂O₃. Hydrogen species dissociatively adsorbed on Pt nano-particles were highly reactive with NO at room temperature, leading to the formation of N₂. In contrast, hydrogen species spilled over onto the fringes of Pt particles reacted with NO to form N₂O.

Keywords

Platinum nano-particle, Infrared spectroscopy, Hydrogen spillover, Nitrogen monoxide

1. Introduction

Supported noble metal (Pt, Rh and Pd) catalysts are widely used in important applications, such as automotive emission control^{1,2}, catalytic combustion^{3,4}, steam reforming⁵ and various hydrogenation reactions^{6,7}. Since the catalytic reaction predominantly occurs on the catalyst surface, the particle size of the noble metal is one of the important factors to determine the catalytic activity. On the other hand, growth of noble metal particles and attendant loss of surface area are often observed under operation conditions, leading to deactivation of the supported noble metal catalysts. In particular, automotive catalysts, typified by the three-way catalyst which simultaneously and efficiently reduces NO and oxidizes CO and hydrocarbons, are exposed to high temperature exhaust gases (~1000 °C), so that sintering of the noble metal particles is one of the major reasons for the catalyst deterioration. Investigations to inhibit the sintering of noble metal particles, especially of Pt, have been extensively carried out^{8)–12)}. For example, Nagai *et al.*¹⁰⁾ reported that Pt in Pt/ceria-based oxide does not sinter after aging treatment at 800 °C in air, but does sinter in Pt/Al₂O₃. This phenomenon was explained by the formation of Pt–O–Ce bonds (*i.e.*, the Pt–oxide–support interaction) which act as an anchor for Pt particles on ceria-based oxides. Datye *et al.*¹⁴⁾ studied the sintering mechanism of Pt

particles supported on Al₂O₃ to try to form noble metal catalysts with greater durability. The sintering mechanism of Pt particles was found to depend on the atmosphere. Sintering in a reducing atmosphere at 600 °C and 700 °C can be explained by particle migration and coalescence, whereas sintering in an oxidizing atmosphere occurs by Ostwald ripening.

The optimum particle size of the noble metal is suspected to depend on the type of catalytic reaction^{15)–18)}. For example, Haruta¹⁶⁾ reported that the turnover frequencies (TOFs) of CO oxidation over Au/TiO₂ sharply increased with decreasing diameter of Au particles from 4 nm and the Pt group metals showed a decreasing or steady TOF. Denton *et al.*¹⁸⁾ investigated the influence of platinum dispersion on the activity of Pt/Al₂O₃ and Pt/SiO₂ catalysts for NO reduction with propene, and reported that the intrinsic activity increased with decreasing platinum dispersion, suggesting that platinum dispersion is the key factor. Therefore, investigation of methods to control the particle size of noble metal and to understand the catalytic performance is very important.

The present study prepared Pt/Al₂O₃ with different Pt dispersions by controlling the preparation conditions, and investigated the dispersion state of Pt particles by the gas chemisorption technique, showing that the amount of chemisorption of H₂ and CO on Pt/Al₂O₃ is quite different depending on the particle size of Pt. The behavior of hydrogen species adsorbed on Pt/Al₂O₃ with different Pt dispersion is discussed on the basis of the difference in the reactivity of hydrogen species

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toward NO.

2. Experimental

1 wt% Pt/Al₂O₃ was prepared by impregnation of Al₂O₃ (Sumitomo Chemicals, AKP-G015) with a solution of Pt(NO₂)₂(NH₃)₂, followed by drying and calcination at 500 °C for 3 h in air. The sample was further calcined at 700 °C for several hours to obtain different Pt dispersions. Heating rate for calcination was fixed at 10 °C · min⁻¹. A scanning electron microscope (SEM, JEOL-JSM7000F) was used for analysis of the dispersion state of Pt particles in the Pt/Al₂O₃ samples. The dispersion of Pt was calculated from H₂ or CO chemisorption measured by the pulse method at room temperature, in which the sample was first reduced with H₂ at 400 °C for 1 h and then cooled to room temperature in flowing He.

Fourier transform infrared (FT-IR) spectra of adsorbed hydrogen species were taken with a JASCO FT/IR 4200 spectrometer at a resolution of 4 cm⁻¹ under a static condition. Prior to each experiment, a self-supporting sample disk (14 mg · cm⁻²) was placed in an IR cell with CaF₂ windows, pretreated with hydrogen at 13.3 kPa for 1 h, and then evacuated at 400 °C for 1 h. The background spectrum of the treated surface was measured for spectral correction at room temperature. Observation of surface species was carried out after introduction of hydrogen at 6.67 kPa at room temperature.

The reactivity of hydrogen species adsorbed on Pt/Al₂O₃ was measured by the pulse method at 50 °C. The sample (0.1 g) was first reduced with H₂ at 400 °C for 1 h, then cooled to 50 °C in flowing He. After adsorption of H₂ at 50 °C, the physically adsorbed H₂ species was purged with He. Several pulses of NO (1.2 mL, 5 % NO in He) were then introduced to the sample to examine the reactivity of adsorbed hydrogen species. The gas composition desorbed from the sample was analyzed with a quadrupole mass spectrometer (M-201QA-TDM, Canon Anelva).

3. Results and Discussion

3.1. Morphology and Dispersion of Pt Supported on Al₂O₃

Figures 1(a) and 1(b) show the secondary electron image (SEM) and reflection electron image (REM) of Pt/Al₂O₃ calcined at 500 °C for 3 h and at 700 °C for 10 h, respectively. The SEM shows only surface morphology, whereas REM indicates the composition. No large Pt particles were identified in the REM image of Pt/Al₂O₃ calcined at 500 °C (Fig. 1(a)). Pt seems to be highly dispersed as nano-sized particles on the Al₂O₃ support. After calcination at 700 °C for 10 h, aggregates of Pt particles were observed in the REM image

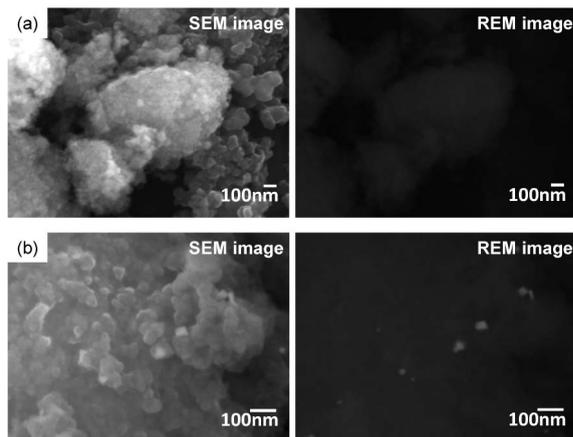
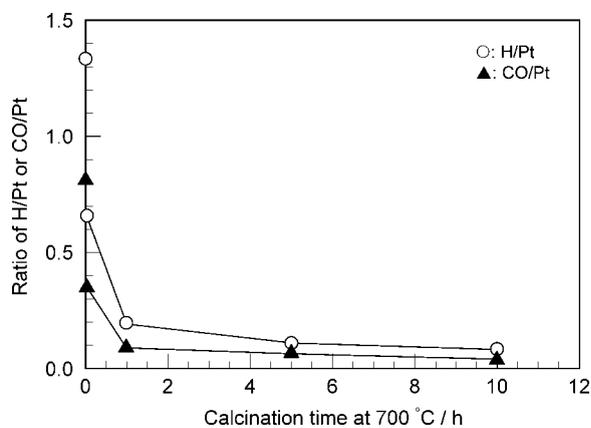


Fig. 1 SEM and REM Images of Pt/Al₂O₃ Calcined at (a) 500 °C for 3 h and (b) 700 °C for 10 h



(○) H/Pt measured by H₂ chemisorption, (▲) CO/Pt measured by CO chemisorption.

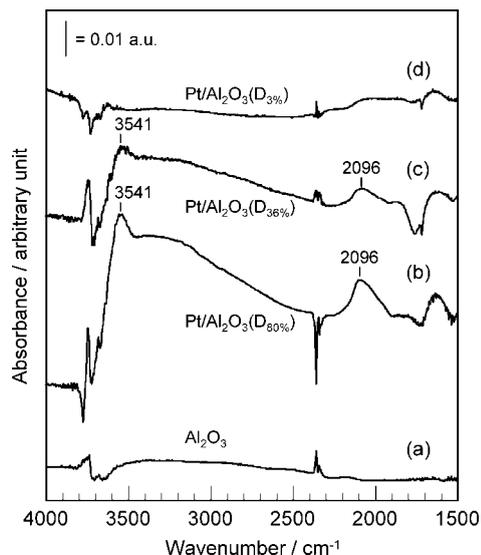
Fig. 2 Changes in H₂ and CO Chemisorption on Pt/Al₂O₃ as a Function of Calcination Time at 700 °C

(Fig. 1(b)), indicating sintering of Pt particles.

Figure 2 shows the changes in H₂ and CO chemisorption as functions of calcination time at 700 °C. H₂ and CO chemisorption monotonously decreased with increasing calcination time, suggesting that Pt dispersion can be controlled by changing the calcination time. In agreement with the results of SEM observation (Fig. 1), the sintering of Pt particles proceeds with time, leading to low Pt dispersion. Figure 2 shows that H₂ chemisorption was greater than CO chemisorption over the entire range of Pt dispersion. Pt dispersion beyond 100 % was estimated for Pt/Al₂O₃ with nano-sized Pt particles by H₂ chemisorption. This result suggests that H₂ can be adsorbed on both Pt particles and Al₂O₃ support.

3.2. Evidence of Hydrogen Spillover

In many cases, the dispersion of Pt on the Al₂O₃ support would be correctly measured by CO adsorption¹⁹⁾.



(a) Al_2O_3 , (b) $\text{Pt}/\text{Al}_2\text{O}_3$ ($D_{80\%}$), (c) $\text{Pt}/\text{Al}_2\text{O}_3$ ($D_{36\%}$) and (d) $\text{Pt}/\text{Al}_2\text{O}_3$ ($D_3\%$).

Fig. 3 FT-IR Difference Spectra of Adsorbed Hydrogen after Introduction of 6.67 kPa of H_2 at Room Temperature

However, the observation that a quite large amount of H_2 was chemisorbed on Pt nano-particles suggests the possibility of hydrogen spillover. The spillover phenomenon in heterogeneous catalysts was well summarized by Conner and Falconer²⁰. Since hydrogen spillover takes place at the interface between the metal particle and support *via* the dissociation of H_2 on the metal particles, the presence of nano-sized metal particles would be favorable. However, direct evidence of hydrogen species has often not been observed in ordinary $\text{Pt}/\text{Al}_2\text{O}_3$.

In order to confirm the possibility of hydrogen spillover on $\text{Pt}/\text{Al}_2\text{O}_3$ with high Pt dispersion, FT-IR spectra were measured to detect hydrogen species on Al_2O_3 and $\text{Pt}/\text{Al}_2\text{O}_3$ calcined at 500°C for 3 h and at 700°C for 1 min and 10 h. The dispersion of Pt on the sample calcined at 500°C was estimated to be 80 % by CO adsorption, so that the sample is here named “ $\text{Pt}/\text{Al}_2\text{O}_3$ ($D_{80\%}$)” whereas for samples calcined at 700°C are named “ $\text{Pt}/\text{Al}_2\text{O}_3$ ($D_{36\%}$)” and “ $\text{Pt}/\text{Al}_2\text{O}_3$ ($D_3\%$)” respectively. As shown in **Fig. 3**(b), in the case of $\text{Pt}/\text{Al}_2\text{O}_3$ ($D_{80\%}$) with high Pt dispersion, a distinct IR band due to hydrogen species dissociatively adsorbed on Pt was observed at 2096 cm^{-1} ²¹. In addition, the IR band due to OH group on Al_2O_3 at 3541 cm^{-1} was clearly increased after exposure to H_2 . Interestingly, a decrease in the intensity of IR bands due to hydrogen species (2096 cm^{-1}) and OH group on Al_2O_3 (3541 cm^{-1}) was observed when hydrogen was adsorbed on $\text{Pt}/\text{Al}_2\text{O}_3$ ($D_{36\%}$) (**Fig. 3**(c)). Furthermore, in the case of $\text{Pt}/\text{Al}_2\text{O}_3$ ($D_3\%$) (**Fig. 3**(d)), no increase in the IR bands due to hydrogen species and OH group on Al_2O_3 was

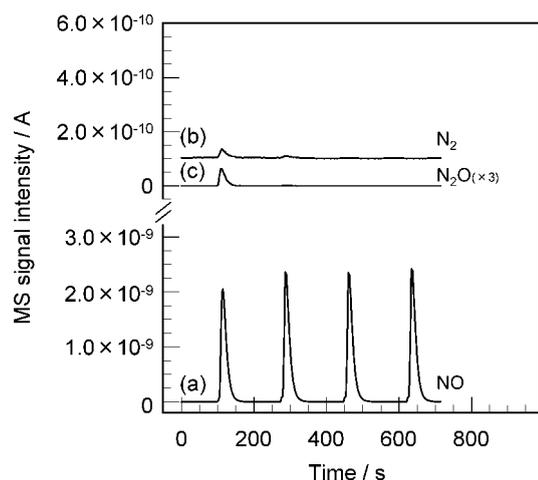
observed. Also, no change in the IR bands due to OH group on Al_2O_3 was observed for Al_2O_3 after the adsorption of H_2 (**Fig. 3**(a)). Sato *et al.*²² reported that adsorption of hydrogen on 2 wt% $\text{Ru}-\text{CsOH}/\text{MgO}$ causes the appearance of an IR band due to hydrogen species dissociatively adsorbed on Ru at 1687 cm^{-1} as well as increased band due to OH group on MgO at 3500 cm^{-1} . This phenomenon was explained by a spillover of hydrogen species from Ru to MgO, because increment of OH group on MgO decreased with decreasing Ru dispersion. Based on the observation that exposure of $\text{Pt}/\text{Al}_2\text{O}_3$ with high Pt dispersion to H_2 caused an increase in OH group on Al_2O_3 , we can conclude that hydrogen spillover takes place on nano-sized Pt particles supported on Al_2O_3 .

3.3. Reactivity of Adsorbed Hydrogen Species with NO

Hydrogen species dissociatively adsorbed on metal and spilling over to the support oxide can be expected to promote several catalytic reactions involving hydrogen as a reactant. For example, the participation of hydrogen species spilling over onto the support in hydrogenation reactions was reported by many researchers^{20,23)~26)}. However, in most cases, the reactivity of the spilled-over hydrogen was not directly evaluated because it seems to be difficult to distinguish between hydrogen species adsorbed from gas phase and those spilled-over from metal particles. On the other hand, hydrogen species can also act as the reducing agent for the reduction of oxidizing agents such as nitrogen oxide (NO_x).

In the present study, the reactivity of adsorbed and spilled-over hydrogen species with NO was examined at 50°C . NO can easily react with hydrogen adsorbed on Pt to form N_2 and N_2O . The distribution of N_2 and N_2O as a product for NO reduction may be different depending on the reactivity of the hydrogen species adsorbed on $\text{Pt}/\text{Al}_2\text{O}_3$. The reactivity of hydrogen species adsorbed on Pt surface was first evaluated, in which NO pulses were injected to $\text{Pt}/\text{Al}_2\text{O}_3$ ($D_3\%$) after H_2 adsorption at 50°C . No hydrogen spillover phenomenon was observed for $\text{Pt}/\text{Al}_2\text{O}_3$ ($D_3\%$). **Figure 4** shows the changes in the gas composition of NO (at $m/e = 30$), N_2 (at $m/e = 28$) and N_2O (at $m/e = 44$) as a function of reaction time. Simultaneous formation of very small amounts of N_2 and N_2O was apparently observed. The reaction of NO with H_2 over Pt has been proposed^{27)~29)} to proceed *via* the following set of elementary steps:





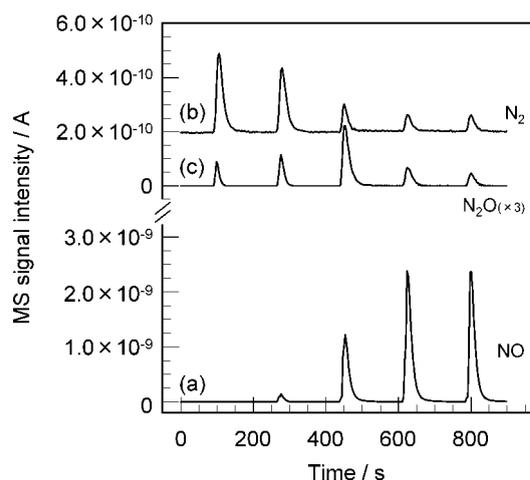
The sample was exposed to H₂ at 50 °C for 10 min and then purged with He at 50 °C for 10 min before introduction of the NO pulses.

Fig. 4 Analysis by Mass Spectrometry of (a) NO (mass 30), (b) N₂ (mass 28) and (c) N₂O (mass 44) Formed during the Introduction of NO Pulses over Pt/Al₂O₃ (D₃%) at 50 °C

Competitive formation of N₂ and N₂O seems to occur *via* dissociative adsorption of NO on the Pt surface. N₂ is formed by recombination of N atoms, whereas N₂O formation proceeds through the reaction of N atoms and NO molecules. The observation that N₂ and N₂O were simultaneously formed for the reaction of NO with hydrogen species adsorbed on Pt/Al₂O₃ (D₃%) suggests that the series of elementary steps (1)-(5) represents the reaction pathway.

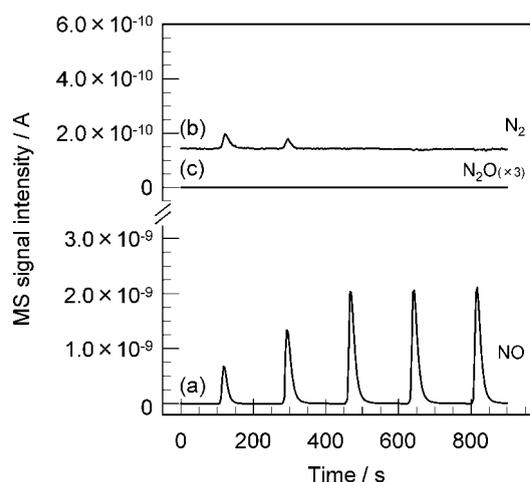
On the other hand, quite different behavior for the formation of N₂ and N₂O was observed, when NO pulses were exposed to Pt/Al₂O₃ (D₈₀%) after H₂ adsorption at 50 °C. As shown in **Fig. 5**, the formation of N₂ was clearly observed, and the amount decreased with increasing pulse number. In accordance with the results obtained for Pt/Al₂O₃ (D₃%), hydrogen species adsorbed on Pt surface is highly reactive for the reduction of NO to N₂. However, the amount of N₂O formation increased with pulse number and reached the maximum at the 3rd pulse. Therefore, the reaction pathways for N₂O formation may be different from those for N₂ formation.

The dissociation of NO (step (2)) on the Pt surface is probably the important step for the formation of N₂ and N₂O. As shown in **Fig. 6**, when NO pulses were passed over Pt/Al₂O₃ (D₈₀%) without H₂ adsorption, only trace amounts of N₂ were observed, clearly suggesting that dissociation of NO (step (2)) and subsequent recombination of N atoms leading to N₂ formation are accelerated by the adsorbed hydrogen species. Therefore, NO species may directly react with hydrogen species to form atomic nitrogen *via* adsorption on the Pt surface, and then the N atoms quickly recombine to form N₂.



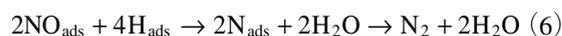
The sample was exposed to H₂ at 50 °C for 10 min and then purged with He at 50 °C for 10 min before introduction of the NO pulses.

Fig. 5 Analysis by Mass Spectrometry of (a) NO (mass 30), (b) N₂ (mass 28) and (c) N₂O (mass 44) Formed during the Introduction of NO Pulses over Pt/Al₂O₃ (D₈₀%) at 50 °C



The sample was not exposed to H₂ before introduction of the NO pulses.

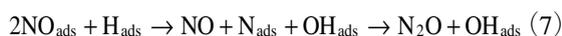
Fig. 6 Analysis by Mass Spectrometry of (a) NO (mass 30), (b) N₂ (mass 28) and (c) N₂O (mass 44) Formed during the Introduction of NO Pulses over Pt/Al₂O₃ (D₈₀%) at 50 °C



Since four atoms of hydrogen are necessary for step (6) to occur, NO reduction to N₂ preferentially proceeds on a Pt surface with a large amount of hydrogen species. Therefore, the amount of N₂ formation decreased with the number of NO pulses (**Fig. 5**).

On the other hand, as shown in **Fig. 5**, N₂O formation reached the maximum at the 3rd pulse of NO over Pt/Al₂O₃ (D₈₀%). The presence of isolated hydrogen species on Pt surface seems to be important for N₂O formation. The following reaction pathway involving

one hydrogen atom can be proposed:



In addition to isolated hydrogen species on the Pt surface, hydrogen species migrating to either the fringes of Pt particles or the Al₂O₃ support can participate as reactive species in N₂O formation, because a large amount of spilled-over hydrogen species are present on the Al₂O₃ surface surrounding nano-sized Pt particles. This proposal is also supported by the observation that N₂O formation decreased with the number of NO pulses over Pt/Al₂O₃ (D₃%) (Fig. 4), on which no hydrogen spillover phenomenon was observed.

4. Conclusions

The particle size of Pt supported on Al₂O₃ can be controlled by changing the calcination conditions. Pt/Al₂O₃ with Pt dispersion ranging from 80 to 3 % estimated by CO chemisorption was prepared. Comparison of the amounts of CO and H₂ chemisorption showed that chemisorption of H₂ was greater than that of CO over the entire range of Pt dispersion. Pt dispersion beyond 100 % was estimated for Pt/Al₂O₃ with nano-sized Pt particles by H₂ chemisorption. FT-IR measurements of hydrogen species adsorbed on Pt/Al₂O₃ with different Pt dispersion revealed that hydrogen spillover occurs on nano-sized Pt particles supported on Al₂O₃. The reactivities with NO of hydrogen species dissociatively adsorbed on Pt nano-particles and spilled-over hydrogen were different. The former was reactive for the formation of N₂, whereas the latter was reactive for the formation of N₂O.

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要 旨

アルミナ担持白金ナノ粒子上に吸着した水素種のキャラクタリゼーションおよび反応性解析

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アルミナに担持した白金ナノ粒子の分散状態を化学吸着法により検討した。その結果, いずれの白金分散度においても水素の化学吸着量は一酸化炭素と比較して高くなった。特にナノサイズの白金粒子の場合, 水素の化学吸着量からは100%を超える白金分散度が算出された。白金分散度の異なる Pt/Al₂O₃上に吸着した水素種の FT-IR 測定から, ナノサイズの白金粒子上に

解離吸着した水素種はアルミナ上にスピルオーバーすることが推察された。白金ナノ粒子上に解離吸着した水素は室温においても一酸化窒素 (NO) と容易に反応し, 窒素を生成する。一方, 白金粒子とアルミナ担体の界面付近にスピルオーバーした水素種は亜酸化窒素 (N₂O) の生成に寄与することが推察された。

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