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Nitrogen Monoxide and Soot Oxidation in Diesel Emissions with Platinum–Tungsten/Titanium Dioxide Catalysts: Tungsten Loading Effect

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Abstract: Compared with Pt/TiO₂, tungsten-loaded Pt–W/TiO₂ catalysts exhibit improved activity for NO and soot oxidation. Using catalysts prepared by an incipient wetness method, the tungsten loading effect was investigated using Brunauer–Emmett–Teller surface areas, X-ray diffraction, transmission electron microscopy (TEM), CO pulse chemisorption, H₂ temperature-programmed reduction, NH₃ temperature-programmed desorption (NH₃-TPD), and pyridine Fourier transform infrared (FT-IR) spectroscopy. Loading tungsten on the Pt/TiO₂ catalyst reduced the platinum particle size, as revealed in TEM images. CO pulse chemisorption showed that platinum was covered with tungsten and the dispersion of platinum decreased when 5 wt.% or more of tungsten was loaded. The NH₃-TPD and pyridine-FT-IR results demonstrated that the number of strong acid sites and Brønsted acid sites in the catalyst were increased by the presence of tungsten. Therefore, a catalyst containing an appropriate amount of tungsten increased the dispersion of platinum, thereby increasing the number of active sites for NO and soot oxidation, and increased the acidity of the catalyst, thereby increasing the activity of soot oxidation by NO₂.

Keywords: soot; particulate matter (PM); exhaust gas after-treatment; platinum catalyst; oxidation catalyst; Pt/tio₂

1. Introduction

Globally, harmful exhaust emissions regulations have been tightened owing to the increasing use of diesel engines in various fields, such as coal-fired power plants, ships, aviation, and automobiles [1,2]. Exhaust emissions from diesel engines include hydrocarbons, soot, NO_x, SO_x, and carbon monoxide. Among these emissions, soot, which consists of unburned carbon particles, can cause air pollution, various respiratory diseases, and lung cancer. The World Health Organization (WHO) and the California Air Resources Board (CARB) classify soot as a first-level carcinogen [3]. The European Union (EU) introduced the EURO emission regulation in 1994 as a means to reduce the emission of pollutants in the exhaust gas of diesel cars. EURO-6c was introduced in September 2017, which applies the Worldwide Harmonized Light Vehicle Test Procedure (WLTP) and Real Driving Emissions (RDE) instead of the New European Driving Cycle (NEDC), an existing EURO-6 emission measurement method. As a result, it has become more difficult to meet emission limits [4].

Methods for reducing soot include pre-treatment technologies, which involve fuel reforming and improvement of combustion conditions, and post-treatment technologies, which involve the collection

and removal of soot in a diesel particulate filter (DPF) (active regeneration, combination regeneration, and passive regeneration) [5]. The mechanisms of soot oxidation can be summarized as follows.

The reaction to oxidize soot using O_2 , as shown in Equation (1), occurs at temperatures of 550 °C or higher; therefore, post-treatment technologies based on this reaction require a separate heat source to raise the DPF temperature. In addition, when a large amount of soot is combusted, the exothermic reaction may raise the temperature of the catalyst and the DPF to approximately 1000 °C, thereby causing degradation of the catalyst and structural damage to the filter. In contrast, NO, which accounts for 80–90% of NO_x in diesel exhaust gas, can be oxidized using a DPF loaded with a catalyst and the generated NO₂ can then oxidize soot, as shown in Equations (2) and (3). As this process occurs at a lower temperature (250 °C), a separate heat source is not required to increase the temperature of the DPF, and the possibility of durability degradation owing to thermal aging of the catalyst and filter is low [6,7].

As platinum catalysts have high oxidation activities, many studies on soot oxidation have focused on such catalysts. Table 1 provides a summary of platinum catalysts that have been applied for soot oxidation. Oi-Uchisawa et al. [8] studied the characteristics of soot oxidation by loading 0.3 wt.% platinum on TiO₂, ZrO₂, SiO₂, and Al₂O₃ supports. When the reaction gas contained SO₂, the catalyst on the TiO₂ support showed high activity for soot oxidation, whereas the catalysts on SiO₂ and Al₂O₃ supports showed low activities. The specific surface area and the platinum dispersion did not significantly affect the catalytic activities of these catalysts. However, in sulfate accumulation experiments, accumulation of SO₄^{2−} was observed on platinum in the Pt/SiO₂ catalyst and on TiO₂ in the Pt/TiO₂ catalyst, indicating that the activity of platinum, which is an active metal, was maintained.

Table 1. Comparison of the activities of various platinum catalysts for soot oxidation.

Catalyst	Feed	GHSV (h ^{−1}) ^a	Catalyst:Soot	T ₅₀ (°C) ^b	Ref.
Pt[1]/TiO ₂	550 ppm NO, 1.5 ppm SO ₂ , 7.5% O ₂ , 8% H ₂ O, N ₂ bal.	96,000	100:1	415	[8]
Pt[1]/Al ₂ O ₃	1000 ppm NO, 3% O ₂ , He bal.	30,000	9:1	550	[9]
Pt[1]-K[5.4]/Al ₂ O ₃	1000 ppm NO, 3% O ₂ , He bal.	30,000	9:1	450	[9]
Pt[2.5]/CeO ₂	600 ppm NO, 10% O ₂ , Ar bal.	70,000	4:1	390	[10]
Pt[0.5]/MnCeAl	1000 ppm NO, 10% O ₂ , N ₂ bal.	-	10:1	442	[11]
Pt[1]/H-ZSM5	1000 ppm NO, 10% O ₂ , N ₂ bal.	30,000	10:1	440	[12]
Pt[1]/H-ZSM5	500 ppm NO, 10% O ₂ , N ₂ bal.	30,000	5:1	433	[13]
Pt[1]-W[3]/TiO ₂	300 ppm NO, 3 ppm SO ₂ , 10% O ₂ , 5% H ₂ O, N ₂ bal.	50,000	4:1	324	In this study

^a GHSV(h^{−1}) (gas hourly space velocity); ^b T₅₀ (°C) is the temperature required to achieve 50% soot combustion in the soot oxidation experiment; the lower the better.

Matarrese et al. [9] performed soot experiments using a Pt[1]–K[5.4]/Al₂O₃ catalyst and found that the activity of soot oxidation was increased by the NO_x adsorption and desorption characteristics of potassium. Krishna et al. [10] studied soot oxidation using a CeO₂ support with redox properties and an excellent oxygen storage capacity. They explained that the reactive oxygen species present on the CeO₂ support of a Pt[2.5]/CeO₂ catalyst oxidized NO adsorbed on platinum, thereby activating the soot oxidation process. In addition, Liu et al. [11] added MnOx–CeO₂ to Al₂O₃ to enhance the thermal stability of the Pt/Al₂O₃ catalyst and the activity of soot oxidation. This modification lowered T₅₀ (°C) (temperature with a 50% soot conversion rate) from 474 to 442 °C for soot oxidation. However, the active sites of catalysts containing CeO₂ and alkaline metals such as potassium are poisoned during reactions involving SO₂, resulting in catalyst deactivation [10,11].

Liu et al. [12] studied soot oxidation using a Pt/ZSM-5 catalyst to reduce poisoning of the catalyst by SO₂. During NO oxidation in the presence of SO₂, a higher amount of NO₂ was produced at a low temperature when ZSM-5 was used rather than Al₂O₃ as a support for platinum. During soot oxidation in the presence of SO₂, T₅₀ (°C) decreased by 20 °C with the Pt/ZSM-5 catalyst. However, a small amount of platinum was located in the micropores (0.57 nm) of ZSM-5, and it was difficult for soot larger than the pore size of ZSM-5 to come into contact with platinum in the pores. Therefore, to prevent platinum from being present in the zeolite pores, Gao et al. [13] synthesized platinum nanoparticles with an average particle size of 7.5 nm and then loaded the particles on an H-ZSM-5 support. Using this catalyst, T₅₀ (°C) of 433 °C was obtained, even though the amount of NO was reduced to 500 ppm in the soot oxidation experiment. Tungsten is known to increase the acidity and NO_x adsorption properties of catalysts [14]. However, heretofore, there has been no exploration of tungsten-added Pt catalysts for their soot oxidation activity. The exhaust gas temperature required for passive regeneration is gradually being lowered owing to the development of exhaust gas recirculation (EGR) and diesel engine combustion technology. Therefore, to oxidize soot by passive regeneration, it is necessary to develop a catalyst with excellent activity at low temperatures. In this study, we investigated the effect of the tungsten content in a Pt/TiO₂ catalyst on the soot oxidation characteristics at low exhaust gas temperatures. To determine the oxidation characteristics of soot on the catalyst, we confirmed the formation of NO₂, which acts as an oxidant of soot, and examined soot oxidation by NO₂ and NO reaction gases. Moreover, tungsten-loaded Pt/TiO₂ catalysts were characterized and, based on the results, their oxidation characteristics were investigated.

2. Results and Discussion

2.1. Catalyst Characterization

Table 2 summarizes the results of the BET (Brunauer–Emmett–Teller) analysis. When the tungsten loading amount on the catalyst increased to 3 wt.%, the specific surface area increased by approximately 3.3 m²/g relative to that of the catalysts with 0 wt.% tungsten. However, when the tungsten loading amount was more than 5 wt.%, the specific surface area decreased. The specific pore volumes were similar for all the catalysts, but the average pore diameter decreased from 28.9 to 26.6 nm as the tungsten content increased.

Table 2. Analysis of the structural characteristics of Pt–W[x]/TiO₂ catalysts (BET surface area (S_{BET}), external surface area (S_{ext}), pore volume (V_P), and average pore size (D_P)).

Sample	S _{BET} (m ² /g)	S _{ext} (m ² /g)	V _P (m ³ /g)	D _P (nm)
W[0]	51.5	48.1	0.37	28.9
W[1]	54.1	49.5	0.37	27.5
W[3]	54.8	47.7	0.38	27.5
W[5]	54.7	46.4	0.35	25.9
W[7]	52.8	46.3	0.35	26.6

The XRD (X-ray diffraction) patterns of the Pt–W[x]/TiO₂ catalysts are shown in Figure 1. Anatase and rutile peaks, which are characteristic of TiO₂, were observed for all the synthesized catalysts, but no platinum or WO_x peaks were detected. Platinum may not have been observed because the metal loading amount on the catalyst was as low as 1 wt.% [15]. In the case of WO_x, the characteristic peaks (2θ = 23.3°, 24.4°, and 33.8°) were not observed even when the metal loading amount on the catalyst was 7 wt.%. This suggests that amorphous or nano-sized WO_x was well dispersed on TiO₂ [16].

Figure 1. XRD patterns of Pt-W[x]/TiO₂ catalysts.

Figure 2 shows FE-TEM (field emission transmission electron microscopy) images, S-TEM (scanning transmission electron microscopy) images, and the platinum particle size distributions of the Pt-W[x]/TiO₂ catalysts. In the case of the Pt-W[0]/TiO₂ catalyst (Figure 2a) without tungsten, the average particle size of platinum was 2.5 nm. In contrast, the average particle sizes of platinum in Pt-W[3]/TiO₂ (Figure 2a) and Pt-W[5]/TiO₂ (Figure 2c) were 1.8 and 1.6 nm, respectively. The platinum particle size distributions show that the size of the platinum particles decreased and the width of the particle size distribution narrowed as the tungsten content of the catalyst increased. However, tungsten on the surface of TiO₂ was not observed to form clusters (Figure 2b,c). EDS (energy-dispersive

X-ray spectroscopy) mapping was performed to confirm the distribution of platinum and tungsten on the catalyst surface, and the results are shown in Figure 3. Tungsten, which was difficult to observe using S-TEM, was found to be distributed throughout the catalyst.

Figure 2. FE-TEM and S-TEM images and platinum particle size distributions of Pt-W[x]/TiO₂ catalysts: (a) Pt-W[0]/TiO₂, (b) Pt-W[3]/TiO₂, and (c) Pt-W[7]/TiO₂.

Table 3 shows the results of the CO pulse chemisorption analysis for the Pt-W[x]/TiO₂ catalysts. When the tungsten loading amount on the catalyst was less than 3 wt.%, the dispersion and particle size of platinum were not significantly affected. However, when the loading amount was more than 5 wt.%, the dispersion of platinum drastically decreased and the platinum particle size dramatically increased. However, the average particle sizes of platinum obtained from the CO pulse chemisorption and TEM analyses are considerably different. According to the results of the TEM analysis, the amount of CO chemically adsorbed on platinum during CO pulse chemisorption decreased owing to partial blocking of the platinum particles by WO_x.

Figure 3. EDS mapping of the distribution of platinum (red) and tungsten (blue) in the Pt-W[x]/TiO₂ catalysts: (a) Pt-W[3]/TiO₂ and (b) Pt-W[7]/TiO₂.

Table 3. Particle size and dispersion of platinum as determined by CO pulse chemisorption and TEM analysis.

Sample	Pt Loading (wt.%) ^a	Pt Dispersion (%) ^b	Pt Particle Size	
			(nm) ^b	(nm) ^c
W[0]	0.95	22.1	5.1	2.5
W[1]	0.98	17.1	6.6	-
W[3]	1.03	19.8	5.7	1.8
W[5]	0.94	8.8	12.8	-
W[7]	1.08	6.1	18.5	1.6

^a Pt loadings were calculated from ICP-MS (Inductively Coupled Plasma Mass Spectrometer). ^b Pt dispersions and particle sizes were calculated from CO pulse chemisorption. ^c Pt particle sizes from S-TEM images.

Figure 4 shows the H₂-TPR (H₂ temperature-programmed reduction) results for the Pt-W[x]/TiO₂ catalysts. For the catalyst without tungsten, the reduction peaks produced by the strong metal–support interaction (SMSI) effects of PtOx and Pt–TiO₂ appeared at 60 and 170 °C, respectively, and the surface reduction peak of TiO₂ appeared at 320 °C [17]. In contrast, for the catalysts containing tungsten, a new peak was detected at approximately 230 °C, which was considered to be generated by the Pt–W interaction. The reduction peak resulting from the SMSI effect of Pt–TiO₂ shifted to higher temperatures when up to 3 wt.% tungsten was added, but then shifted back to lower temperatures when more than 3 wt.% tungsten was added. This change may have resulted from overloading of tungsten, thereby increasing the W–Ti interaction and decreasing the Pt–TiO₂ interaction [18].

Figure 5 shows the NH₃-TPD (NH₃ temperature-programmed desorption) curves of the Pt-W[x]/TiO₂ catalysts. The NH₃-TPD curves can be deconvoluted into three peaks corresponding to weak, medium, and strong acid sites. The acid site densities of the catalysts with increasing tungsten content were calculated from the peak areas (Table 4). As the tungsten content increased, the total number of acid sites decreased. However, the amount of strong acid sites increased with increasing tungsten content, and broad peaks were detected at 460 and 480 °C in catalysts containing more than 3 wt.% tungsten. Thus, as the tungsten loading amount on the catalyst increased, WOx covered TiO₂, thereby decreasing the amount of TiO₂-related weak and medium acid sites and increasing the amount of WOx-related strong acid sites [19].

Figure 4. H_2 -TPR profiles of Pt-W[x]/TiO₂ catalysts.

Figure 5. NH_3 -TPD profiles of Pt-W[x]/TiO₂ catalysts.

Table 4. Density of acid sites on Pt–W[x]/TiO₂ catalysts as determined by NH₃-TPD analysis.

Sample	Acid Site Density (mmol _{NH3} g _{Cat} ^{−1})			
	Weak	Medium	Strong	Total
W[0]	0.078	0.080	0.071	0.229
W[1]	0.088	0.069	0.086	0.243
W[3]	0.083	0.059	0.091	0.233
W[5]	0.059	0.052	0.098	0.209
W[7]	0.057	0.046	0.073	0.176

To investigate the relative concentrations of Brønsted and Lewis acid sites on the surfaces of the Pt–W[x]/TiO₂ catalysts, FT-IR (Fourier transform infrared) analyses were performed by adsorbing pyridine at 200 °C. At Brønsted acid sites, pyridine is adsorbed as a pyridinium ion after accepting a proton, whereas it is adsorbed as covalently bonded pyridine at Lewis acid sites via electron-pair sharing [20,21]. Figure 6 shows the FT-IR spectra of the pyridine-adsorbed Pt–W[x]/TiO₂ catalysts. Generally, peaks corresponding to the Brønsted acid sites appear at 1545 and 1640 cm^{−1}, whereas those corresponding to the Lewis acid sites appear at 1435 and 1598 cm^{−1} [22,23]. Brønsted acid sites were not detected in the catalyst without tungsten. However, a peak assigned to the Brønsted acid sites (1640 cm^{−1}) slightly increased with increasing tungsten content. Table 5 shows the IR-band area and ratio (B/L ratio) of the Brønsted and Lewis acid sites with increasing tungsten content in Pt–W[x]/TiO₂. Assuming the adsorption sites of pyridine are identical to those of ammonia, the densities of the Brønsted and Lewis sites were calculated by multiplying total acid site density by $\left(\frac{B/L}{B/L+1}\right)$ and $\left(\frac{1}{B/L+1}\right)$, respectively. As the tungsten content in the catalyst increased to 7 wt.%, the peak areas of the Brønsted and Lewis acid sites increased. In addition, the B/L ratio indicated a three-fold increase in the number of Brønsted acid sites. These results reveal that tungsten loading resulted in the formation of Brønsted acid sites and a decrease in the proportion of Lewis acid sites.

Figure 6. FT-IR spectra of Pt–W[x]/TiO₂ catalysts after pyridine adsorption and subsequent desorption at 200 °C.

Table 5. Area and area ratio (B/L ratio) of Brønsted and Lewis acid sites on Pt–W[x]/TiO₂ catalysts.

Sample	B-Acid Area (1640 cm ⁻¹)	L-Acid Area (1435 cm ⁻¹)	B/L Ratio ^b	Acid Site Density (mmol _{NH3} g _{Cat} ⁻¹)		
				Total ^a	Brønsted ^c	Lewis ^c
W[0]	-	8.03	-	0.229	-	-
W[1]	0.75	14.25	0.05	0.243	0.012	0.231
W[3]	0.92	15.95	0.06	0.233	0.013	0.220
W[5]	1.31	17.31	0.08	0.209	0.015	0.194
W[7]	2.15	18.50	0.12	0.176	0.018	0.158

^a The acid site densities were obtained by integrating NH₃-TPD curves in Figure 5. ^b B, L area and B/L ratios were obtained from the pyridine adsorption FTIR spectroscopy results. ^c Brønsted and Lewis acid density were calculated using total acid density and B/L ratio.

2.2. Catalytic Activities of Pt–W[x]/TiO₂ for NO and Soot Oxidation

The catalytic oxidation of NO to NO₂ is an important reaction for NO emitted from diesel engines, as the produced NO₂ can be used as an oxidant in soot oxidation. Figure 7a illustrates the NO oxidation results over the Pt–W[x]/TiO₂ catalysts. The amount of NO₂ produced by NO oxidation increased as the content of tungsten increased at temperatures below 350 °C. At 250 °C, the concentration of NO₂ generated increased approximately 3.5 times as the amount of tungsten in the catalysts increased to 7 wt.%. As revealed by the NH₃-TPD analysis, this phenomenon may occur because the amount of strong acid sites on the surface of the catalyst increased as the tungsten loading amount increased. Thus, the adsorption of NO on the catalyst surface was favored and the adsorbed NO was oxidized to NO₂ on the platinum surface [14].

Next, soot oxidation by NO₂ was performed by supplying 300 ppm NO₂, 3 ppm SO₂, 10% O₂, and balance N₂. Figure 7b shows the experimental results over the Pt–W[x]/TiO₂ catalysts. When 1 wt.% tungsten was loaded on the catalyst, the activity was similar to that of the Pt/TiO₂ catalyst without tungsten. However, when 3 wt.% tungsten was loaded, the soot oxidation rate rapidly increased, and similar reaction results were also observed at tungsten loading amounts of more than 3 wt.%. Thus, as the acidity of the catalyst surface increased, NO_x was more easily absorbed. However, the addition of more than 3 wt.% tungsten did not significantly affect soot oxidation by NO₂.

Figure 7c exhibits the experimental results for the reaction of 300 ppm NO, 3 ppm SO₂, 10% O₂, and balance N₂ over the Pt–W[x]/TiO₂ catalysts. Under these conditions, the soot conversion rate at 300 °C decreased in the order of W[3] > W[5] > W[1] > W[0] > W[7]. Liu et al. explained that the acidity of the catalyst surface acts as a promoter for transferring NO₂ formed on the platinum surface to soot [13]. The dependence of the soot oxidation performance on NO₂ was quite high. Moreover, the experimental results for the oxidation of NO into NO₂ (Figure 7a) and the oxidation of soot using NO₂ (Figure 7b) showed that as the content of tungsten in the Pt/TiO₂ catalyst increased, the supply of NO₂, the oxidant required for soot oxidation, increased. However, the soot oxidation results differed when NO was used (Figure 7c). These experimental results indicate that there was a significant variable other than NO₂ production involved in the soot oxidation reaction.

Figure 7. Cont.

Figure 7. (a) NO_2 concentration profile during the NO oxidation reaction over Pt-W[x]/ TiO_2 catalysts. Reaction conditions: catalyst = 100 g/L; reactant gas = 300 ppm NO, 3 ppm SO_2 , 10% O_2 , 5% H_2O , and N_2 balance; flow = 1.0 L/min; GHSV = 50,000 h^{-1} . (b) Soot oxidation performance of Pt-W[x]/ TiO_2 catalysts using NO_2 . Reaction conditions: catalyst/soot = 8:2; reactant gas = 300 ppm NO_2 , 3 ppm SO_2 , 10% O_2 , 5% H_2O , and N_2 balance; total flow = 0.1 L/min; GHSV = 50,000 h^{-1} . (c) Soot oxidation performance of Pt-W[x]/ TiO_2 catalysts using NO. Reaction conditions: catalyst/soot = 8:2; reactant gas = 300 ppm NO, 3 ppm SO_2 , 10% O_2 , 5% H_2O , and N_2 balance; total flow = 0.1 L/min; GHSV = 50,000 h^{-1} .

Figure 8 shows illustrations of the soot oxidation process using NO based on the analysis of the catalyst properties. As shown in Figure 8a, NO_2 produced on the platinum surface migrates to soot when the platinum and the soot are adjacent to each other, thereby leading to rapid soot oxidation. Thus, the Pt-W[3]/ TiO_2 catalyst, which is loaded with an appropriate amount of tungsten, is considered advantageous for soot oxidation using NO. In contrast, as shown in Figure 8b, when platinum was completely covered by WO_x , gaseous NO could easily react with platinum to generate NO_2 , but contact between soot and platinum, the active site, is difficult. Therefore, soot oxidation is relatively unlikely to occur. Therefore, NO oxidation was dominant in the catalyst loaded with 7 wt.% tungsten, but the soot oxidation rate using NO was relatively low.

Figure 8. Illustration of catalysts covered with tungsten oxide as a function of the tungsten content.

Figure 9 displays the temperature at which soot conversion rates of 10% (T_{10} (°C)) and 20% (T_{20} (°C)) are achieved, as well as the respective regression curves according to the tungsten content of the catalyst. When the catalyst was loaded with 3 wt.% tungsten, the lowest T_{10} (°C) and T_{20} (°C) values of 284 and 301 °C, respectively, were obtained. The regression curves suggest that a tungsten loading of 3.5–4.0 wt.% will result in the lowest temperature for soot conversion.

Figure 9. Temperatures corresponding to soot conversion rates of 10% (T_{10} (°C)) and 20% (T_{20} (°C)) as a function of the tungsten content in Pt-W[x]/TiO₂ catalysts. Reaction conditions: catalyst/soot = 8:2; reactant gas = 300 ppm NO, 3 ppm SO₂, 10% O₂, 5% H₂O, and N₂ balance; total flow = 0.1 L/min; GHSV = 50,000 h^{−1}.

3. Materials and Methods

3.1. Catalyst Preparation

Degussa P-25 was used as the TiO₂ support, ammonium paratungstate (APT, [(NH₄)₁₀(H₂W₁₂O₄₂)·4H₂O]) was used as a precursor for tungsten, and platinum was obtained from a platinum solution (A type, 16.6%, SNS Co., Hwa-seong, Korea). In this study, the content of platinum on the support was fixed at 1 wt.%, and the content of tungsten was 0–7 wt.%. The Pt-W[x]/TiO₂ catalysts (where x is the content of tungsten in wt.%) were prepared as follows. Firstly, calculated APT was added to solution of oxalic acid dehydrate ([HO₂CCO₂H·2H₂O], Sigma-Aldrich, St. Louis, MO, USA). The mixture was stirred at 300 rpm for 10 min until clear solution formed. An APT solution was loaded on 10 g of TiO₂ by an incipient wetness method and then dried at 100 °C for 5 h to prepare W[x]/TiO₂ powder. Next, the calculated platinum solution was loaded on the 10 g of dried W[x]/TiO₂ powder by the incipient wetness method. The Pt-W[x]/TiO₂ catalyst was dried at 100 °C for 24 h and then calcined in an air atmosphere at 500 °C for 4 h using a calcination furnace at a heating rate of 1 °C/min.

For NO oxidation, the Pt-W[x]/TiO₂ catalyst powder was mixed with distilled water (catalyst (g)/water (g) = 0.5) and milled for 30 min using a mortar to prepare a slurry. Next, the catalyst slurry was coated on a cordierite honeycomb (400 cells per square inch (cps) with a height of 0.6 cm) at a rate of 100 g/L. SEM images of the non-catalyst coating and catalyst coating samples are shown in Figure S1, and the properties of cordierite honeycomb are shown in the Table S1.

3.2. Experimental Apparatus and Evaluation Method

3.2.1. NO Oxidation

A tube-type quartz reactor with an inner diameter of 1.6 cm was used to confirm the NO oxidation performance of the Pt-W[x]/TiO₂ catalysts. The prepared honeycomb catalysts were fixed in the quartz reactor, and the NO and NO₂ concentrations after the reaction were analyzed using non-dispersive infrared spectroscopy (Fuji Co., Tokyo, Japan). The experimental conditions for NO oxidation were as follows: 300 ppm NO, 3 ppm SO₂, 10% O₂, 5% H₂O, and N₂ balance. The total flow rate of the reactants was 1.0 L/min (GHSV = 50,000 h⁻¹).

3.2.2. Soot Oxidation

A tube-type quartz reactor with an inner diameter of 0.4 cm was used to confirm the soot oxidation performance of the Pt-W[x]/TiO₂ catalysts. The Pt-W[x]/TiO₂ catalyst powder and soot were mixed (catalyst (g)/soot (g) = 4) using a mortar for 30 min to ensure good contact. The model soot used in the experiment was Printex U (Degussa, 20–30 nm). The experiment was carried out at 200–450 °C under the following reaction conditions: 300 ppm NO or NO₂, 3 ppm SO₂, 10% O₂, 5% H₂O, and N₂ balance. The total flow rate of the reactants was 100 mL/min (GHSV = 50,000 h⁻¹). The concentration of CO₂ generated after soot oxidation was measured at the outlet using gas chromatography (7890A, Agilent Technology Co, Santa Clara, CA., USA) with a thermal conductivity detector and a capillary column (Carboxen 1010 PLOT, 30 m × 0.533 mm, SUPELCO Co., St. Louis, MO, USA).

3.3. Catalyst Characterization

The BET surface areas and pore characteristics of the Pt-W[x]/TiO₂ catalysts were measured using a Micromeritics ASAP 2020 instrument.

XRD (D/max-2200/PC, Rigaku Co., Tokyo, Japan) with CuK α radiation was conducted at 40 kV and 200 mA in the 2 θ range of 10–100° to confirm the crystal structure as the tungsten content of the catalyst increased.

To determine the platinum particle size, tungsten loading state, and dispersion of the catalyst, FE-TEM (JEM-2200FS, JEOL Co., Tokyo, Japan) was used. To analyze the size and distribution of platinum particles on TiO₂ accurately, S-TEM was used. The elemental composition of the catalyst surface was analyzed by EDS mapping. For these measurements, the sample was dispersed in ethanol and prepared on a copper grid (300 mesh).

CO pulse chemisorption, H₂-TPR, and NH₃-TPD were performed using a Micromeritics Autochem 2920 instrument. CO pulse chemisorption was performed to determine the platinum particle size and dispersion of the catalyst. The catalyst was subjected to reduction treatment by maintaining a temperature of 300 °C for 1 h while injecting a mixed gas of 10% H₂/Ar. Then, He gas was injected for 30 min to remove adsorbed hydrogen. Next, the temperature was lowered to room temperature, and 10% CO/He was pulse injected at a flow rate of 50 mL/min to measure the particle size and dispersion of platinum based on the amount of adsorbed CO.

H₂-TPR analysis was performed to determine the reducing ability of the catalyst according to temperature. The calcined sample was heated to 800 °C at a heating rate of 5 °C/min while injecting a mixed gas of 10% H₂/Ar. NH₃-TPD was conducted to analyze the acid sites in the catalyst. The calcined sample was activated by maintaining a temperature of 300 °C for 1 h under a mixed gas of 10% H₂/Ar. After exposure to a mixed gas of 15% NH₃/He at room temperature for 1 h, the temperature of the sample was raised to 100 °C to desorb any NH₃ physically adsorbed on the surface of the catalyst, and then He was injected for 30 min. Subsequently, the analysis was conducted by raising the sample temperature to 600 °C at 10 °C/min while flowing He at 50 mL/min.

To determine the distribution of Brønsted and Lewis acid sites on the catalyst, pyridine was adsorbed, and FT-IR spectra (FTLA2000-104, ABB Co., Zürich, Switzerland) were obtained. The sample was mounted on a diffuse reflection infrared Fourier transform (DRIFT) cell, and a background IR

spectrum was obtained after degassing in a 300 °C vacuum atmosphere for 2 h. Next, the pyridine solution was injected into the DRIFT cell using a syringe, and pyridine molecules were adsorbed on the catalyst. The adsorption process was allowed to proceed at 200 °C for 30 min to saturate the acid sites on the catalyst surface with pyridine, and IR spectra were obtained.

4. Conclusions

In this study, a Pt–W[x]/TiO₂ catalyst showing excellent soot oxidation was developed. As the content of tungsten in the Pt–W[x]/TiO₂ catalyst increased, the amount of strong acid sites and Brønsted acid sites increased, and the catalytic activity for the oxidation of NO to NO₂ increased. The catalysts with 3 wt.% or more tungsten showed similar activities for soot oxidation by NO₂. In contrast, the catalyst loaded with 3 wt.% tungsten showed the highest activity for soot oxidation using NO. Although increased oxidation of NO to NO₂ occurred at higher tungsten loadings, the surface of the active metal, platinum, was covered by WO_x, making it difficult to deliver the produced NO₂ to soot and thus lowering the reaction activity. We confirmed that an appropriate surface acidity and coverage of platinum by tungsten were important in the Pt–W[x]/TiO₂ catalysts for effective soot oxidation. In this study, we found that the Pt–W[3]/TiO₂ catalyst showed the highest rate of soot oxidation.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/11/1283/s1>, Figure S1: SEM image of the honeycomb sample; (a) Non-catalyst coating (b) catalyst coating (100 g/L), Table S1: Properties of the honeycomb using the catalyst coating.

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