Platinum-Based Catalyst for Diesel Hydrocarbon Oxidation

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Abstract: The catalytic performance of Pt-based catalysts for the total oxidation of hydrocarbons was investigated. The activity of supported Pt catalysts (Pt/Al₂O₃, Pt/ZrO₂, Pt/TiO₂, and Pt/H-ZSM-5) depends on the metal oxide support. Pt/Al₂O₃ showed the highest catalytic activity when the catalysts were aged at 750 °C for 50 h in air. The activity of Pt/Al₂O₃ was dependent on the valence state of the Pt surface. Pt/Al₂O₃ with the Pt surface in the metallic state was more active than with the surface in the cationic state. The surface density of acid and basic sites on the Al₂O₃ support controlled the valence state of the Pt surface and stability of the Pt particles in the highly dispersed state, respectively.

Key words: diesel oxidation catalyst; platinum; alumina; valence state of platinum surface; surface acid-base property

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A diesel oxidation catalyst (DOC) is used for the total oxidation of CO, unburned hydrocarbons (HCs), and soluble organic fraction (SOF) of particulates in a diesel exhaust [1–3]. The DOC is also used to burn a large amount of fuel, which are periodically supplied by post-injection, in order to raise the soot oxidation temperature for the regeneration of the diesel particulate filter (DPF) [4]. A large amount of exhaust gas recirculation (EGR) in the system is applied to efficiently lower NO_x from the engine, so the temperature of the exhaust gas from the diesel engine is low. Therefore, the DOC is required to oxidize CO and HCs completely at low temperatures. In order to satisfy this requirement, relatively large amounts of Pt are used for the DOC. However, the use of minimal Pt is now receiving extensive attention because the demand for Pt for automotive catalysts is growing due to increasing environmental awareness [5].

Extensive research have been performed to improve the activity and durability of a DOC, e.g., the chemical deactivation of supported Pt DOC catalysts by sulfur oxide and contaminants like phosphorus, zinc and calcium from lubricant oil has been extensively studied to get information for the development of a highly durable DOC [6–8]. Recently, Aluha et al. [9] reported that a Pt-Pd bimetallic catalyst supported on Al₂O₃ modified with MoO₃ showed high catalytic activity for CO and C₃H₈ oxidation even in the presence of 20 ppm SO₂. Diehl et al. [10] studied the total oxidation of 48 hydrocarbons over Pt/Al₂O₃ and reported that light alkenes were much more reactive than light alkanes,

while the opposite was observed with long chain hydrocarbons. Although many research works have been performed to improve the supported Pt catalysts, fewer studies have been performed to understand the essential features in the catalysis by supported Pt catalysts that can lead to significant improvement of the catalytic performance. In the present work, we investigated in detail the catalytic performance of Pt-based catalysts for the total oxidation of HCs in order to gain knowledge that will be useful for the use of minimal Pt for the DOC.

1 Experimental

1.1 Preparation of the samples

Supported Pt (1 wt%) catalysts were prepared by the impregnation of metal oxide supports (Al₂O₃ (Sasol), ZrO₂ (Daiichi Kigenso Kagaku Kogyo Co., Ltd., RSC-H), TiO₂ (Degussa, P-25), H-ZSM-5 (Tosoh, HSZ-830NHA, Si/Al₂=28)) with a solution of Pt(NO₂)₂(NH₃)₂ (Tanaka Kikinzoku Kogyo; Pt: 4.595 wt% in solution). Four different Al₂O₃ (Al₂O₃-A: Sasol; Al₂O₃-B: Mizusawa Chemicals, GP-20; Al₂O₃-C: Sumitomo Chemical, NK-324; Al₂O₃-D: JRC-ALO-8), which have different physicochemical properties, were used. The catalyst precursors obtained were dried and then calcined at 600 °C for 5 h in air (fresh sample). The catalyst samples were further calcined at 750 °C for 50 h in air (aged sample).

1.2 Characterization of the samples

The BET surface area of the samples was determined using a volumetric adsorption apparatus (Quantachrome, Nova-4200e) by N_2 adsorption at $-196\text{ }^\circ\text{C}$. The dispersion of Pt was calculated from CO chemisorption measured by the pulse method at $50\text{ }^\circ\text{C}$. Before the measurement, the sample was first reduced with H_2 at $400\text{ }^\circ\text{C}$ for 1 h and then cooled to $50\text{ }^\circ\text{C}$ in flowing He. Fourier transform infrared (FT-IR) spectra of adsorbed CO, used as the probe molecule, were obtained with a flow of 0.5% CO-99.5% He at $50\text{ }^\circ\text{C}$ over the catalyst with a Nicolet 6700 FT-IR spectrometer at a resolution of 4 cm^{-1} . A self-supporting sample disk of 14 mg/cm^2 placed in an IR cell with CaF_2 windows was used. This was pretreated at $500\text{ }^\circ\text{C}$ in a flow of 10% O_2 -90% He and then cooled to $50\text{ }^\circ\text{C}$ in the same atmosphere. Temperature-programmed desorption of ammonia (NH_3 -TPD) and CO_2 (CO_2 -TPD) were performed using a TPD-1-AT-SP (Bell Japan Inc.) to estimate the acid and basic sites, respectively, on Al_2O_3 . The catalyst sample was pretreated in a flow of He at $600\text{ }^\circ\text{C}$. After cooling to $100\text{ }^\circ\text{C}$ in flowing He, ammonia adsorption was carried out by passing a gas mixture of 0.5% NH_3 -99.5% He through the sample bed at $100\text{ }^\circ\text{C}$ for 1 h. CO_2 adsorption was carried out by passing a gas mixture of 0.5% CO_2 -99.5% He through the sample bed at $50\text{ }^\circ\text{C}$ for 1 h. After the adsorption gas was purged with He to remove physically adsorbed ammonia and CO_2 at each adsorption temperature, NH_3 -TPD and CO_2 -TPD measurements were carried out by heating to $600\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C/min}$ in flowing He at a flow rate of $60\text{ cm}^3/\text{min}$. A quadrupole mass spectrometer was used to measure the desorbed ammonia.

1.3 Activity test

The catalytic activity was evaluated using a fixed-bed

continuous flow reactor. A reaction gas mixture containing NO (200 ppm), *n*-decane (1780 ppm C), 1-methylnaphthalene (220 ppm C), O_2 (5%), and H_2O (10%) diluted in He as the balance gas was fed to a catalyst sample (10 mg), which had been pretreated in situ in a flow of 5% O_2 -95% He at $500\text{ }^\circ\text{C}$ for 1 h at a flow rate of $100\text{ cm}^3/\text{min}$. The activity was measured while decreasing the temperature from 500 to $100\text{ }^\circ\text{C}$ at a rate of $2\text{ }^\circ\text{C/min}$. The effluent gas was analyzed by two online gas chromatographs equipped, respectively, with a Molecular Sieve 5A column (for the analysis of CO) and a Porapak Q column (for the analysis of CO_2).

2 Results and discussion

2.1 Activity of the samples

In the present study, a mixture of *n*-decane and 1-methylnaphthalene was employed as the hydrocarbon source. We have measured the activity of the supported Pt catalysts for the oxidation of *n*-decane in another set of experiment and found that *n*-decane was oxidized at lower temperatures than 1-methylnaphthalene for all the supported Pt catalysts tested (results not shown). In order to simulate a diesel exhaust, the reaction gas with NO included was used. The selective reduction of NO with HCs occurred at the temperatures at which the oxidation of HCs began. The presence of NO did not affect the activity of the supported Pt catalysts for the total oxidation of HCs (not shown).

Figure 1(a) shows the activity of the supported Pt catalysts (fresh sample) for the total oxidation of HCs. Pt/ TiO_2 was the least active catalyst, while Pt/ Al_2O_3 , Pt/ ZrO_2 , and Pt/H-ZSM-5 showed similar catalytic activities. On the other hand, as shown in Fig. 1(b), when the catalysts were aged at $750\text{ }^\circ\text{C}$ for 50 h, a decrease of the catalytic activity was observed for all the catalysts. Among the catalysts tested, Pt/ Al_2O_3 showed the highest catalytic activity. This

Fig. 1. Activity of the supported platinum catalysts for the total oxidation of HCs. (a) Fresh samples; (b) Aged samples. Reaction conditions: NO = 200 ppm, *n*-C₁₀H₂₂ = 1780 ppm C, 1-methylnaphthalene = 220 ppm C, O_2 = 5%, H_2O = 10%, He balance, catalyst = 10 mg, total flow rate = $100\text{ cm}^3/\text{min}$, heating rate = $2\text{ }^\circ\text{C/min}$.

showed that Pt/Al₂O₃ was relatively stable under high temperature aging.

2.2 Characterization results

Table 1 gives a summary of the BET surface area and Pt dispersion of fresh and aged catalysts. Since significant decreases in Pt dispersion after aging were observed, the decrease in catalytic activity can be ascribed to the sintering of Pt particles. However, no clear correlation between Pt dispersion and catalytic activity was observed. That is, Pt/ZrO₂ which has the highest Pt dispersion (CO/Pt = 0.24) exhibited a lower catalytic activity than Pt/Al₂O₃ (CO/Pt = 0.01). This suggested that the metal oxide support played an important role in the total oxidation of HCs.

Table 1 Physical properties of the supported platinum catalysts

Catalyst	BET surface area (m ² /g)		Pt dispersion (Pt/CO)	
	Fresh	Aged	Fresh	Aged
Pt/Al ₂ O ₃	156	147	0.40	0.01
Pt/ZrO ₂	56.6	25.8	1.00	0.24
Pt/TiO ₂	50.0	7.7	0.12	< 0.01
Pt/H-ZSM-5	350	n.a.	0.20	0.02

In order to understand the effect of the metal oxide support, Pt/Al₂O₃ catalysts were prepared using four different Al₂O₃ supports. Their catalytic activity and physical properties were measured. Figure 2 shows the activity of the four Pt/Al₂O₃ catalysts for the total oxidation of HCs. Table 2 gives a summary of the BET surface area and Pt dispersion of the Pt/Al₂O₃ samples. Although Pt/Al₂O₃-A and Pt/Al₂O₃-D have similar BET surface areas, the Pt dispersion was higher on Pt/Al₂O₃-D than on Pt/Al₂O₃-A. As can be seen in Fig. 2, Pt/Al₂O₃-D showed a higher activity than Pt/Al₂O₃-A, suggesting the importance of Pt dispersion on the activity for the total oxidation of HCs. On the other

Fig. 2. Activity of Pt/Al₂O₃ for the total oxidation of HCs. Reaction conditions are the same as for Fig. 1.

Table 2 Physical properties, CO₂ formation rate, and TOF at 230 °C for the total oxidation of HCs over Pt/Al₂O₃

Catalyst	BET surface area of Al ₂ O ₃ (m ² /g)	Dispersion of Pt (Pt/CO)	CO ₂ formation rate at 230 °C (mol/g)	TOF at 230 °C (mol/(min·mol))
Pt/Al ₂ O ₃ -A	156	0.40	4.29 × 10 ⁻⁴	0.209
Pt/Al ₂ O ₃ -B	182	0.63	3.54 × 10 ⁻⁴	0.110
Pt/Al ₂ O ₃ -C	314	0.63	2.35 × 10 ⁻⁵	0.007
Pt/Al ₂ O ₃ -D	156	0.85	5.20 × 10 ⁻⁴	0.119

hand, the activity of Pt/Al₂O₃-B was higher than that of Pt/Al₂O₃-C although their Pt dispersions were similar. In order to clarify the importance of the Pt dispersion, the TOF (expressed as moles of CO₂ formed per mole of surface Pt atoms per minute) was calculated for 230 °C. As shown in Table 2, the TOF values differ and depended on the Al₂O₃ support employed. Pt/Al₂O₃-A gave a relatively high TOF value, while Pt/Al₂O₃-C gave a low TOF value. Similar TOF values were obtained for Pt/Al₂O₃-B and Pt/Al₂O₃-D. These results suggested that the activity of Pt/Al₂O₃ was dependent on not only the Pt dispersion but also other features of the Al₂O₃ support.

Since Al₂O₃ itself did not show oxidation activity (results not shown), Pt was the catalytically active component for the total oxidation of HCs. The HC oxidation activity of supported Pt is known to depend on the valence state of its surface [11,12]. In order to characterize the valence state of the Pt surface supported on Al₂O₃, FT-IR spectra of CO adsorbed on Pt/Al₂O₃, which had been oxidized by pre-treatment to be similar to the conditions of the catalytic reaction that was carried out under oxidizing condition, were measured. As shown in Fig. 3, exposure of CO to Pt/Al₂O₃ gave an IR band at around 2100 cm⁻¹ due to CO linearly adsorbed on Pt [13–17]. However, its band position was slightly different depending on the Al₂O₃ support. CO species adsorbed on Pt/Al₂O₃-A, Pt/Al₂O₃-B, and Pt/Al₂O₃-D gave a strong IR band at 2104 cm⁻¹, while that on Pt/Al₂O₃-C gave the IR band at 2115 cm⁻¹. The interaction between CO and the Pt surface, which is reflected in the wavenumber of the IR band, is strongly dependent on the valence state of the Pt surface [13,16–19]. That is, CO bonded on Pt in the metallic state gives rise to an IR band at a lower wavenumber compared with that on Pt in a slightly cationic state. Therefore, the surfaces of Pt supported on Al₂O₃-A, Al₂O₃-B, and Al₂O₃-D were in the metallic state, while that on Al₂O₃-C was in the cationic state. As can be seen in Fig. 2, the first three catalysts, Pt/Al₂O₃-A, Pt/Al₂O₃-B, and Pt/Al₂O₃-D, showed higher activities for the total oxidation of HCs than the latter catalyst. This result suggested that Pt in the metallic state supported on Al₂O₃ is the catalytically active site for the total oxidation of HCs.

The valence state of Pt supported on a metal oxide is

Fig. 3. FT-IR spectra of CO adsorbed on Pt/Al₂O₃-A, Pt/Al₂O₃-B, Pt/Al₂O₃-C, and Pt/Al₂O₃-D. All the spectra were recorded after flushing with He at 50 °C, following exposure to 0.5% CO-99.5% He at 50 °C for 0.5 h.

known to be different depending on the surface acidity of the metal oxide support. Yazawa et al. [11] investigated the valence state of Pt supported on various metal oxides by Pt L_{III}- and L_{III}-edge XANES, and found that Pt on acidic supports was less oxidized than that on basic supports in an oxidizing atmosphere. This indicated that the oxidation-resistance of Pt was enhanced by an increase in the acid strength of the support. On the other hand, Nagai et al. [20] reported that the use of a basic support can stabilize Pt particles in a highly dispersed state. By taking into account these results in the literature [11,20], the difference in the valence state of the Pt surface observed for the Pt/Al₂O₃ samples in this study was attributed to the difference in the surface acid-base property of the Al₂O₃ supports.

In order to get information on the surface acidity and basicity of the Al₂O₃ supports, NH₃-TPD and CO₂-TPD measurements were carried out. The NH₃-TPD and CO₂-TPD profiles of Al₂O₃-B and Al₂O₃-C were measured because the dispersions of Pt supported on these two Al₂O₃ were similar (Table 2) while the valence states of the Pt surfaces were different (Fig. 3). Figure 4 shows the NH₃-TPD profiles of the two Al₂O₃ supports. The shapes of the NH₃-TPD profiles were similar, suggesting there was no significant difference in the acid strength. The amount of NH₃ desorbed from Al₂O₃-C (0.363 mmol/g) was more than that from Al₂O₃-B (0.217 mmol/g), indicating that Al₂O₃-C has more acid sites. However, as can be seen in Table 2, the surface area of Al₂O₃-C was larger than that of Al₂O₃-B. Therefore, the amount of acid sites normalized by surface area, which corresponds to the surface density of acid sites, was evaluated. The surface density of acid sites was slightly higher on Al₂O₃-B (1.20×10^{-6} mol/m²) than on Al₂O₃-C (1.16×10^{-6}

Fig. 4. NH₃-TPD profiles of Al₂O₃-B (1) and Al₂O₃-C (2).

mol/m²). A high surface density of acid sites on the Al₂O₃ support appears to be important for stabilizing the Pt surface in the metallic state.

Figure 5 shows the CO₂-TPD profiles of the two Al₂O₃ supports. Both Al₂O₃ supports showed similar CO₂-TPD profiles, indicating there was no difference in their surface basic property (basic strength and amount of basic site, the amount of CO₂ desorbed from Al₂O₃-B and Al₂O₃-C were 0.0726 and 0.0768 mmol/g, respectively). The surface density of basic sites was higher on Al₂O₃-B (0.40×10^{-6} mol/m²) than on Al₂O₃-C (0.24×10^{-6} mol/m²). It is suggested that Pt particles are stabilized in the highly dispersed state on Al₂O₃-B under the reaction conditions for the total oxidation of HCs.

Fig. 5. CO₂-TPD profiles of Al₂O₃-B (1) and Al₂O₃-C (2).

Although further experimental details are necessary, the surface acidity and basicity of the Al₂O₃ support can be concluded to be an important factor that also determines the activity of supported Pt for the total oxidation of HCs.

3 Conclusions

The activity of supported Pt catalysts for the total oxidation of hydrocarbons depended on the metal oxide support. Pt/TiO₂ was the least active catalyst, while Pt/Al₂O₃, Pt/ZrO₂, and Pt/H-ZSM-5 showed similar activities. The activity of the supported Pt catalysts decreased after aging at 750 °C for 50 h in air. Pt/Al₂O₃ showed the highest activity after aging. The activity of Pt/Al₂O₃ for the total oxidation of HCs strongly depended on the valence state of the Pt surface. Pt/Al₂O₃ with the surface of Pt in the metallic state showed higher activity than with the surface in the cationic state. The surface densities of acid and basic sites on Al₂O₃ were responsible for the valence state of the Pt surface and stability of Pt particles in the highly dispersed state, respectively.

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