Effect of Aging Atmosphere on Catalytic Activity for NO–CO– C₃H₆–O₂ Reaction of CeO₂-Containing Oxide Supported Pd Catalysts

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Abstract The catalytic activity for CO, hydrocarbon and NO removal on Al_2O_3 and CeO_2 based oxides supported Pd catalysts were studied under switching of aging condition between air and N₂ atmosphere. For CeO₂-containing Pd catalysts, the deterioration of catalytic activities by aging in N₂ was improved by oxidative treatment. Based on results of XPS and FT-IR measurements, it was presumed that the catalytic activity of Pd catalysts was strongly affected by the adsorbed form of CO on Pd, which occurs owing to a change of the chemical state of Pd.

Keywords Palladium · Cerium oxide · Oxidation

1 Introduction

Pd has widely used in three-way catalysts (TWCs) of automobile for active species which oxidize carbon monoxide (CO) and hydrocarbons (HC) [1–4]. And there have been several studies on the properties of reduction for nitrogen oxides (NO_x) in Pd catalysts for the alternative material of

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S. Kato · M. Ogasawara · S. Nakata Department of Applied Chemistry, Graduate School of Engineering and Resource Science, Akita University, 1-1 Tegatagakuen-machi, Akita 010-8502, Japan rhodium [5–7]. TWCs has used under fluctuating atmosphere of the ratio air/fuel at high temperature. Recently, an improvement of TWCs performance and an efficient use of the precious metals are demanded in order to accommodate the global new legislation and the rising precious metal prices. Therefore it will be needed saving the consumption of precious metal and preventing the catalyst from the deterioration of purification performance for exhaust gas under atmosphere fluctuating O₂ concentration at high temperature. There have been a number of reports on the deactivation of Pd catalyst [5, 8-10]. It is known that changes in the chemical states of Pd affect remarkably the catalytic activity and thermal stability of Pd catalyst [8, 11-14]. Since the vapor pressure of Pd metal is higher than that of PdO, PdO decomposition temperature and oxygen partial pressure affect the sintering of Pd [8, 11]. To suppress sintering of dispersed Pd particles, attempts to increase PdO decomposition temperature have been made by doping the electronegative promoters such as alkaline earth metal in a carrier [5]. Hinokuma et al. [15] has reported that the Pd/CeO₂ catalyst by the treatment of thermal aging at 900 °C in air was remarkably increased catalytic activities for the ambient-temperature CO oxidation. However improved phenomenon of the deteriorated purification performance for the CeO₂ containing Pd catalysts have not been investigated in detail.

In this work, we studied the catalytic activity for NO– CO–C₃H₆–O₂ reaction and surface states of dispersed Pd on γ -Al₂O₃, CeO₂ or CeO₂–ZrO₂ mixed oxides under the switch of aging condition using by air and nitrogen (N₂) atmosphere as simple endurance test of TWCs. Consequently, it was found that the deteriorated purification performance of the CeO₂ containing Pd catalysts by the aging in N₂ atmosphere was recovered by the aging in air.

2 Experimental

2.1 Sample Preparation

The catalyst powder loaded 1 mass% Pd supported on γ -Al₂O₃, CeO₂ or CeO₂–ZrO₂ mixed oxides were prepared by impregnation of Pd(NO₃)₂ solution (Tanaka Noble Metals Co, Ltd), followed by drying at 100 °C and calcinations at 600 °C for 3 h in air. CeO₂ and CeO₂–ZrO₂ mixed oxides powder used as supports were prepared using a precipitation method [16]. La doped γ -Al₂O₃ (Sasol, Ltd.) was used as a support for Pd/ γ -Al₂O₃ catalyst. The slurry prepared by mixing of each powders and inorganic binder were coated 100 g/L on a ceramics honeycomb (NGK INSULATORS, LTD.), followed by drying at 90 °C for 15 min and calcinations in air at 600 °C for 3 h.

Aging of the catalysts was performed at 900 °C under air and N_2 atmosphere shown in Table 1. Hereinafter, aging atmospheres of air and N_2 are denoted as A and N, respectively. CeO₂–ZrO₂ is denoted as CZ-X/Y, where X and Y indicate the weight percentage of CeO₂ and ZrO₂, respectively.

2.2 Catalytic Activity Test and Characterization

Catalytic activity test was performed raising the temperature from 100 to 500 °C in a simulated stoichiometric gas containing CO (0.69 vol.%), C_3H_6 (400 ppm), NO (500 ppm), O_2 (0.5 vol.%), CO_2 (14 vol.%), H_2O (10 vol.%) and N_2 balance. The total gas flow during the experiments was 25 L/min, GHSV 20,000 h⁻¹, and the heating rate of the furnace was 20 °C/min. The experimental set-up for the activity measurements is presented in Fig. 1. The concentration of CO, C_3H_6 and NO in the effluent gas was continuously monitored by infrared (IR), flame ionization and chemiluminescence detectors with an on-line gas analyzer (Horiba, MEXA7100).

The characterization of catalyst which was stripped from the coated ceramics honeycomb after the aging treatment was carried out. The dispersion of Pd on Pd/CeO₂, Pd/ γ -Al₂O₃ and Pd/CeO₂--ZrO₂ catalysts was measured by using CO pulse method [17]. The 0.2 g of catalyst was loaded into a quartz tube reactor. The catalyst heated to 400 °C at

 Table 1
 Schematic table of aging condition of Pd catalysts

Symbol	Atmosphere
Aged A	Aged for 4 h in air
Aged N	Aged for 4 h in N ₂
Aged AA	Aged for 8 h in air
Aged AN	Switched to aging for 4 h in air after aging for 4 h in N_2
Aged NA	Switched to aging for 4 h in N_2 after aging for 4 h in air



Fig. 1 Schematic drawing of the catalytic reactor

10 °C/min and held for 10 min in flowing air at 100 cm³/min. Then, the catalysts were purged with He fed at 100 cm³/min for 1 min, and then held for 10 min in flowing H₂ at 100 cm³/min. Subsequently the catalyst cooled down to 50 °C under He atmosphere, and the catalyst held at 50 °C under switched feed gases. The order of feed gases was as follows, air (5 min), He (1 min), CO₂ (10 min), He (1 min), H₂ (5 min) and He 5 min at 100 cm³/min. The CO pulse adsorption was performed at 50 °C. CO concentration in the effluent gas was evaluated using a Shimadzu GC-8A gas chromatograph with TCD. Based on an assumed stoichiometry of one adsorbed CO molecule per exposed Pd atom, the particle size of Pd was calculated by using Eq. (1) [18].

Dispersion = 1.1/d (nm)(1)

A specific surface area was estimated by N₂ adsorption measurement using Brunauer–Emmett–Teller (BET) method (Quantachrome Instrument, Quadrasorb SI). X-ray diffraction (XRD) patterns of the crystal phases of the aged Pd catalysts were recorded using a Rigaku RINT-TTRIII diffract meter with Cu K α radiation. The data for stepscanning XRD were recorded at 0.02° intervals in the range $30.0^{\circ} \le 2\theta \le 50.0^{\circ}$ with 10 s count accumulation per a step. Chemical states of Pd on supports were investigated by X-ray photoelectron spectroscopy (XPS, Shimazu, KRATOS AXIS-ULTRA DLD). XPS measurement was performed using monochromatic Al K α X-rays (15 kV, 10 mA). The peak position was calibrated using the binding energy of C 1s (284.6 eV). Fourier transform infrared

spectroscopy (FT-IR) experiments were carried out using a JASCO FT/IR-6200 spectrometer equipped with MCT detector and KBr beam splitter. Spectrum was obtained with 64-scan data acquisition at resolution of 4 cm⁻¹ in controlled gas atmosphere and temperature, employing a diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy cell. The sample was pretreated in N₂ flow at 600 °C for 30 min and then cooled to 50 °C in N₂. The background spectrum of the surface was measured for spectral correction. Measurement of spectra was carried out after introducing 25 vol.% CO with the balance of N₂ at a flow rate of 0.1 L/min.

3 Result and Discussion

3.1 Catalytic Activity and Pd Dispersion

The catalytic activities for NO-CO-C₃H₆-O₂ reaction using a simulated stoichiometric exhaust gas over Pd/ CeO₂, Pd/ γ -Al₂O₃ and Pd/CZ were investigated and evaluated the temperature at which conversion is attained to 50 % (T₅₀) and a conversion at 500 °C (η_{500}) of CO, C₃H₆ and NO. Figures 2, 3, 4, 5 and 6 shows values of T_{50} and light-off curves of conversions for the fresh and aged (at 900 °C) Pd catalysts, respectively. As shown in Figs. 3, 4, 5 and 6, η_{500} of CO, C_3H_6 and NO were reached nearly 100 % in all catalysts. Pd/CeO2 catalyst exhibited the highest activity for both CO/C3H6 oxidation and NO reduction, except for the aged-N catalysts. T₅₀ for CO, C₃H₆ and NO of fresh Pd/γ-Al₂O₃ catalyst shifted from 221 to 265 °C for the fresh catalyst to over 300 °C after the aging at 900 °C (Fig. 2). On the other hand, the T_{50} for CO of Pd/CeO₂ shifted higher temperature from 176 °C for the fresh catalyst to 348 °C for the aged-N catalyst, and shifted lower temperature, 185 °C, which is close to that of the fresh catalyst, after the following oxidative treatment (aged-NA). This activity recovery behavior also appeared in the case of C₃H₆ and NO, and the temperature shift became larger with increasing CeO₂ contents. Additionally, the T₅₀ for CO of Pd/CeO₂ shitted slightly lower from 176 °C for the fresh catalyst to 167 °C after oxidative treatment (aged-A). However, after the following aging in N2, it raised to 200 °C (aged-AN). T50 for CO of Pd/CeO2 after oxidative treatment, aged-A and AA, were close to each other, such as 167 and 169 °C, respectively. Similar behaviors of T₅₀ for C₃H₆ and NO were also observed for the CeO₂ containing Pd catalysts. These results suggest that the catalytic activities over CeO₂ containing Pd catalysts were affected by the aging atmosphere. In addition, it was found that the catalytic activity of CeO2 containing Pd catalyst was deteriorated by aging in N2 and recovered by the following aging in air.



Fig. 2 Light-off temperature of 50 % conversion rate in NO–CO– C_3H_6 –O₂ reaction over Pd catalysts

The BET surface area and Pd dispersions (CO/Pd) on each sample for fresh and aged at 900 °C are shown in Table 2. The BET surface area of fresh catalysts for Pd/ γ -Al₂O₃, Pd/CeO₂, Pd/CZ-50/50 and Pd/CZ-30/70 were 178, 91, 83 and 90 m^2/g , respectively. The surface area of the catalysts aged for 8 h (aged-AA) is smaller than that for 4 h (aged-A), suggesting that sintering of the support and Pd proceeded with aging time. The surface areas of Pd/ γ -Al₂O₃, for fresh and after aging under all the aging conditions were higher than those of CeO₂-containing Pd catalysts. On the other hand, surface area of the Pd/ γ -Al₂O₃ after aged-AA treatment was the lowest among the aged Pd/γ -Al₂O₃ catalysts, indicating that aging process in oxidative atmosphere causes to decrease surface area. CO/Pd of fresh catalysts, Pd/γ-Al₂O₃, Pd/CeO₂, Pd/CZ-50/50 and Pd/CZ-30/70 were 0.130, 0.559, 0.429 and 0.430,



Fig. 3 Conversion curves of CO, C3H6 and NO over Pd/CeO2 for NO-C3H6-CO-O2 reaction



Fig. 4 Conversion curves of CO, C3H6 and NO over Pd/Al2O3 for NO-C3H6-CO-O2 reaction



Fig. 5 Conversion curves of CO, C_3H_6 and NO over Pd/CZ (C/Z = 50/50) for NO- C_3H_6 -CO- O_2 reaction

respectively. CO/Pd of each aged Pd catalysts decreased in the sequence of Pd/CeO₂ > Pd/CZ-50/50 > Pd/CZ-30/ $70 > Pd/\gamma$ -Al₂O₃, except for the catalysts after aged-N treatment. This sequence is inconsistent with that of the surface area. In the case of CeO₂-containing Pd catalysts after aging, except for the aged-N catalyst, CO/Pd decreased with increasing CeO_2 contents in the support. After aging in the absence oxygen atmosphere (aged-N), the CO/Pd of CeO₂-containing Pd catalysts was significantly small, but recovered by following oxidative treatment



Fig. 6 Conversion curves of CO, C_3H_6 and NO over Pd/CZ (C/Z = 30/70) for NO- C_3H_6 -CO- O_2 reaction

Table 2 Surface area and Pd dispersion in Pd catalysts after aging at 900 °C

	Surface area (m ² /g) Aged at 900 °C						Dispersion: CO/Pd Aged at 900 °C						
	Fresh	А	Ν	AA	AN	NA	Fresh	А	Ν	AA	AN	NA	
Pd/γ-Al ₂ O ₃	178	102	131	94	105	104	0.13 (8.6)	0.04 (32.0)	0.03 (36.2)	0.03 (40.0)	0.02 (53.4)	0.04 (27.3)	
Pd/CeO ₂	91	54	59	46	52	43	0.56 (2.0)	0.47 (2.4)	0.01 (160.2)	0.41 (2.7)	0.29 (3.8)	0.31 (3.7)	
Pd/CZ-50/50	83	46	73	41	44	50	0.44 (2.6)	0.18 (6.3)	0.03 (38.7)	0.12 (9.4)	0.02 (56.1)	0.13 (8.6)	
Pd/CZ-30/70	90	52	70	48	52	51	0.43 (2.6)	0.08 (13.8)	0.03 (44.9)	0.06 (20.4)	0.01 (112.1)	0.10 (11.4)	

() The particle size of Pd species (nm)

(aged-NA). The change of CO/Pd for the aged-N and NA catalysts exhibited similar behavior with T_{50} of CO, C_3H_6 and NO, namely T_{50} shifted higher temperature with decreasing CO/Pd. This result suggests that CO/Pd of the CeO₂-containing Pd catalysts was independent on the surface area and the oxidation of Pd species leads to higher dispersion of Pd on CeO₂. Similar behavior has been reported for Pd/ γ -Al₂O₃ catalyst by Xu et al. [19] that Pd sintering was not influenced by the sintering of support. Nagai et al. [20] has reported that the interaction between Pt and CeO₂ at 800 °C under oxidizing condition causes redispersion of as grown Pt crystallites in Pt/CeO₂ catalyst. In the present study, the redispersion behavior of Pd on CeO₂-containing catalysts was found.

Table 3 and Fig. 7 shows BET surface area, CO/Pd and value of T_{50} for the Pd catalysts aged at 950 and 1,000 °C, respectively. The surface area of Pd/CeO₂ catalyst aged at 1,000 °C was lower than that of the catalyst aged at 900 °C in both aged-N and aged-NA conditions. CO/Pd of Pd/CeO₂ catalysts after the aged-N and aged-NA treatment at 950 °C were 0.01 and 0.21, respectively, indicating that redispersion of Pd occurred by the aged-NA treatment. After the aged-NA treatment at 1,000 °C, the CO/Pd was lower than that after the treatment at 900 °C. This phenomenon would be caused by PdO decomposition to

metallic Pd, leading to faster Pd sintering at the higher temperature in air. T_{50} of CO was 356 and 226 °C after aged-N and aged-NA treatment at 950 °C, respectively, indicating that the catalytic activity at lower temperature was improved by the oxidative treatment after N₂ treatment. A similar phenomenon was also observed for C_3H_6 oxidation and NO reduction over the Pd/CeO₂ and for the catalysts aged at 1,000 °C. On the other hand, for Pd/ γ -Al₂O₃ catalysts, T_{50} of CO, C_3H_6 and NO were shifted high temperature with increasing the aging time and temperature.

Figure 8 shows T_{50} of CO plotted as function of CO/Pd for Pd/ γ -Al₂O₃, Pd/CeO₂, Pd/CZ-50/50 and Pd/CZ-30/70 catalysts. It was found that the value of T_{50} is correlated with CO/Pd. As the results mentioned above, the value of CO/Pd for the aged-NA catalyst was higher than that for the aged-N catalyst in CeO₂-containing Pd catalysts. These results suggest that the recovery behavior of the catalytic activity after aging in air is attributed to a characteristic of Pd surface on the support.

In order to determine Pd species on the catalysts, XRD experiments were carried out. The XRD patterns of Pd/ γ -Al₂O₃ and Pd/CeO₂ for the aging at 900 °C are shown in Fig. 9. In Fig. 9a, the most of peaks are consistent with the characteristic peaks of cubic CeO₂, and metallic Pd

	Surface a	rea (m ² /g)			Dispersion: CO/Pd				
	Aged at 9	950 °C	Aged at 1	,000 °C	Aged at 950 °C		Aged at 1,000 °C		
	N	NA	N	NA	N	NA	N	NA	
Pd/y-Al ₂ O ₃	128	104	123	103	0.03	0.03	0.02	0.03	
Pd/CeO ₂	39	34	20	20	0.01	0.21	0.01	0.02	

Table 3 Surface area and Pd dispersion in Pd catalysts after aging at 950 and 1,000 $^\circ C$



Fig. 7 Light-off temperature of 50 % conversion rate in a simulated exhaust gas over Pd catalysts for aging at 950 and 1,000 $^{\circ}$ C

 $(2\theta = 40.1^{\circ})$ was detected in the aged-N and aged-AN Pd/ CeO₂ catalyst. The crystallite sizes of metallic Pd estimated by Scherrer's equation for the aged-N and aged-AN catalysts were 46.8 and 55.9 nm, respectively. The peak observed at $2\theta = 40.1^{\circ}$ was disappeared in the case of the catalyst after the treatment in inert and following oxidative atmosphere (aged-NA). The strongest peak of PdO $(2\theta = 33.8^{\circ})$ could not be observed in all Pd/CeO₂, due to the existence of the peak of CeO₂ in the region of $2\theta = 31-35^{\circ}$. Figure 9b shows the XRD patterns for Pd/ γ -



Fig. 8 Relationships between CO/Pd and T₅₀ of CO

Al₂O₃. Metallic Pd for the aged-AN and aged-N catalysts and PdO for the aged-A and NA catalysts were detected. These crystallite sizes of metallic Pd and PdO were 16-21 nm. This crystallite sizes are not correlated the particle size of Pd species which estimated from CO/Pd in Table 2. Xu et al. [21] has reported that the correlation of Pd metal particle size was obtained between TEM, XRD, H_2 chemisorption and CO oxidation in Pd/ θ -Al₂O₃ catalyst. In their study, the sample was immediately quenched in liquid N₂ after N₂ aging to prevent oxidation of metallic Pd into polycrystalline PdO. The difference between particle sizes estimated by XRD and CO adsorption in the present study would be attributed to the existence of polycrystalline which formed during the cooling after N₂ aging and the adsorbed form of CO on Pd species such as Pd⁰-CO, $(Pd^{0})_{2}$ -CO and $(Pd^{0})_{3}$ -CO. These results suggest that a number of CO absorption sites on Pd affected the catalytic activity. In order to clarify the recovery behavior of the catalytic activity of Pd/CeO₂ catalysts, the chemical state of Pd and a form of adsorbed CO were investigated.

3.2 The Chemical State of Pd

The change in the chemical state of Pd on the catalysts treated each aging condition at 900 °C were studied using XPS. Pd 3d XPS spectra of Pd/CeO₂ and Pd/ γ -Al₂O₃ catalysts aged under the each condition are shown in Fig. 10.





The Pd 3d_{5/2} peaks of Pd/CeO₂ catalysts were observed in the region of 334-339 eV (Fig. 10a). It is reported that Pd $3d_{5/2}$ peak of metallic Pd (Pd⁰), PdO (Pd²⁺) and PdO₂ (Pd⁴⁺) are shown at 335.2, 336.7 and 337.5 eV, respectively [22–27]. The peak observed at 337.7 eV for the fresh of Pd/CeO₂ catalysts was assigned to Pd⁴⁺. The peak of Pd⁴⁺ was observed for the aged-A and NA catalysts after oxidative treatment, and it was also observed the aged-AN catalyst after aging in inert atmosphere. For the aged-N catalyst, the weak peak observed at 335.4 eV was assigned to Pd⁰. The reason for this result of the aged-N catalyst may be due to a decrease of Pd atoms on the catalyst. These results indicate that reduction of Pd^{4+} on CeO_2 after the oxidative treatment at 900 °C is difficult and the chemical state of Pd⁰ for the aged-N easily changes to that of the fresh catalyst by oxidative treatment at 900 °C (the aged-NA). On the other hand, the peaks observed at 334.8 and 336.7 eV for the Pd/ γ -Al₂O₃ catalysts were assigned to Pd⁰ and Pd²⁺ (Fig. 10b). The peaks of Pd⁰ were observed for the catalyst aged under inert atmosphere (aged-N and AN). Pd²⁺ were observed for the catalyst aged under oxidative atmosphere (aged-A and aged NA), namely the chemical state of Pd on Al₂O₃ was easily changed by the aging atmosphere. From these results of the XPS measurement, it was found that the chemical state of Pd on CeO₂ was higher oxidation state than that of γ -Al₂O₃ under oxidative atmosphere.

There are a number of reports about the existence of Pd^{4+} . Otto et al. [25] have reported that PdO_2 was stabilized by an interaction of a highly dispersed Pd with an

oxide support and Moroseac et al. [28] have suggested that the metal-support interactions may stabilize PdO_2 for Pd/SnO_x catalyst in hydrogen containing air, respectively. On the other hand, Colussi et al. [29] reported the formation of a square planer PdO_4 unit for Pd^{2+} state in Pd-O-Ce surface of Pd/CeO_2 catalyst as revealed by density-functional theory (DFT) calculations on the basis of high-resolution TEM data.

3.3 A Form of Adsorbed CO Over Pd Catalysts

The DRIFT spectra of adsorbed CO at 50 °C on Pd/CeO₂ and Pd/γ -Al₂O₃ catalysts aged under each condition at 900 °C are shown in Fig. 11. Figure 11a shows the DRIFT spectra of CO adsorbed Pd/CeO₂ catalysts. It is reported that the bands for linearly adsorbed CO on Pd^{0} , Pd^{+} , Pd^{2+} and the bridge bonded \overrightarrow{CO} on $\overrightarrow{Pd^0}$ [($\overrightarrow{Pd^0}_2$ - \overrightarrow{CO}] appear near 2085, 2110, 2156 and 2000, 1960 cm⁻¹ for the Pd/CeO₂ catalysts, respectively [12, 30-36]. For the fresh catalyst, the bands observed at 2,089 and 2,140 cm^{-1} were assigned to linear Pd⁰-CO and Pd²⁺-CO. Intensity of these band decreased by aging and the band assigned to linear Pd⁺-CO appeared at 2,118 cm⁻¹ after oxidative treatment (aged-A, NA and AN). For the aged-N catalyst, these linear Pd-CO bands were absent, but the other band was observed at 1,997 cm⁻¹, which is assigned to bridge (Pd⁰)₂–CO. It was found that the Pd in aged-N catalyst is present as metallic state. The bands of Pd⁰-CO and Pd²⁺-CO disappeared for the aged-N catalyst, but they were observed by oxidative treatment (aged-NA) again. These results were Fig. 10 Pd 3d XPS peaks of Pd catalysts: a Pd/CeO₂ and b Pd/ Al_2O_3



Fig. 11 DRIFT spectra of CO adsorbed on the Pd catalysts in a flow of 25 vol.% CO and balance N_2 at 50 °C for 10 min: a Pd/CeO₂ and b Pd/Al₂O₃

suggested that the adsorbed form of CO on Pd was changed by the chemical state of Pd on CeO₂, and the lowest CO/Pd for the aged-N (Table 2) would be caused by absence of adsorbed linear carbonyl on Pd⁰. In Pd/CeO₂ catalysts, no bands assigned to adsorb CO on Pd⁴⁺ were observed for the fresh, aged-A, aged-AN and aged-NA. Figure 11b shows the DRIFT spectra of CO adsorbed on Pd/γ -Al₂O₃ catalysts. It is reported that the bands for linearly adsorbed of CO on Pd^0 , Pd^+ , the bridge bonded of CO on Pd^0 and the three-fold bonded of CO on Pd^0 [(Pd^0)₃–CO] had shown near 2080, 2158, 1975 and 1911 cm⁻¹ for the Pd/γ -Al₂O₃ catalysts, respectively [6,

34, 37, 38]. The weak bands observed at 1,989 and 2,094 cm⁻¹ were assigned to bridge $(Pd^0)_2$ -CO and Pd^0 -CO for the fresh catalyst. After aging under the each condition, the band at 2,094 cm⁻¹ disappeared and intensity of the band at 1,989 cm⁻¹ decreased. No bands of linear carbonyl on Pd²⁺ for the fresh, aged-A and aged-NA were observed except for the fresh catalyst. These results for the Pd/Al₂O₃ catalysts are suggested Pd²⁺ was reduced to Pd⁰ in 25 vol.% CO/N₂ flow.

Figure 12 shows the DRIFT spectra during a flow of 25 vol.% CO and balance N2 over the aged-A Pd/CeO2 catalyst at 50 °C. The bands observed at 2,089 and 2,140 cm⁻¹ were assigned to linear Pd⁰-CO and Pd²⁺-CO after a flow of CO/N_2 gas. The bands observed at 2,300–2,400 cm⁻¹ were assigned to CO2 (g). As from 3 min, intensity of band assigned to linear Pd²⁺-CO decreased with the exposure time. On the other hands, intensity of band assigned to linear Pd⁰-CO increased with the exposure time, and the band clearly appeared at 2,118 cm⁻¹ (linear Pd⁺–CO) as from 10 min. It was suggested that oxidized Pd species were reduced to Pd^+ or metallic Pd in the flow of CO/N₂ gas. Therefore, no bands assigned to adsorb CO on Pd⁴⁺ would be observed Pd/CeO₂ catalysts in this study. From these results of the FT-IR experiments, it was found that the adsorbed forms of CO on Pd/CeO2 and Pd/Al2O3 catalysts after the oxidative treatment were linear and bridge carbonyl types, respectively. And it was found that the difference between the crystallite sizes of Pd species estimated by Scherrer's equation and the CO adsorption are caused by the adsorbed form of CO on Pd. Fernández-Garciá [32] and Martínez-Arias et al. [33] has reported that linear carbonyl type was easily desorbed at lower temperature than bridged carbonyl type on Pd, and it was suggested that the generated metallic adsorption sites by desorption of CO was became adsorption sites of NO for CO–NO– O_2 reaction. Moreover Craciun et al. [12] has reported that the higher dispersion and catalytic activity showed with increasing the ratio of linear carbonyl to bridged carbonyl peak areas for methane steam reforming. Therefore it was thought that CO/Pd and the catalytic activity were affected by the difference of the adsorbed form of CO on Pd.

From the above-mentioned results, it was found that the catalytic activity of CeO_2 containing Pd catalyst was deteriorated by the aging in N₂ but it was recovered by the oxidative treatment. And the catalytic activity is depended on CO/Pd. The deterioration of catalytic activity for the aged-N in CeO₂ containing Pd catalysts was caused by the decrease in CO/Pd, which takes place by the change of adsorbed form of CO on Pd from linear Pd–CO for fresh catalyst to bridge $(Pd^0)_2$ –CO for the aged-N. This adsorbed form of CO on Pd was affected the chemical state of Pd. The chemical state of Pd on CeO₂ by the oxidative treatment was existed higher oxidation state (Pd^{4+}) than that of



Fig. 12 DRIFT spectra of CO adsorbed on the aged-A Pd/CeO_2 catalyst in a flow of 25 vol.% CO and balance N_2 at 50 °C. Exposure time: 0, 1, 3, 5, 10, 15 and 30 min

 γ -Al₂O₃. Reduction of Pd⁴⁺ formed by the oxidative treatment at 900 °C was difficult, and the chemical state of Pd⁰ for the aged-N returned easily to that of the fresh catalyst by oxidative treatment at 900 °C.

4 Conclusion

In the present study, we studied the catalytic activity Pd catalysts under the switch of aging condition using by air and N₂ atmosphere, and found the catalytic activity of CeO₂-containing Pd catalysts improved by oxidative treatment at 900 °C. It was shown that Pd/CeO₂ catalysts exhibited higher catalytic activities for CO, C₃H₆ and NO than Pd/γ -Al₂O₃ and Pd/CZ catalysts, except that for the aged-N. For CeO2-containing Pd catalysts, the deterioration of catalytic activities for the aged-N was improved by oxidative treatment at 900 °C. The catalytic activity was correlated with CO/Pd rather than BET surface area and the crystallite size of Pd species. The XPS results indicated that the chemical state of Pd on CeO₂ performed the oxidative treatment was highly ionic state than that of γ -Al₂O₃. And the FT-IR measurement revealed that the adsorbed form of CO on Pd/CeO₂ catalysts was linear carboxyl and that of CO on Pd/Al₂O₃ catalysts was bridge carboxyl type. Based on these results, it was presumed that the catalytic activity for Pd catalysts was strongly affected by the adsorbed form of CO on Pd, which takes place by a change of the chemical state of Pd.

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