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Propene oxidation over palladium catalysts supported on zirconium rich ceria–zirconia

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ABSTRACT

Ceria–zirconia solid solution with the Ce/Zr ratio of 1/3 was prepared and used as support material for palladium catalysts. The palladium catalysts supported on the zirconium rich ceria–zirconia (Pd/CZ) were studied for propene oxidation reaction. In the activity tests, the influences of palladium loadings, pretreatment conditions, and reaction conditions were investigated. The catalytic activities of Pd/CZ with small amount of palladium component were strongly affected by the pretreatment conditions such as oxidative or reductive atmosphere. From IR measurements, it was suggested that the palladium species with high reducibility should be active for the complete oxidation of propene. The initial activities of Pd/CZ catalysts under the insufficient oxygen condition were equivalent to the activities under the stoichiometric condition due to the property of high oxygen storage capacity (OSC). It was revealed that CZ support helped the high dispersion of palladium oxide particles and its OSC property assisted the propene oxidation reaction.

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1. Introduction

Automobile has been an indispensable means of transportation for human life over the decades. Recently, some electric vehicles are available in several countries, whereas the automobile that runs on gasoline still remains the majority. In the case of the gasoline-fueled automobile, the treatment of exhaust gases as carbon monoxide (CO), hydrocarbon (HC), nitrogen oxide (NO_x), and sulfur oxide (SO_x) is a significant technology, because the gases have a large impact on human body and the global environment. For example, it is believed that the photochemical oxidants are produced by the photochemical reaction of hydrocarbons and NO_x, and the oxidants induce the air pollution such as photochemical smog. The gases of NO_x and SO_x would be the main reason of acid rain and air pollution. Therefore, various types of automotive catalysts have been developed to remove their harmful gases. One of the most famous catalysts is three-way catalyst (TWC), which is composed of precious metal, ceria–zirconia, and alumina. Especially, the ceria–zirconia (CZ) solid solution has the superior characters of high thermal stability and high oxygen storage capacity (OSC) [1–3], and it has already been put into practical use as the promoter of automotive catalysts. Furthermore, it was reported that the growth of platinum particles was inhibited by the strong interaction with ceria–zirconia system under oxidative condition. The unique effect of CZ solid solution was named as “anchor effect” [4,5]. The catalysts with CZ mixed oxide were investigated for not only the purification of exhaust gases [6,7] but also some kinds of oxidation reaction. For instance, CeO_2–ZrO_2 doped with transition metals and rare earth elements [8] was studied for soot combustion, and Co_3O_4/CeO_2–ZrO_2 composite oxide catalyst [9,10] and CeO_2–ZrO_2 [11] were investigated on total methane oxidation at low temperature. Methane combustion [12,13], toluene combustion [14], and methanol decomposition to synthesis gases [15] over palladium catalysts supported on ceria–zirconia have also been reported by several researchers. Almost all researches, however, were conducted on catalysts with cerium rich ceria–zirconia. There are only a few researches about Zr rich ceria–zirconia supported palladium catalysts for total oxidation of hydrocarbon such as methane [16,17]. Ce element is classified with the rare earth element, and the price of precious metals is extremely expensive. Therefore, the decreases of precious metals and cerium usage are desired in addition to the achievement of high catalytic performance for the strict regulation of exhaust gases such as EURO6.

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In this study, ceria–zirconia solid solution with 25% of cerium and 75% of zirconium were used for the support material, and the influence of palladium amount was carefully investigated for propene (C_3H_6) oxidation as the fundamental reaction of exhaust gas treatment. In addition, the effects of reaction conditions and pretreatment to catalysts were researched by using the different atmosphere, because the automotive catalysts were exposed to both lean and rich conditions.

2. Experimental

2.1. Preparation of CZ support and Pd/CZ catalysts

Palladium catalysts supported on ceria–zirconia were prepared according to the following procedure. First, ceria–zirconia powder was synthesized by the coprecipitaion method. Cerium ammonium nitrate (Wako Pure Chemical) and zirconyl nitrate (Wako Pure Chemical) were sufficiently mixed with pure water, and excess ammonium hydroxide was added to the mixed solution. The precipitated powder was washed in pure water and dried at 110 °C for 1 day. The resultant powder was preheated at 600 °C for 3 h in air to remove the residual nitrate compounds, and calcined at 800 °C for 3 h in air for thermal stability improvement. By this process, the CZ(1/3) support with the chemical formula of $Ce_{0.25}Zr_{0.75}O_x$ was obtained.

Secondly, Pd component was loaded on the CZ(1/3) support by the conventional impregnation method. The powder of CZ support was impregnated with a nitrate solution of $Pd(NO_2)_2(NH_3)_2$ (Tanaka Kikinzoku Kogyo), and it was dried at 110 °C for 1 day. After the heat-treatment at 600 °C for 3 h, the catalyst was also calcined at 800 °C for 3 h in air as well as CZ support. The loadings of palladium in the samples were set at 0.04, 0.2, 1.0 and 5.0 wt.%. The *y* wt.% Pd/CZ(1/3) catalysts were hereinafter called "yPd/CZ".

2.2. Propene oxidation tests

The activities of Pd/CZ catalysts for propene oxidation were measured with a typical fixed-bed flow reactor. The as-calcined catalysts with the amount of 100 mg were pretreated at 600 °C in a flow of 10% O_2/N_2 (50 ml min^{-1}) in the reactor, and then the catalytic reaction tests were carried out by passing gaseous mixtures composed of propene (3345 ppmC), O_2 (0.5% or 0.4%), and N_2 gas as diluted gas with a total flow rate of 500 ml min^{-1} (space velocity: 300,000 ml g^{-1} h^{-1}). The oxygen concentration of 0.5% and 0.4% corresponds to the stoichiometric condition and the oxygen deficient condition of 20%, respectively, when the catalytic reaction proceeds as the total oxidation ($C_3H_6 + 9/2O_2 \rightarrow 3CO_2 + 3H_2O$). The reacted gases were analyzed by a flame ionization detector (FID) (Shimadzu, VMS-1000F) and a portable gas analyzer (HORIBA, PG-230). The propene conversion to CO_2 was calculated with CO_2 concentration at reactor outlet. The temperature was increased from 50 to 600 °C at a rate of 10 °C min^{-1}. After the reaction test, the catalyst was heat-treated at 600 °C under a flow of 10% H_2/N_2 (50 ml min^{-1}), and the same reaction test was conducted for the investigation of the effect of pretreatment condition. The amount of catalyst was set at 100 mg, and the thickness of catalytic layer in the reactor was about 2 mm. Therefore, it is considered that the temperature around samples must be homogeneous.

2.3. Characterization of Pd/CZ(1/3) catalysts

Several kinds of characterization of as-calcined catalysts were carried out so as to reveal the correlation between catalytic activities and the loading of palladium, and to realize the variation of activities due to pretreatment and reaction conditions. The BET surface area of the catalysts was estimated by TriStar II (micromeritics®), after the heat treatment at 300 °C for 3 h under vacuum. X-ray diffraction (XRD) analysis and Raman spectroscopy were conducted with MiniFlex II (Rigaku) and NRS-3100 (JASCO), respectively, in order to investigate the crystal phase and structure. The XRD patterns were recorded by using Cu Kα radiation. In the Raman spectroscopy, the Nd: YVO_4 laser with a 532 nm line was used at around 10 mW power. In addition, the O_2–CO_2–H_2–CO pulse method [18] was performed to estimate the more precise dispersion of palladium particles. The microstructures of catalysts were observed by transmission electron microscopy equipped with field emission gun (FE-TEM) (JEM2100F, JEOL) at the accelerating voltage of 200 kV. TEM images were recorded by CCD camera.

Fourier transform infrared (FT-IR) spectroscopy, temperature-programmed reduction (TPR) measurement and evaluation of oxygen storage capacity (OSC) were also carried out to investigate the chemical properties of prepared catalysts. FT-IR spectra of adsorbed CO were acquired with FT/IR-4200 (JASCO) at a resolution of 4 cm^{-1}. After a sample disk was pretreated at 400 °C for 1 h in 26.7 kPa (200 Torr) of oxygen or hydrogen, it was evacuated at 400 °C for 1 h. Then, IR cell with pretreated catalyst was filled with 6.7 kPa (50 Torr) of CO gas at room temperature. After the cell was evacuated, IR spectra were carefully recorded. The reducibility of Pd/CZ catalysts, in other words, the reactivity of oxygen species in catalysts was investigated by TPR measurement. The as-calcined catalyst was heated in 5% H_2/Ar at a heating rate of 10 °C min^{-1}, and the outlet gas was recorded by TCD detector (BP-1, HEMMI Slide Rule). After H_2-TPR measurement, the amount of adsorbed oxygen was evaluated by the pulse method of oxygen gas. The as-calcined catalysts were pretreated at 300 or 400 °C before the several characterizations. The chemical state of catalysts would not change due to the pretreatments, because the catalysts were calcined at higher temperature of 800 °C.

3. Results and discussion

3.1. Catalytic activities on propene oxidation

The results of propene oxidation tests under stoichiometric condition (O_2: 0.5%) over Pd/CZ catalysts after the oxidation and reduction treatment are shown in Fig. 1. A reaction test without catalyst was performed, and the curve of CO_2 yield was added to Fig. 1(a). After the oxidation treatment (Fig. 1(a)), the propene oxidation reaction was initiated at 200 °C over all Pd/CZ, and the ignition temperature was *ca.* 250 °C over CZ support. In the case of the catalysts with Pd loadings of 0.2, 1.0, and 5.0 wt.%, the total oxidation of propene was achieved under 500 °C. On the other hand, the propene conversion over 0.04Pd/CZ was 70% even at 600 °C, whereas the light off temperature was 200 °C and its activity was higher than that of CZ. The order of catalytic performance (5.0 > 1.0 > 0.2 > 0.04Pd/CZ > CZ) after the oxidation treatment was same with the order after the reduction, as can be seen in Fig. 1(b). The activities of 0.04, 0.2 and 1.0Pd/CZ, however, were improved by the reduction treatment, and the total oxidation of propene was achieved at 450 °C over 0.04Pd/CZ reduced in hydrogen. This result indicated that the chemical state of palladium species should be significant, as discussed in Section 3.5.

Fig. 2 shows the results of propene oxidation tests under insufficient oxygen condition (O_2: 0.4%). After the oxidation at 600 °C (Fig. 2(a)), the ignition temperatures on Pd/CZ catalysts were around 200 °C, and the light off curves below the conversion of 20% were similar with the curves of Pd/CZ under stoichiometric condition (Fig. 1(a)). In the conversion over 20%, however, the catalytic performances under insufficient oxygen conditions were inferior to the performances of Pd/CZ under stoichiometric condition. The improvements of catalytic activities by the reduction

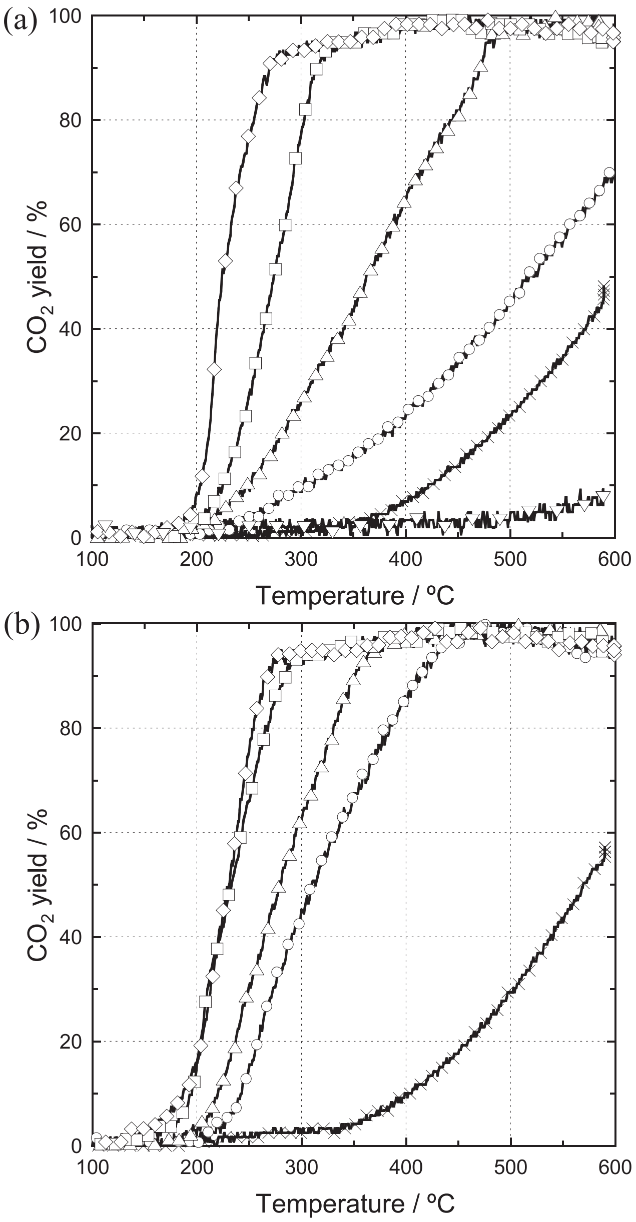

Fig. 1. CO_2 yield over CZ(1/3) and Pd/CZ(1/3) catalysts after heat-treatment in (a) oxidation and (b) reduction atmosphere. (×) CZ, (◯) 0.04Pd/CZ, (△) 0.2Pd/CZ, (□) 1.0Pd/CZ, (◊) 5.0Pd/CZ, (▽) no catalyst. Reaction conditions: propene, 3345 ppmC; O_2, 0.5%; N_2, balance; total flow rate = 500 ml min^{-1}; S.V. = 300,000 ml g^{-1} h^{-1}.

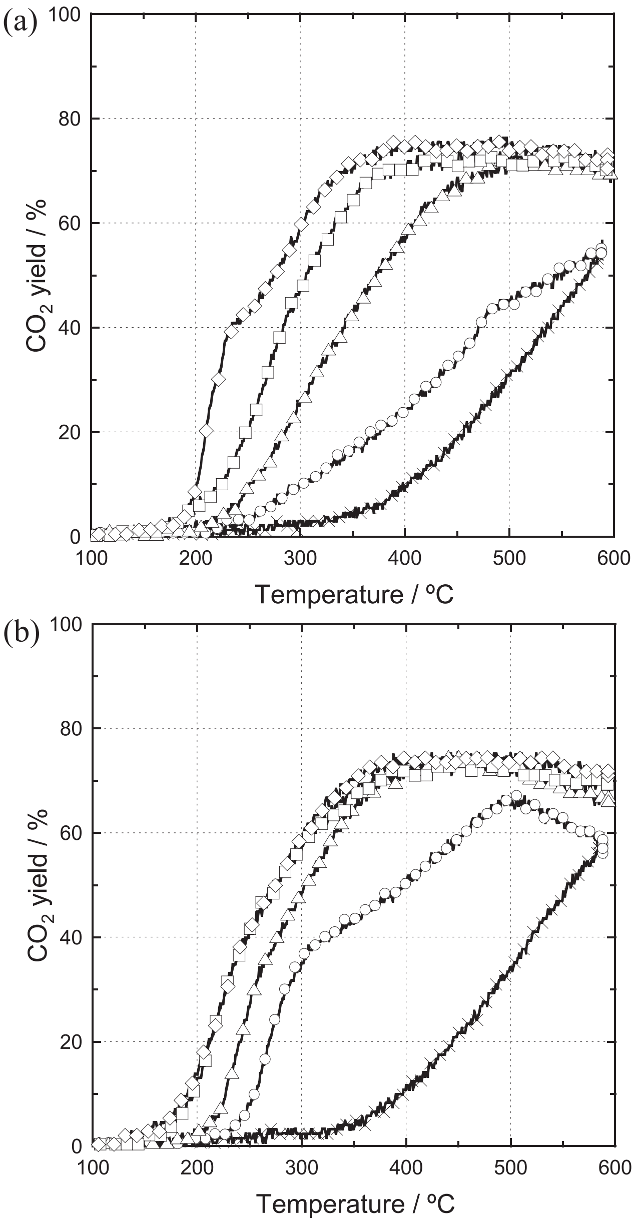

Fig. 2. CO_2 yield over CZ(1/3) and Pd/CZ(1/3) catalysts after heat-treatment in (a) oxidation and (b) reduction atmosphere. (×) CZ, (◯) 0.04Pd/CZ, (△) 0.2Pd/CZ, (□) 1.0Pd/CZ, (◊) 5.0Pd/CZ. Reaction conditions: propene, 3345 ppmC; O_2, 0.4%; N_2, balance; total flow rate = 500 ml min^{-1}; S.V. = 300,000 ml g^{-1} h^{-1}.

treatment were confirmed in the reduced samples (Fig. 2(b)). The total decomposition of propene was achieved due to the formation of by-products such as CO, while the yields of CO_2 did not reach to 100% even at high temperature such as 500 °C. This is because O_2 concentration was set as 80% (O_2: 0.4%) for total propene oxidation (O_2: 0.5%).

3.2. Structure of CZ support and Pd/CZ catalysts

The Pd/CZ catalysts were characterized to investigate the cause of difference in catalytic activities. The fundamental properties of BET surface areas, dispersion and diameter of Pd particles, and OSC values were summarized in Table 1. The surface area of CZ support was 64.2 m^2 g^{-1}, and those of Pd/CZ catalysts were more than 45 m^2 g^{-1}, even after the heat treatment at 800 °C. The high thermal stability of CZ powder was confirmed by the measurements. Fig. 3 shows XRD patterns of as-calcined catalysts. In the pattern of CZ support, only a fluorite type structure was observed, though the peaks were a little broad. Therefore, the CZ powder prepared by the coprecipitation method seems to be composed of the homogeneous solid solution of ceria and zirconia despite a large amount of zirconium component. The crystal phases derived from palladium species were not detected in all Pd/CZ catalysts. This might be due to the small amount and low crystallinity of palladium component. The difference of diffraction patterns was not shown by XRD analysis, whereas the Raman spectra of the as-calcined catalysts were gradually changed with the increase of Pd loadings (Fig. 4). The Raman spectra of CZ support, 0.04Pd/CZ and 0.2Pd/CZ were assigned to a tetragonal fluorite structure, as reported by Hirata [19]. Meanwhile, in the case of 1.0 and 5.0Pd/CZ, the Raman spectra were totally broad, and the peaks of F_{2g} band (*ca.* 460 cm^{-1}) were shifted to a lower frequency. Therefore, it was indicated that the Raman spectra were weakened by the palladium species at top surface of CZ support. Furthermore, the variation of lattice structure

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Table 1
BET surface area, dispersion, diameter of palladium particles and OSC value of Pd/CZ catalysts.

Sample	BET surface area ($m^2 g^{-1}$)	CO/Pd (%)[a]	Diameter of palladium particles (nm)	OSC (μmol g^{-1})
CZ(1/3)	64.2	–	–	400.4
0.04Pd/CZ	55.8	31.7	4.7	400.2
0.2Pd/CZ	59.8	37.4	3.9	411.3
1.0Pd/CZ	55.0	35.9	4.1	446.1
5.0Pd/CZ	46.3	11.2	13.2	620.8

[a] Dispersion of Pd particles was estimated by the O_2–CO_2–H_2–CO adsorption method at 50 °C [18].

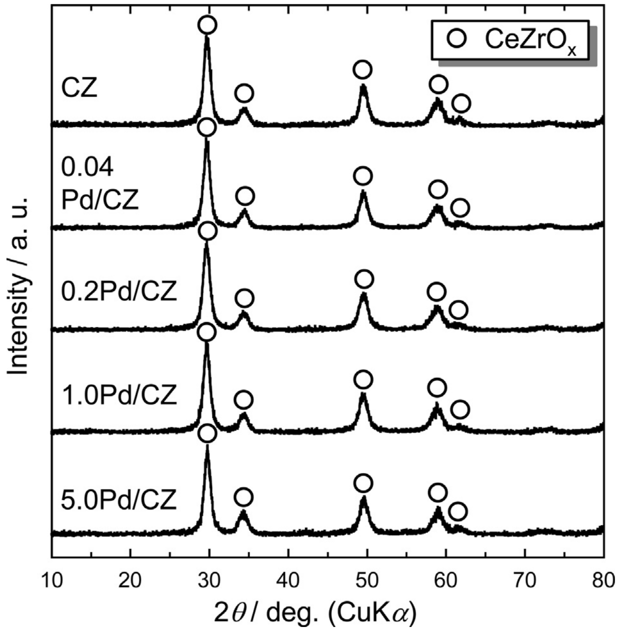

Fig. 3. XRD patterns of CZ(1/3) and Pd/CZ(1/3) catalysts.

was induced by the loading of palladium component and calcination at high temperature. In other words, a part of palladium species might dissolve into the lattice of CZ support. This would be the reason of the shift of F_{2g} band from 460 to 430 cm^{-1}. In several reports [20–23], a B_{1g} vibration mode of palladium oxide was clearly measured at 650 cm^{-1}, and the weak Raman peaks were also observed at 445 and 1,120 cm^{-1}. In this study, however, the peaks assigned as PdO were not identified due to the strong spectra of CZ support.

TEM observation was carried out in order to reveal the morphology and state of palladium species in Pd/CZ catalysts. TEM image of 1.0Pd/CZ calcined at 800 °C for 3 h are shown in Fig. 5(a). The fine particles with the size of *ca.* 2 nm were clearly observed on the surface of CZ support, as indicated by white arrows. It was confirmed that the palladium species were highly dispersed on CZ support. The

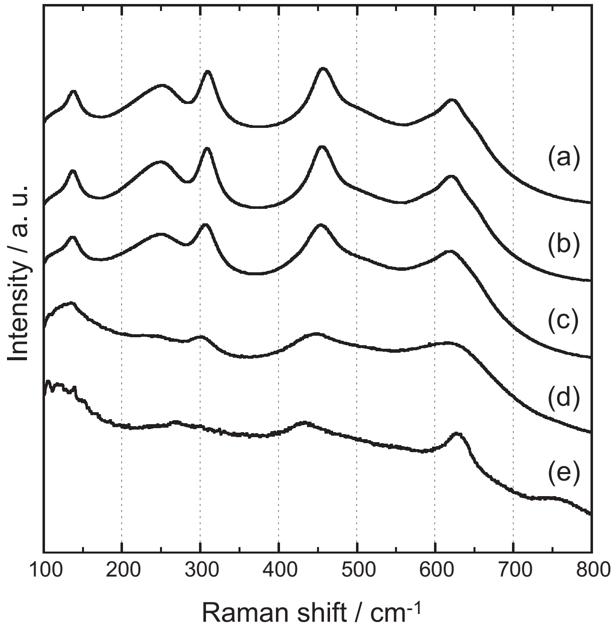

Fig. 4. Raman spectra of CZ(1/3) and Pd/CZ(1/3) catalysts. (a) CZ support, (b) 0.04Pd/CZ, (c) 0.2Pd/CZ, (d) 1.0Pd/CZ, (e) 5.0Pd/CZ.

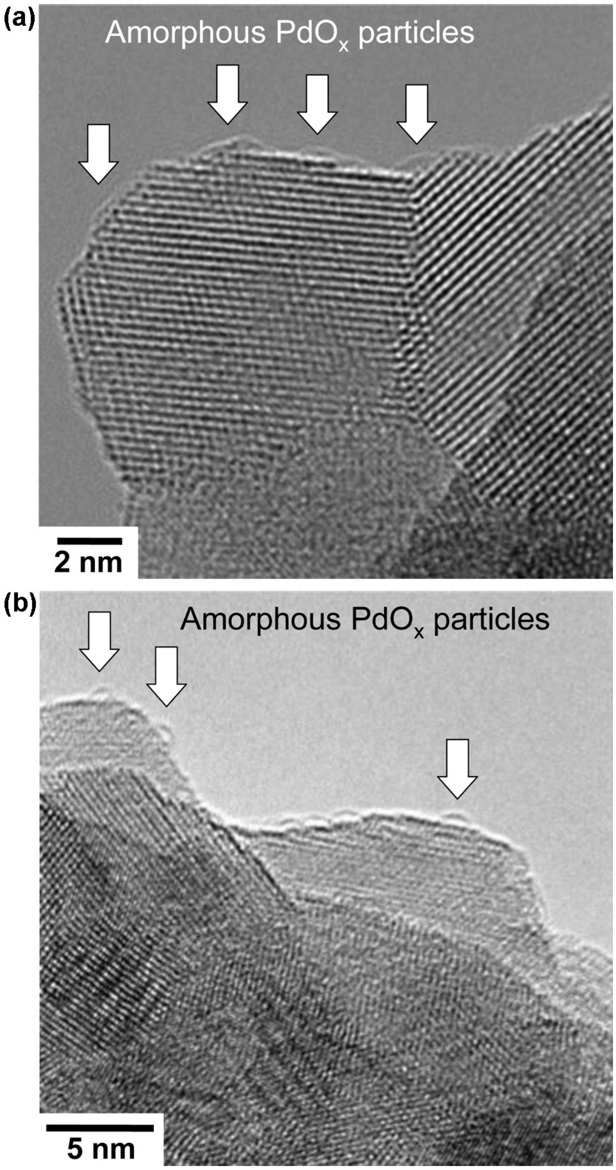

Fig. 5. TEM images of 1.0Pd/CZ catalyst: (a) after calcination at 800 °C for 3 h, and (b) after propene oxidation test.

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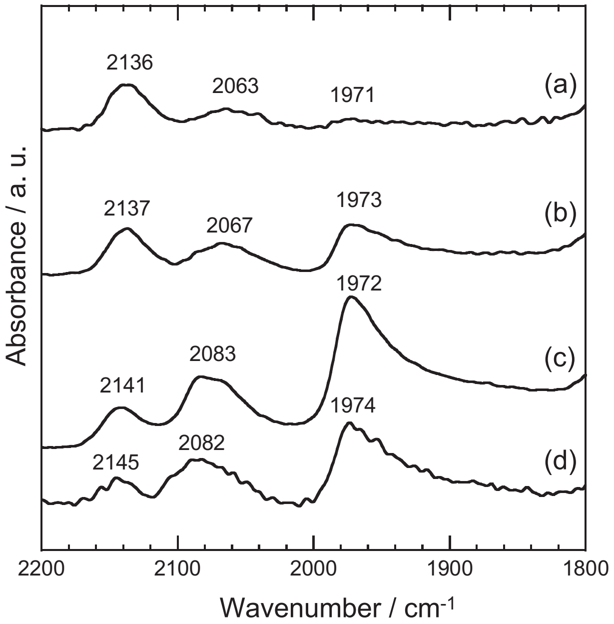

Fig. 6. FT-IR spectra of CO species adsorbed on Pd/CZ with various Pd loadings after oxidation treatment at 400 °C. (a) 0.04Pd/CZ, (b) 0.2Pd/CZ, (c) 1.0Pd/CZ (d) 5.0Pd/CZ.

catalyst of 1.0Pd/CZ after propene oxidation test under insufficient oxygen was also observed by FE-TEM. As can be seen in Fig. 5(b), the nano-sized particles existed on CZ support. The small particles in Fig. 5 must be the palladium oxide with the amorphous state, because the lattice images were not observed. TEM observation revealed that the palladium particles maintained the highly dispersed state, even after the propene oxidation test at 600 °C. Thereby, the strong interaction between palladium and CZ support seems to inhibit the particle growth of palladium.

In the CO chemisorption experiments (O_2–CO_2–H_2–CO pulse method), the mean diameters of Pd particles in Pd/CZ catalysts were calculated as 4–13 nm by the assumption of linear CO adsorption, as summarized in Table 1. On the contrary, the size of palladium oxide particles in TEM images was *ca.* 2 nm. The discrepancy between the diameters calculated from CO chemisorption and the size obtained from TEM observation could be explained by the underestimation of the CO adsorption amount. In fact, not only linear but also bridged CO adsorption was confirmed in FT-IR measurements, as mentioned in next section (Figs. 6 and 7). The bridged CO adsorption causes the underestimation of the amount of CO adsorption. Therefore, the calculated diameters via CO chemisorption experiments were larger than the diameters of PdO_x particles observed by TEM.

3.3. *FT-IR spectroscopy*

The chemical states of palladium species in Pd/CZ catalysts were investigated by FT-IR measurements. FT-IR spectra of CO species adsorbed on Pd/CZ catalysts heat-treated at 400 °C in O_2 and H_2 gas atmosphere are shown in Figs. 6 and 7, respectively. After the oxidation treatment (Fig. 6), three kinds of IR bands (1970, 2065 and 2140 cm^{-1}) were ascribed to bridged CO adsorbed to Pd^0, linear CO on Pd^0, and linear CO on Pd^{2+} [24]. Although palladium species must be in oxidized state after the oxidation treatment, a part of palladium oxide seems to be easily reduced by CO gas below 50 °C. When IR cell was filled with CO gas at room temperature, the yellow–brown color of sample disks was quickly changed to dark gray. The change in color also implicated that the top surface of Pd/CZ catalysts should be easily reduced. Thus, the existence of metallic Pd was confirmed by FT-IR spectroscopy. It was suggested that the reducibility of palladium oxide supported on CZ should be very high. The reducibility was examined by TPR measurement in the next section. The wide IR bands from 1200 to 1700 cm^{-1} were detected and identified as carbonate species adsorbed on CZ support [25]. After the reduction treatment at 400 °C, on the other hand, IR bands assigned as bridged and linear CO on Pd^0 were obtained around 1960 and 2025 cm^{-1}, as shown in Fig. 7. In 0.04Pd/CZ catalyst, the IR band of linearly adsorbed CO was relatively stronger than that of bridged CO. This result indicates that palladium species in Pd/CZ catalysts with low Pd loading were highly dispersed in atomic state.

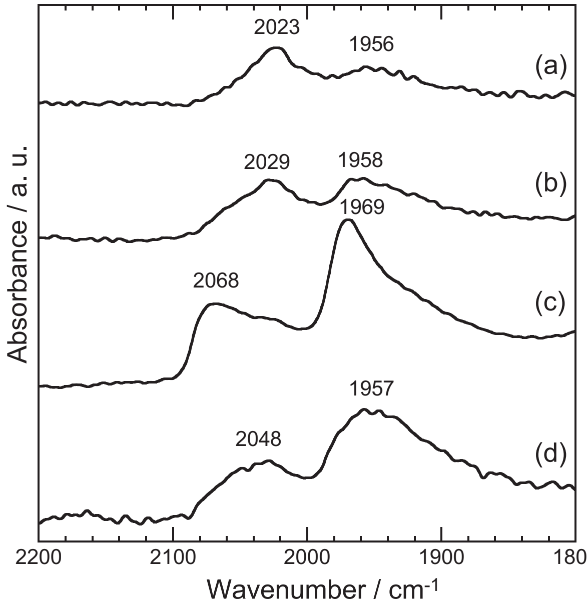

Fig. 7. FT-IR spectra of CO species adsorbed on Pd/CZ with various Pd loadings after reduction treatment at 400 °C. (a) 0.04Pd/CZ, (b) 0.2Pd/CZ, (c) 1.0Pd/CZ (d) 5.0Pd/CZ.

3.4. *TPR measurement*

The reducibility of catalyst is important for oxidation reaction, especially under insufficient oxygen condition, because the oxygen species in catalysts assist the chemical reaction with oxygen. So, the reducibility was examined by H_2-TPR measurements, and the profiles are summarized in Fig. 8. As can be seen in Fig. 8, a broad peak of oxygen release was observed at 300–700 °C in CZ support without palladium component. In the case of 0.04 and 0.2Pd/CZ, on the contrary, the consumption of hydrogen gas was recorded as a sharp peak at 50–140 °C. It was revealed that the oxygen release was drastically accelerated by a tiny amount of palladium, whereas the OSC values of 0.04 and 0.2Pd/CZ were almost same with CZ material (Table 1). The reduction temperature of PdO_x should be strongly affected by particle size and morphology. In addition, palladium could assist the dissociation and spillover of H_2, resulting in the decrease of reduction temperature. A weak and broaden peaks at 90–140 °C were confirmed in 1.0 and 5.0Pd/CZ, and a peak at 80 °C was reversely recorded in 5.0Pd/CZ. The negative peak should be assigned to the hydrogen desorption from palladium hydride, because the metallic palladium has the property of hydrogen storage capacity. The similar results were reported for PdO/SnO_2 catalysts by Takeguchi et al. [26]. The hydrogen consumption due to OSC property of Pd/CZ catalyst simultaneously proceeded with the hydrogen release from metallic palladium particles. This is why the strong peak was not detected at around 80 °C in 1.0Pd/CZ. The OSC value of 5.0Pd/CZ was much larger than the

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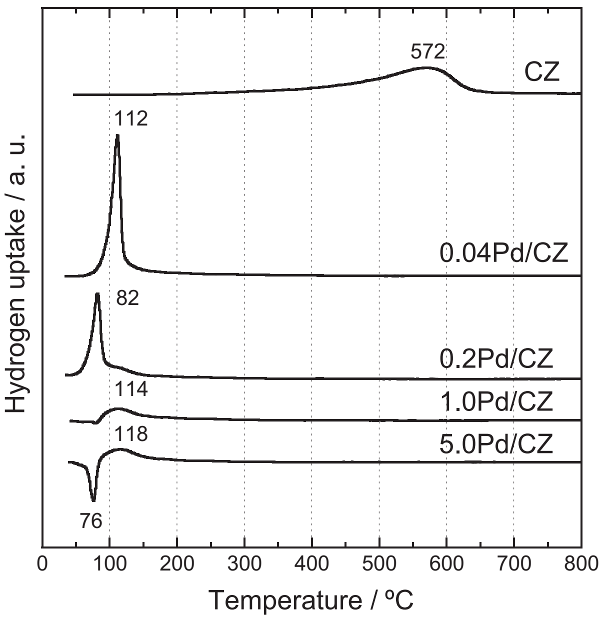

Fig. 8. H_2-TPR profiles of CZ and Pd/CZ catalysts.

others. Therefore, the palladium component in Pd/CZ should be easily reduced and oxidized as well as CZ material.

3.5. Discussion

The difference of catalytic activities due to Pd loading, pretreatment conditions, and oxygen concentration should be carefully discussed on the basis of the results of characterization. With the increase of Pd loading, Pd/CZ catalysts exhibited higher activities, regardless of pretreatment and reaction conditions. Therefore, it was suggested the palladium species must be the active site of propene oxidation. After the reduction treatment (Fig. 1(b) and Fig. 2(b)), the catalytic performance of 1.0Pd/CZ was almost equivalent to that of 5.0Pd/CZ. The Pd loading amount of 5.0 wt.% was enough large to decompose propene gas, and some part of palladium component seems not to play a role as active site. This assumption was supported by the low dispersion of palladium and calculated diameter of palladium particles in 5.0Pd/CZ, as can be seen in Table 1.

The effects of pretreatment conditions were explained by the results of IR measurement with CO adsorption (Figs. 6 and 7). The catalysts of Pd/CZ reduced at 600 °C in hydrogen exhibited higher activities than the oxidized Pd/CZ catalysts (Figs. 1 and 2). The palladium species in reduced catalysts existed in metallic state, and the chemical state of palladium in the catalysts after oxidation treatment was metallic and oxidized state. This means that metallic palladium (Pd^0) shows higher activities for propene oxidation than oxidized palladium (Pd^{2+}). In addition, the existence of metallic palladium was confirmed even after the heat treatment at 600 °C in O_2 gas. This is because a part of oxidized palladium was rapidly reduced in CO atmosphere. The reactive palladium species should be the active site. Thereby, the performance of 0.04Pd/CZ after the oxidation treatment was extremely low, because the IR bands ascribed as metallic palladium (1971 and 2063 cm^{-1}) were weaker than the other Pd/CZ catalysts, as shown in Fig. 6. In the case of 5.0Pd/CZ, the existence of metallic palladium was confirmed by the negative peak derived from the desorption of hydrogen gas. So, the light off curves of 5.0Pd/CZ in Fig. 1(a) was similar to the curves of reduced 5.0Pd/CZ (Fig. 1(b)) with no relation to the pretreatment conditions. Several researchers have reported that the complex oxides such as $Ce_{1-x}Pd_xO_{2-\delta}$ or $Ce_{1-x-y}Zr_xPd_yO_{2-\delta}$ enhanced the catalytic activities in methane oxidation and CO/NO reaction [27,28]. In this study, the dissolution of palladium into the lattice of CZ support was intimated by Raman spectroscopy. However, the enhancement of activities by the formation of $Ce_{1-x-y}Zr_xPd_yO_{2-\delta}$ was not verified for propene oxidation reaction.

The oxygen concentration in propene oxidation reaction test also affected the catalytic performance. However, the initial activities below 20% of CO_2 yields were not changed, whether the oxygen concentration was set at stoichiometric (0.5%) or insufficient condition (0.4%). The reducibility of Pd/CZ catalyst, which was investigated by TPR measurements (Fig. 8), would play an important role for the oxidation of propene under the insufficient oxygen condition. In other words, the property of oxygen storage capacity (OSC) of Pd/CZ catalysts should assist the complete oxidation of propene. The temperature, at which the OSC property of catalysts works, depends on the amount of palladium. As mentioned in Section 3.4, H_2-TPR profiles indicated that the order of reduction temperature was 5.0, $1.0Pd/CZ < 0.2Pd/CZ < 0.04Pd/CZ \ll CZ$. Therefore, the order of catalytic performances was also $5.0Pd/CZ > 1.0Pd/CZ > 0.2Pd/CZ > 0.04Pd/CZ \gg CZ$. In the activity tests of propene oxidation, the reducing agent is not H_2 gas but propene, and the oxygen in samples should be released at higher temperature. The variations in slopes of light off curves were confirmed in the insufficient oxygen condition (Fig. 2(a) and (b)). The variation was clearly observed in 5.0Pd/CZ under the 0.4% of oxygen concentration, as can be seen in Fig. 2(a). The results implicated that the propene oxidation reaction proceed with two reaction mechanisms. As discussed above, the OSC property of CZ support helps the propene oxidation at low temperature and under 0.4% of oxygen concentration. At high temperature, on the contrary, the amount of lattice oxygen from CZ material would not be enough to decompose propene gas. Thereby, the rate of total oxidation of propene reduced over the 40% of CO_2 yields.

4. Conclusions

The propene oxidation tests over CZ(1/3) and Pd/CZ(1/3) treated in oxidation and reduction atmosphere were conducted, and the effects of Pd loadings, pretreatment conditions, and oxygen concentration were investigated. The Pd/CZ catalysts exhibited higher activities, with the increase of Pd loadings, after the reduction treatment in hydrogen, and under 0.5% of oxygen concentration (stoichiometric condition). Consequently, it was concluded that the reactive palladium species with high reducibility were active for propene oxidation. The high dispersion of PdO_x particles was achieved due to the strong interaction between PdO_x particles and CZ support, and the dispersion was maintained after the propene oxidation tests. Furthermore, the lattice oxygen of CZ material assists the complete oxidation of propene, especially under the insufficient oxygen condition. In the future, it is necessary to investigate the activities of Pd/CZ(1/3) catalysts in the other purification reaction of hydrocarbons and CO, or three way catalytic reaction.

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References

[1] M. Ozawa, M. Kimura, A. Isogai, J. Alloys Compd. 193 (1993) 73–75.
[2] M. Ozawa, J. Alloys Compd. 275–277 (1998) 886–890.
[3] M. Sugiura, M. Ozawa, A. Suda, T. Suzuki, T. Kanazawa, Bull. Chem. Soc. Jpn. 78 (2005) 752–767.

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[4] Y. Nagai, T. Hirabayashi, K. Dohmae, N. Takagi, T. Minami, H. Shinjoh, S. Matsumoto, J. Catal. 242 (2006) 103–109.
[5] Y. Nagai, K. Dohmae, Y. Ikeda, N. Takagi, N. Hara, T. Tanabe, G. Guilera, S. Pascarelli, M.A. Newton, N. Takahashi, H. Shinjoh, S. Matsumoto, Catal. Today 175 (2011) 133–140.
[6] S. Matsumoto, Catal. Today 90 (2004) 183–190.
[7] J. Kaspar, P. Fornasiero, M. Graziani, Catal. Today 50 (1999) 285–298.
[8] E. Aneggi, C. de Leitenburg, G. Dolcetti, A. Trovarelli, Catal. Today 114 (2006) 40–47.
[9] L.F. Liotta, G.D. Carlo, G. Pantaleo, G. Deganello, Catal. Commun. 6 (2005) 329–336.
[10] L.F. Liotta, G.D. Carlo, G. Pantaleo, G. Deganello, Appl. Catal. B: Environ. 70 (2007) 314–322.
[11] S. Pengpanich, V. Meeyoo, T. Rirksomboon, K. Bunyakiat, Appl. Catal. A: Gen. 234 (2002) 221–233.
[12] S. Specchia, E. Finocchio, G. Busca, P. Palmisano, V. Specchia, J. Catal. 263 (2009) 134–145.
[13] C. Bozo, N. Guilhaume, J.M. Herrmann, J. Catal. 203 (2001) 393–406.
[14] Z. Qingbao, Z. Leihong, T. Botao, X. Yunlong, Y. Lei, Chin. J. Catal. 29 (2008) 373–378.
[15] Y. Liu, T. Hayakawa, T. Ishii, M. Kumagai, H. Yasuda, K. Suzuki, S. Hamakawa, K. Murata, Appl. Catal. A: Gen. 210 (2001) 301–314.
[16] D. Ciuparu, L. Pfefferle, Appl. Catal. A: Gen. 218 (2001) 197–209.
[17] D. Ciuparu, L. Pfefferle, Catal. Today 77 (2002) 167–179.
[18] T. Takeguchi, S. Manabe, R. Kikuchi, K. Eguchi, T. Kanazawa, S. Matsumoto, W. Ueda, Appl. Catal. A: Gen. 293 (2005) 91–96.
[19] T. Hirata, J. Phys. Chem. Solids 56 (1995) 951–957.
[20] J.R. McBride, K.C. Hass, W.H. Weber, Phys. Rev. B 44 (1991) 5016–5028.
[21] K. Otto, C.P. Hubbard, W.H. Weber, G.W. Graham, Appl. Catal. B: Environ. 1 (1992) 317–327.
[22] G.W. Graham, A.E. O'Neill, D. Uy, W.H. Weber, H. Sun, X.Q. Pan, Catal. Lett. 79 (2002) 99–105.
[23] H. Liang, J.M. Raitano, G. He, A.J. Akey, I.P. Herman, L. Zhang, S.W. Chan, J. Mater. Sci. 47 (2012) 299–307.
[24] A. Bensalem, J.C. Muller, D. Tessier, F. Bozon-Verduraz, J. Chem Soc, Faraday Trans. 92 (1996) 3233–3237.
[25] A. Holmgren, B. Andersson, D. Duprez, Appl. Catal. B: Environ. 22 (1999) 215–230.
[26] T. Takeguchi, T. Okanishi, S. Aoyama, J. Ueda, R. Kikuchi, K. Eguchi, Appl. Catal. A: Gen. 252 (2003) 205–214.
[27] S. Colussi, A. Gayen, M.F. Camellone, M. Boaro, J. Llorca, S. Fabris, A. Trovarelli, Angew. Chem. Int. Ed. 48 (2009) 8481–8484.
[28] L. Meng, J.J. Lin, Z.Y. Pu, L.F. Luo, A.P. Jia, W.X. Huang, M.F. Luo, J.Q. Lu, Appl. Catal. B: Environ. 119–120 (2012) 117–122.