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Liquid-phase oxidation of propylene glycol using heavy-metal-free Pd/C under pressurized oxygen

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ABSTRACT

The liquid-phase oxidation of propylene glycol using Pd/C undoped with any heavy metal such as tellurium in the presence of aqueous NaOH under pressurized oxygen resulted in a significant production of lactic acid and a minimal amount of hydroxyl acetone, although, under these conditions, sodium lactate as sodium analogue of lactic acid has been known to easily convert to sodium pyruvate. The advantageous effect of doping Pd/C with a heavy metal, which has been reported for various catalytic reactions in an aqueous phase, was not observed in the present oxidation. Previous papers have reported that oxidation using heavy-metal-free Pd/C and Pd/C doped with a heavy metal at atmospheric pressure and a pH 8 produced pyruvic acid via the formation of hydroxyl acetone and lactic acid, respectively, and that Pd/C doped with a heavy metal rather than Pd/C was suitable for the formation of pyruvic acid from propylene glycol. However the results of the present study show that the use of pressurized oxygen conditions as used in the present study can result in the exclusion of doping with a heavy metal in the preparation of the catalyst, which is amenable to green chemistry.

1. Introduction

The reaction network concerning propylene glycol shown in Scheme 1 has attracted attention, since this shows the possibility of an alternative route for the preparation of pyruvic acid [1–4]. Although pyruvic acid is used as an important feedstock for various industries [5,6], it is still produced from the dehydrative decarboxylation of tartaric acid using large quantities of $KHSO_4$ per batch [7]. An alternative approach to pyruvic acid and the related compounds, which bypasses the use of expensive tartaric acid and the waste of $KHSO_4$, has been accomplished by the catalytic oxidation of propylene glycol and related compounds, as shown in Scheme 1. In the liquid-phase oxidation of propylene glycol using Pd/C and related catalysts in our laboratory (Scheme 1), Pd/C has shown great activity for the production of pyruvic acid through hydroxyl acetone, while Pd/C doped with heavy metals has shown activity for the formation of pyruvic acid through lactic acid under atmospheric pressure and alkaline conditions [2]. The doping of Pd, Pt or Au catalysts with heavy metals such as Pb, Te, and/or Bi [1–4] and the use of alkaline conditions [1–4] made common sense for the obtainment of great catalytic activities. Although the noble metallic catalysts doped with those heavy metals are still used widely in industry [8], green chemistry dictates that a heavy-metal-free catalytic process should be developed. Indeed, recent reports have indicated that heavy-metal-free Pd/C shows significant activity for the conversion of sodium lactate to sodium pyruvate under pressurized oxygen without adjustment of the solution pH [9,10], which indicates that the doping of Pd/C with heavy metals may not be needed even in the reaction network (Scheme 1). To confirm the advantageous effect of the use of pressurized oxygen using heavy-metal-free Pd/C, the liquid-phase oxidation of propylene glycol was examined using heavy-metal-free Pd/C and Pd/C doped with Te under pressurized oxygen.

2. Experimental

Pd/C (with Pd of 5 wt%) was purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan and used as supplied. The BET

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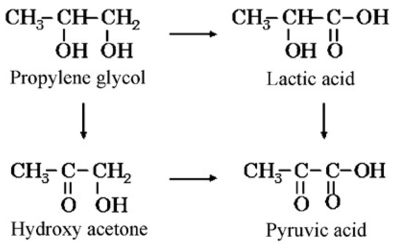

Scheme 1. Reaction network from propylene glycol.

surface area of Pd/C was 946 m^2/g. Pd/C catalyst doped with Te (Te/Pd/C) was prepared by impregnating the commercially available Pd/C with a given amount of H_6TeO_6 (Wako) dissolved in distilled water. Ethylene glycol (Wako) was added to the suspension and stirred for 5 h at 423 K to reduce Te cations [11]. After the reduction, the suspension was cooled to room temperature and isolated by filtration. The solid obtained was washed with distilled water and dried overnight at 343 K. Since previous reports established that an atomic ratio of Te/Pd = 0.03 showed the greatest activity for oxidative dehydrogenation of sodium lactate to pyruvate using Te/Pd/C [10], the catalyst containing the same ratio of Te/Pd was used in the present study. The BET surface area of Te/Pd/C was 883 m^2/g. Unless otherwise noted, catalytic activity was tested in a magnetically stirred stainless steel autoclave reactor (85 mL) [10] using the following procedure. Into the stainless steel autoclave reactor, 25 mL of an aqueous reaction solution containing propylene glycol (12.5 mmol: Kanto Chemical Co., Inc. Tokyo, Japan) and a solution of NaOH (0–25 mmol: Kanto) was added. After the autoclave was filled with 100% O_2, the reaction temperature was adjusted to 358 K in the presence of Pd/C (0.125 g), and the solution was stirred at 700 rpm. In the present study, the pressure in the autoclave was kept constant (1 MPa) by the addition of 100% O_2 to the autoclave during the reaction. After the reaction was allowed to proceed for 5 h, the solution was filtered. The reaction solution thus obtained was analyzed using FID-GC (GC-8AP, Shimadzu Corp., Kyoto, Japan). Propylene glycol and hydroxyacetone were directly analyzed with a 3 mm × 3 m stainless steel column (Gasukuropack 55, Shimadzu). Lactic acid and pyruvic acid were analyzed as ethyl esters after the following treatment. Aliquots (5 mL) of the reaction solution were filtered to remove the catalyst and then treated with aq. NaOH to completely convert these acids to the corresponding sodium salts. After the solution was completely evaporated to dryness, an ethanol solution of BF_3-etherate (Wako) was added to convert the sodium salts to the corresponding ethyl esters. Ethyl pyruvate and ethyl lactate thus obtained were analyzed with a 3 mm × 3 m stainless steel column (PEG6000/Uniport B, GL Science Inc., Tokyo, Japan). The catalysts were characterized by X-ray diffraction (XRD; Rigaku RINT 2500X using monochromatized Cu Kα radiation) and by extended X-ray absorption fine structure (EXAFS). Analysis of EXAFS near the Pd K edge was carried out at the High Energy Accelerator Research Organization with a storage ring current of 400 mA (6.5 GeV). The X-rays were monochromatized with Si(3 1 1) at an NW-10A station. The absorption spectra were observed using ionization chambers in the transmission mode. Since it was impossible to compress Pd/C and Te/Pd/C into a disk with diluents, the catalysts were carefully placed into a hand-made sample holder with 2 polypropylene windows. The photon energy was scanned in a range of 24,080–25,600 eV for the Pd K edge. Details of the calculation procedure have been previously reported [12]. Specific surface area was calculated from adsorption isotherms obtained with a conventional BET nitrogen adsorption apparatus (BELSORP-18SP, Bell Japan Inc., Osaka, Japan).

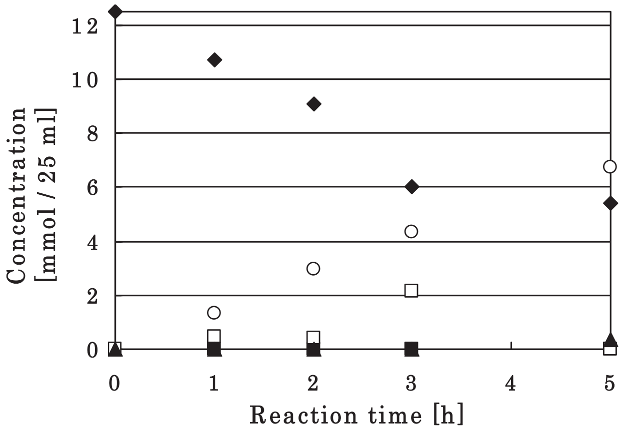

Fig. 1. Time-course of the oxidative dehydrogenation of propylene glycol at 1.0 MPa using Pd/C at 358 K. Symbols: (○) lactic acid (■) pyruvic acid (△) hydroxy acetone (♦) propylene glycol (□) by-product.

3. Results and discussion

3.1. Comparison of the catalytic activity for the oxidation of propylene glycol under atmospheric pressure and that under pressurized oxygen using Pd/C

As previously reported, the liquid phase oxidation of propylene glycol (50 mmol in 100 mL) using Pd/C (2.0 g) at 338 K at a pH 8

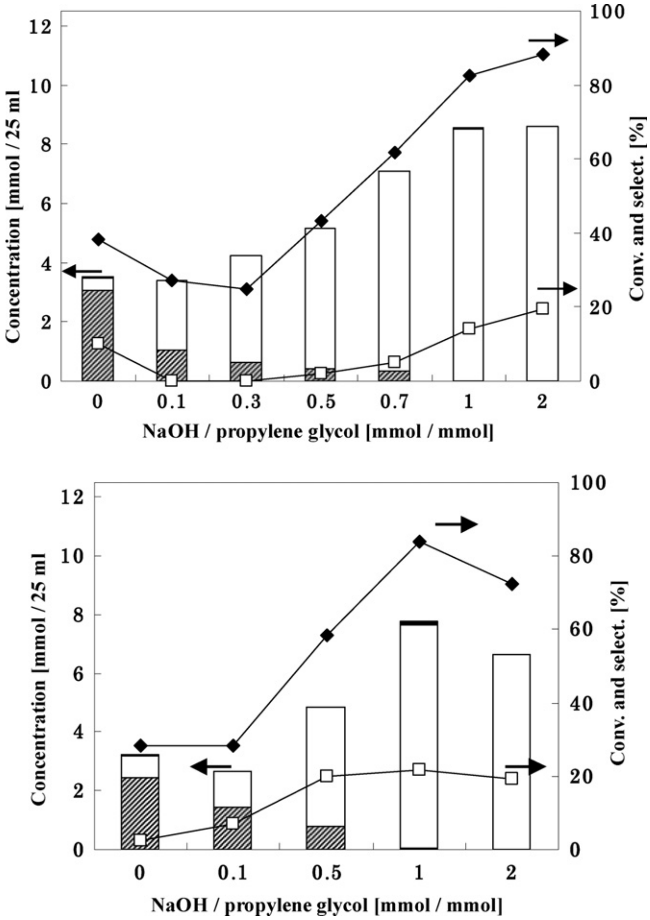

Fig. 2. Effect of NaOH concentration on the oxidative dehydrogenation of propylene glycol (12.5 mmol/25 mL) using Pd/C (A) and Te/Pd/C (B) (both 0.125 g) after 5 h at 358 K. Symbols: (□) lactic acid (■) pyruvic acid (▨) hydroxy acetone (♦) propylene glycol (□) by-product.

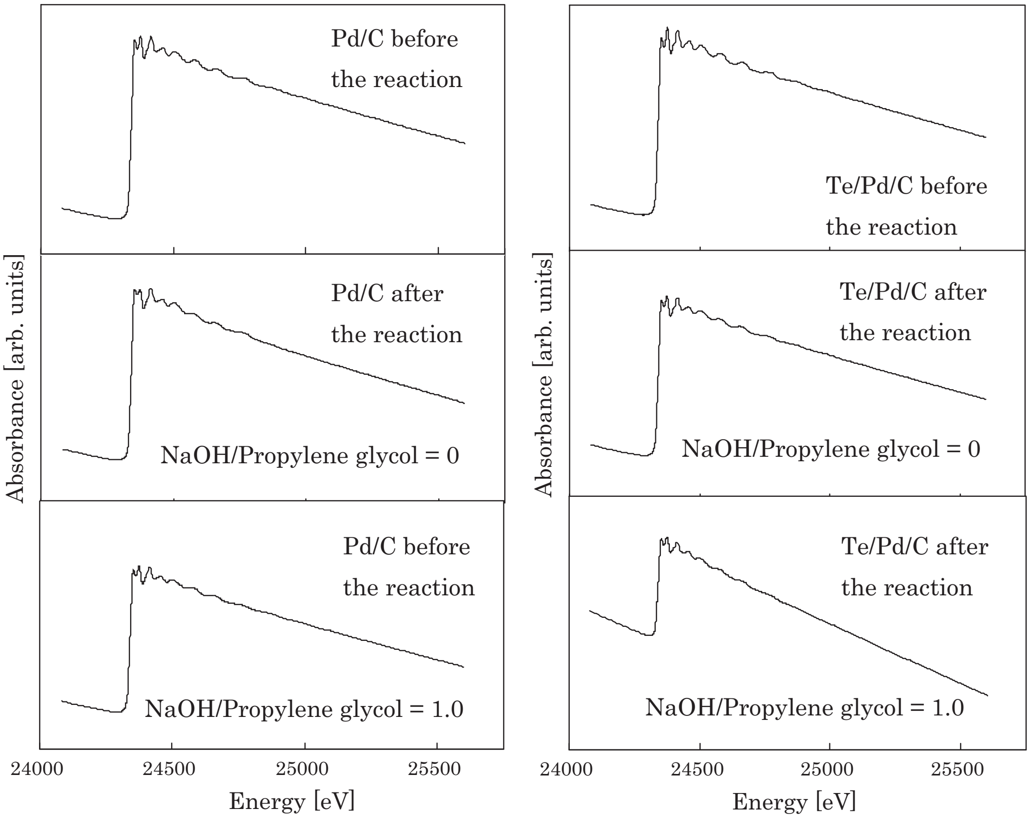

Fig. 3. Pd K-edge EXAFS spectra of Pd/C and Te/Pd/C before and after the oxidation of propylene glycol under pressurized oxygen.

(adjusted with aq. NaOH) for 5 h at atmospheric pressure resulted in the unselective formation of lactic acid, hydroxyl acetone and pyruvic acid (approximately 1:1:0.5 by molar ratio) with 85.5% of the conversion of propylene glycol [2]. In contrast, lactic acid was selectively produced from the oxidation of propylene glycol (12.5 mmol in 25 mL) after 5 h at 1 MPa of oxygen gas using a small amount of Pd/C (0.125 g) in the presence of NaOH (0.7 of NaOH/propylene glycol by molar ratio) with 61.7% of the conversion of propylene glycol (Fig. 1). As previously reported, the oxidation of propylene glycol at atmospheric pressure produced pyruvic acid through hydroxyl acetone using Pd/C, and through lactic acid using Pd/C doped with Pb or Te [2]. It should be noted that lactic acid was produced selectively from the oxidation of propylene glycol under pressurized oxygen even using Pd/C as shown in Fig. 1. When the oxidation of sodium lactate was examined separately under pressurized oxygen, sodium pyruvate acid was selectively produced, as shown in our previous study [9,10]. Therefore, the reaction route from propylene glycol to pyruvic acid would be strongly influenced by the pressurized oxygen, but not by the dopant added to Pd/C. In our previous paper, it has been already pointed out that the catalytic activity of Pd/C for the oxidative dehydrogenation is improved due to the enhancement of oxygen solubility in the reaction solution under pressurized oxygen [10]. Furthermore the presence of NaOH seems to be suitable for the present reaction using Pd/C since some free organic acids react with metallic Pd to form Pd-salts of the free organic acids, resulted in the decrease of the activity of the metallic Pd catalyst. Similar roles of pressurized oxygen and the base has been described in the oxidation of glycerol on Pt/C and Au/C in the presence of NaOH by Carrettin et al. [13]. They proposed that role of base was to aid the dehydrogenation through H-abstraction from one of the primary OH groups of glycerol. Therefore the combination of these roles of pressurized oxygen and the base seem to result in the enhancement of the catalytic activity for the present reaction using Pd/C catalyst.

3.2. Effects of the concentration of NaOH on the oxidation of propylene glycol under pressurized oxygen using Pd/C and Te/Pd/C

In the present system, the formation of free acids such as lactic acid and pyruvic acid is unfavorable to the present catalytic reaction since acidic conditions resulted in the deactivation of Pd/C and Pd/C doped with heavy metal [10]. For example, the conversion of propylene glycol remained unchanged from 3 h to 5 h (Fig. 1), indicating that an amount of NaOH may be insufficient due to consumption of NaOH by the reaction with the base and the free acids formed during the reaction. Therefore, solution pH was controlled to alkaline conditions by the addition of aq. NaOH into the reaction solution, as shown in most of the studies of the present system, in which free acid was converted to the corresponding sodium salt [2–4]. Since it is rather difficult to add aq. NaOH solution into the reaction solution in the present autoclave reactor, aq. NaOH solution was added into the reaction solution at the start of the reaction. In Fig. 2(A and B), the effects of the molar ratio of NaOH through propylene glycol in the reaction solution on the oxidative dehydrogenation of propylene glycol (12.5 mmol/25 mL) using 0.125 g of Pd/C and Te/Pd/C catalysts after 5 h, respectively, are described. The reaction temperature and the pressure were adjusted to 358 K and 1.0 MPa using oxygen gas. As shown in Fig. 2(A), when the concentration of NaOH was increased in the aqueous reaction solution before the reaction, the production of lactic acid also increased while that of hydroxy acetone decreased. Finally, no hydroxy acetone was detected at molar ratios of 1.0 and 2.0 of NaOH through propylene glycol. Similar results were also observed using Te/Pd/C (Fig. 2(B)) while the catalytic activity using Te/Pd/C was evidently lower than that using Pd/C. It should be noted that the selectivities to by-product shown in Fig. 2(A and B), which were calculated from the balance of propylene glycol converted and hydroxy acetone and pyruvic acid formed, were from 0 to 20%. The selectivity to by-product showed a tendency of the increase as the concentration

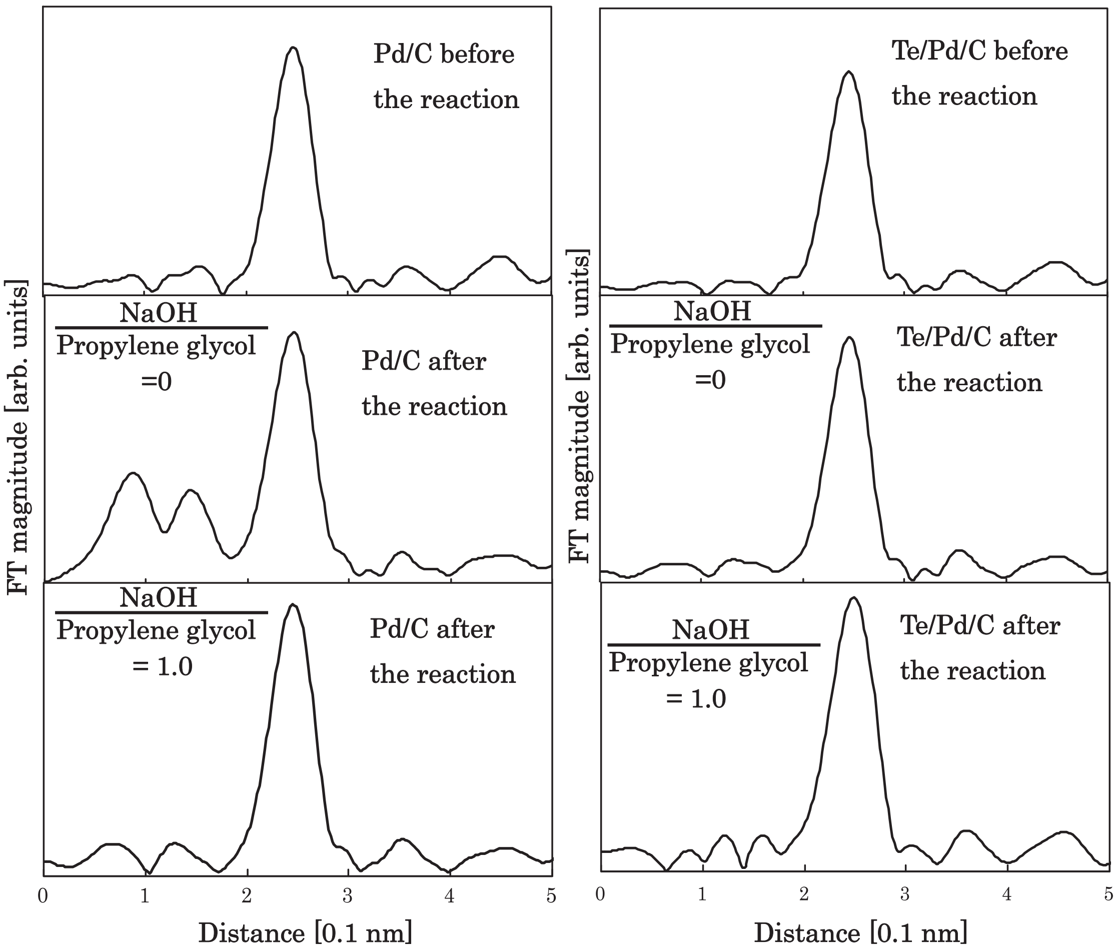

Fig. 4. Fourier transformation of Pd/C and Te/Pd/C before and after the oxidation of propylene glycol under pressurized oxygen.

of NaOH was increased, regardless of the presence and absence of Te in the catalyst. This indicates that the doping with Te of Pd/C is not needed for the present reaction system, although previous reports maintain that the selection of the pathway from propylene glycol to pyruvic acid depended on the presence or absence of heavy metal such as Te or Pb in Pd/C catalysts when doped with these heavy metals at atmospheric pressure [2]. However, the present results reveal that the selection of the pathway depends on the amount of NaOH added to the reaction solution under pressurized oxygen. It should be noted that no pyruvic acid was detected in the present study, although the oxidative dehydrogenation of propylene glycol gave pyruvic acid using Pd/C and Pd/C doped with Pb [2] together with Pt catalysts doped with some heavy metals under atmospheric pressure [3]. Similar results such as the production of lactic acid, but not pyruvic acid, from propylene glycol were also reported in the same reaction in the presence of NaOH using a supported catalyst consisting of Au and/or Pd at 1 MPa of oxygen gas [4]. In order to characterize the by-product in Figs. 1 and 2, GC–MS analysis was employed, indicating that the by-product may be polyhydric alcohol.

3.3. The oxidation of hydroxyl acetone and lactic acid under pressurized oxygen using Pd/C

It is odd that pyruvic acid was not detected in the present system since previous studies found that the oxidative dehydrogenation of sodium lactate using Pd/C under pressurized oxygen produced sodium pyruvate under the same reaction conditions [9,10]. As shown in Scheme 1, two possibilities for the formation of pyruvic acid are present in the oxidative dehydrogenation of propylene glycol to pyruvic acid through intermediates such as hydroxyl acetone or lactic acid. Therefore, the oxidations of hydroxyl acetone and lactic acid (both 12.5 mmol/25 mL) were examined separately using Pd/C (0.125 g) at 358 K and 1.0 MPa using oxygen gas in the presence of NaOH (molar ratio of NaOH/intermediate = 0.7). Although 99.6 and 15.7% of hydroxyl acetone and lactic acid, respectively, were converted during 5 h, the formation of pyruvic acid was not detected at all. Therefore, under pressurized oxygen, deep oxidation of pyruvic acid further proceeded to unidentified species, due to an excess solubility of oxygen gas into the reaction solution. It should be noted that deep oxidation can be avoided if sodium salt in the absence of NaOH instead of free acid in the presence of NaOH is used as a substrate [9,10].

Table 1
Results of curve-fitting analyses for Pd/C and Te/Pd/C before and after the oxidation of propylene glycol under pressurized oxygen.

Sample	Molar ratio[a]	$r_{\text{Pd–Pd}}$ (nm)[b]	N[c]	σ[d] (nm)	*R*[e]
Pd/C	Fresh	0.274	8.18	0.066	0.482
Pd/C	0	0.274	7.44	0.074	1.540
Pd/C	1	0.275	8.01	0.075	0.889
Te/Pd/C	Fresh	0.273	9.29	0.066	0.342
Te/Pd/C	0	0.275	7.60	0.071	0.622
Te/Pd/C	1	0.275	9.74	0.075	1.419

[a] NaOH/Propylene glycol.
[b] Nearest-neighbor distance around Pd.
[c] Coordination number.
[d] Debye–Waller (like) factor.
[e] Reliability factor.

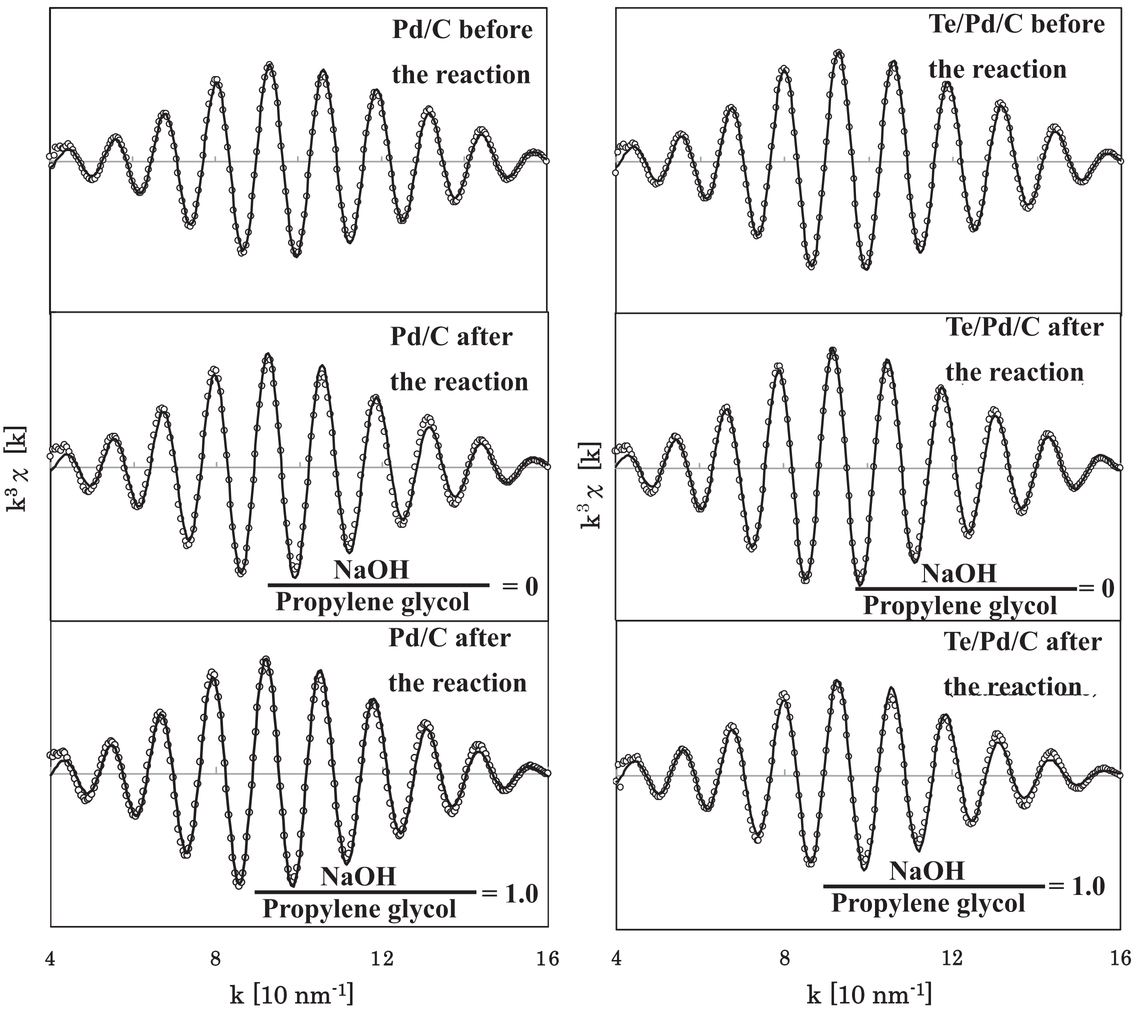

Fig. 5. Curve-fitting near Pd K-edge of Pd/C and Te/Pd/C before and after the oxidation of propylene glycol under pressurized oxygen.

3.4. Effects of the addition of NaOH into the reaction solution on fine structure changes around Pd in Pd/C and Te/Pd/C

As shown in the present study, the catalytic activities for the oxidation of propylene glycol under pressurized oxygen were strongly influenced by the addition of NaOH into the reaction solution. To examine the effects of the addition of NaOH into the reaction solution on fine structure changes around Pd in Pd/C and Te/Pd/C, EXAFS was analyzed near the Pd K edges using Pd/C and Te/Pd/C previously used for obtaining the results shown in Fig. 2(A and B), that is, before and after the reaction at NaOH/propylene glycol = 0 or 1 (Fig. 3). The Pd K edge EXAFS spectra showed that the absorption due to Pd in Pd/C and Pd/Te/C before and after the reaction in the presence and absence of NaOH were essentially identical, which was due to the metallic Pd [10]. Furthermore XRD peaks due to metallic Pd (JCPDS 461043) were detected from these samples (not shown). The corresponding Fourier transformation near the Pd K-edge for these samples showed one signal characteristic metallic Pd [10,14] (Fig. 4); the exception was that obtained from Pd/C previously used in the absence of NaOH (middle on the left column in Fig. 4), in which some signals were also detected at a distance smaller than 0.2 nm. Regardless of the presence and absence of Te in the catalysts, the nearest-neighbor distance around the Pd increased from 0.273 to 0.274 nm before the reaction to 0.274–0.275 nm after the reaction (Table 1). This result may be explained by the incorporation of either hydrogen or carbon into Pd bonds during oxidation [15]. Based on these results, the metallic nature of Pd was maintained even after the oxidation of propylene glycol in the presence and absence of NaOH using Pd/C and Pd/Te/C under pressurized O_2 (Fig. 5).

4. Conclusion

Previous reports on the oxidation system of propylene glycol using Pd/C and related catalysts at atmospheric pressure found a significant dependence on the doping of Pd/C with heavy metals. However, the results of the present study obtained under pressurized oxygen revealed that the catalytic activity is not dependent on doping, but is instead dependent on the molar ratio of NaOH added into the reaction solution against propylene glycol. Therefore, the doping of Pd/C with heavy metals is unnecessary in the present oxidation system under pressurized oxygen.

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