

Application of Heavy-Metal-Free Pd/C Catalyst for the Oxidative Dehydrogenation of Sodium Lactate to Pyruvate in an Aqueous Phase under Pressurized Oxygen

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According to previous reports, the oxidative dehydrogenation of lactic acid to pyruvic acid in an aqueous phase does not proceed with Pd/C, while Pd/C doped with Te or Pb has catalytic activity at atmospheric pressure and 363 K in an aqueous NaOH solution at a pH of 8. Since use of heavy metals, such as Te or Pb, is inconsistent with green chemistry, a heavy-metal-free Pd/C catalyst is employed in the present study. The oxidative dehydrogenation of sodium lactate to sodium pyruvate in an aqueous phase at 358 K under pressurized oxygen at 1 MPa proceeded favorably using Pd/C with no adjustment of solution pH. Under pressurized oxygen, the catalytic activity of Pd/C was similar to that of Pd/C doped with either Te or Pb. This result suggests that a heavy-metal-free Pd/C catalyst might also be applied to other catalytic reactions. As an alternative to doping Pd/C with Te or Pb, the dissolution of gaseous oxygen into the reaction solution significantly enhanced the catalytic activity of Pd/C. To show the contribution of the dissolution of gaseous oxygen, the effects of the volume of oxygen in the reactor (stainless autoclave) on the reaction rate and the activity were examined. The activation parameters thus obtained reveal that the volume of oxygen in the reactor is a more important determinant of catalytic activity than the activation of the reaction itself.

Introduction

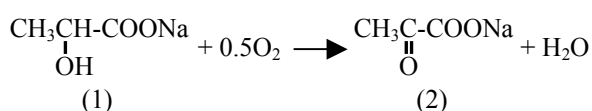
Palladium doped with a heavy metal has been used as an active catalyst for various catalytic reactions for a long time. One of the most important catalysts is the Lindlar catalyst (Pb/Pd/CaCO₃) (Lindlar, 1952), and Pb/Pd/SiO₂ (Stachurski and Thomas, 1988) catalyzes the selective hydrogenation of acetylene to olefins. As another example of a heavy-metal-doped palladium catalyst, Te/Pd/C is a unique catalyst for diacetoxylation of 1,3-butadiene (Takehira *et al.*, 1979). Recently, palladium doped with a heavy metal has attracted attention, particularly for industrial applications. For example, Te/Pd catalysts supported on various oxides and active carbons have been used for the production of $\alpha\beta$ -unsaturated carboxylic acid (Himeno and Yasukawa, 2009).

Palladium doped with a heavy metal also shows an interesting property in the production of pyruvic acid. Pyruvic acid is widely used in various industries because it is an attractive intermediate of various fine chemicals (Corma *et al.*, 2007). Present technology for the production of pyruvic acid remains based on the

classic preparation procedure that involves dehydrative decarboxylation of tartaric acid (Erlenmeyer, 1881). Although the classic procedure produces pyruvic acid in good yield, the required use of an excess amount of KHSO₄ powder per batch is a serious disadvantage. Therefore, development of a new process for the production of pyruvic acid is desirable. Hayashi *et al.* developed a reaction system that produces pyruvic acid via the oxidative dehydrogenation of lactic acid in an aqueous phase using a palladium catalyst doped with either lead or tellurium supported on active carbon (Tsujino *et al.*, 1992; Hayashi *et al.*, 1993, 1994). They found no absorption of oxygen in the attempted oxidative dehydrogenation of lactic acid on Pd/C. By contrast, a spectacular change in the oxidation activity in favor of the formation of pyruvic acid from lactic acid was observed in the presence of Pd/C doped with either lead or tellurium. Addition of a heavy metal had a similar effect on the catalytic oxidation of D-gluconic acid. The primary hydroxyl group was preferentially oxidized on Pt/C, while the use of Pb/Pt/C resulted in preferential oxidation on the hydroxyl group at the α -position (Smits *et al.*, 1986, 1987). Therefore, in the

field of palladium and platinum catalytic chemistry, the use of catalysts doped with heavy metals for the oxidation of the hydroxyl group at the α -position, such as during the conversion of lactate to pyruvate, is considered to be common sense. Additionally, in the oxidative dehydrogenation of lactic acid to pyruvic acid, the solution pH must be adjusted to 8 by the use of a considerable amount of aqueous NaOH (Tsujino *et al.*, 1992; Hayashi *et al.*, 1993, 1994). Thus, sodium lactate rather than lactic acid might be a more suitable raw material for an oxidative dehydrogenation that does not require adjustment of the solution pH.

Although palladium catalysts doped with a heavy metal are still used widely in industry, green chemistry dictates that a heavy-metal-free catalytic process should be developed. Thus, the present study evaluates the oxidative dehydrogenation of sodium lactate (1) to sodium pyruvate (2) using either Pd/C or Pd/C doped with tellurium or lead (Te-Pd/C or Pb-Pd/C) in an aqueous phase without adjustment of the solution pH using a stainless steel autoclave in order to resolve the afore-mentioned problems associated with the current catalytic reaction.



1. Experimental

Pd/C (5 wt%) was purchased from Wako Pure Chemical Industries, Ltd. (BET surface area: 946 m²/g) and was used as supplied, unless otherwise stated. The Te-Pd/C and Pb-Pd/C were prepared by impregnating the commercially available 5 wt% Pd/C with a given amount of H₆TeO₆ (Wako Pure Chemical Industries, Ltd.) or (CH₃COO)₂Pb (Kanto Chemical Co., Inc.), respectively, dissolved in distilled water. For the preparation of Pb-Pd/C, an aqueous solution of Na₃PO₄ (Wako Pure Chemical Industries, Ltd.) was added to the dissolved solution to convert all of the lead into an insoluble phosphate (Hayashi *et al.*, 1994). The catalyst thus obtained was isolated by filtration and washed with hot water. The impregnated catalysts were reduced with a formalin solution (37%, Wako Pure Chemical Industries, Ltd.) at 343 K for 2 h. The suspension was filtered, and the residue was washed and then dried at 343 K overnight *in vacuo*. When the Pd/C that had been previously reduced was used for the oxidative dehydrogenation of sodium lactate, the same reduction procedure was employed. Loading with these heavy metals (M = Pd or Te) was quantified as an atomic ratio relative to palladium (M/Pd). Catalytic activity was tested as previously reported (Sugiyama *et al.*, 2009). Into a stainless steel autoclave (85 mL), 50 or 25 mL of an aqueous reaction solution containing sodium lactate (25 or 12.5 mmol) was added. After the autoclave was

filled with 100% O₂, the reaction temperature was adjusted to 358 K in the presence of the catalyst (0.250 or 0.125 g) and the solution was stirred at 700 rpm. In some cases, 20% O₂ that had been diluted with N₂ was used instead of 100% O₂. In the present study, the pressure in the autoclave was kept constant by the addition of 20% or 100% O₂ to the autoclave during the reaction. In all experiments, except for the kinetic studies, the reaction was allowed to proceed for 5 h. Then, the solution was filtered, and the filtrate was treated with dilute HCl to convert the sodium salts into the corresponding free acids. In the kinetic studies, the reaction solution was similarly treated after 10, 20 and 30 min. The free acids in the solution were analyzed using FID-GC (GC-8A, Shimadzu Co.) with a 3.2 mm × 1.6 m glass column (Thermon-3000/SHINCARBON A). The yield of sodium pyruvate was calculated from the conversion of sodium lactate and the selectivity to sodium pyruvate (=Conversion × Selectivity/100). The catalysts were characterized by X-ray diffraction (XRD; Rigaku RINT 2500X using monochromatized Cu K α 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(311) at an NW-10A station. The absorption spectra were observed using ionization chambers in the transmission mode. Because it was difficult to compress Pd/C into a disk with diluents, the catalyst was carefully placed into a hand-made sample holder with two polypropylene windows. The photon energy was scanned in the range of 24,080 – 25,600 eV for the Pd-edge. Details of the calculation procedure have been previously reported (Sugiyama *et al.*, 2008). Specific surface area was calculated from adsorption isotherms obtained with a conventional BET nitrogen adsorption apparatus (BELSORP-18SP, Bell Japan Inc.).

2. Results and Discussion

2.1 Oxidative dehydrogenation of sodium lactate using Pd/C

The sodium pyruvate concentration and yield obtained after 5 h of the oxidative dehydrogenation of sodium lactate using Pd/C for 5 h are shown in **Figure 1**. The oxidative dehydrogenation of sodium lactate to sodium pyruvate using Pd/C and 100% oxygen proceeded slowly at atmospheric pressure (Figure 1). A similar result was observed previously for the conversion of lactic acid to pyruvic acid using Pd/C at a constant pH of 8 (Tsujino *et al.*, 1992; Hayashi *et al.*, 1993, 1994). It should be noted that the volume of the reaction solution was 50 mL in the present study. However, the activity of Pd/C, which was used as supplied and had not been previously reduced, was dramatically improved by increasing the oxygen

pressure, and a sodium pyruvate yield of 45.8% was obtained at 1.0 MPa (Figure 1). Therefore, in contrast to previous studies of Pd/C catalytic activity under atmospheric pressure (Tsuji *et al.*, 1992; Hayashi *et al.*, 1993, 1994; Smits *et al.*, 1986, 1987), Pd/C appears to be an active catalyst for the oxidative dehydrogenation of the hydroxyl group at the α -position under high-pressure conditions. The activity of Pd/C at 1.0 MPa (Figure 1) for the oxidative dehydrogenation of sodium lactate to pyruvate was equivalent to that of lactic acid to pyruvic acid with Pd/C doped with either Te or Pb at a constant pH of 8 and atmospheric pressure (Tsuji *et al.*, 1992; Hayashi *et al.*, 1993, 1994). Thus, the results shown in Figure 1 indicate that doping of Pd/C is not needed for the oxidative dehydrogenation of the hydroxyl group at the α -position when high pressure is employed during the reaction.

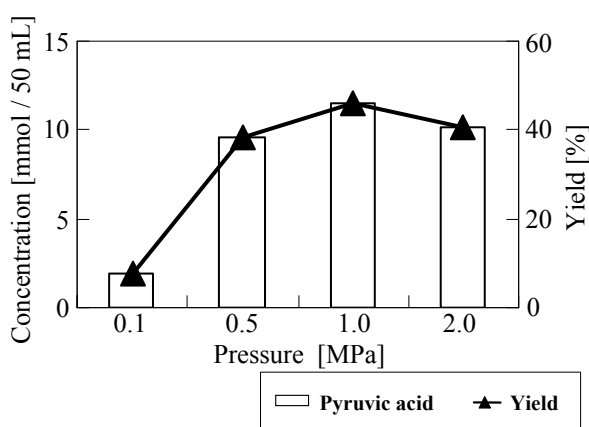


Fig. 1 Effects of oxygen (100% O₂) pressure on the oxidative dehydrogenation of sodium lactate to pyruvate using Pd/C at 358 K (solution volume = 50 mL)

Although the benefit of using high-pressure oxygen is evident during the oxidative dehydrogenation of sodium lactate to pyruvate, the use of air rather than pure oxygen in the present system is desirable. Therefore, 20% oxygen that had been diluted with nitrogen gas was used instead of pure oxygen gas for the oxidative dehydrogenation catalyzed by Pd/C. First, 50 mL of the reaction solution and 0.250 g of Pd/C were used for the reaction, resulting in a 35 mL space volume in the reactor. The sodium pyruvate yield was 7.6, 17.6 and 18.5% at 0.1 (atmospheric pressure; not shown), 1.0 and 2.0 MPa, respectively. Therefore, the enhanced activity that resulted from the use of pure oxygen gas (Figure 1) was not observed when 20% oxygen gas was used (Figure 2A). It should be noted that the solubility of 100% oxygen in water is different from that of 20% oxygen diluted with nitrogen. Thus, the solubility of oxygen in water was estimated using ASPEN PLUS according to the non-random two-liquid (NRTL) activity coefficient model (Poling *et al.*, 2001). As shown in Table 1, the solubility of 100% oxygen at

increased pressure was greater than that of 20% oxygen diluted with nitrogen. Therefore, efficient dissolution of gaseous oxygen into the reaction solution is important for enhancement of catalytic activity using 20% oxygen diluted with nitrogen. In the autoclave used in the present study, the total effective volume for the reaction solution was 85 mL, as described above, of which ca. 35 mL was the volume of the tube and not the reactor itself. Therefore, when 50 mL of the reaction solution was added to the reactor, the volume of the 20% oxygen gas present in the reactor might have been insufficient. The inadequate volume might be a disadvantage of 20% oxygen gas under high pressure. When such a small volume of 20% oxygen gas is used, dissolution of oxygen into the reaction solution is likely to be insufficient due to incomplete mixing of the reaction solution.

Table 1 Estimated solubility of oxygen in water (mmol/ 50 mL H₂O) at 358 K under various pressures using 100% O₂ or 20% O₂ diluted with N₂

Gas	Pressure [MPa]				
	0.1	0.5	1.0	1.5	2.0
100% O ₂	0.93	2.69	5.74	8.78	11.83
20% O ₂	0.19	0.54	1.15	1.75	2.36

Therefore, 25 mL of the reaction solution and 0.125 g of Pd/C, which had not been previously reduced and was used as supplied, were used for oxidative dehydrogenation. Consequently, the volume available for 20% oxygen gas in the reactor was ca. 60 mL (Figure 2B). In this case, the sodium pyruvate yield was dramatically improved: 24.4 and 45.9% at 1.0 and 2.0 MPa, respectively. Therefore, adequate volume is required for the use of 20% oxygen gas diluted with N₂ to enhance the oxidative dehydrogenation of sodium lactate under high pressure.

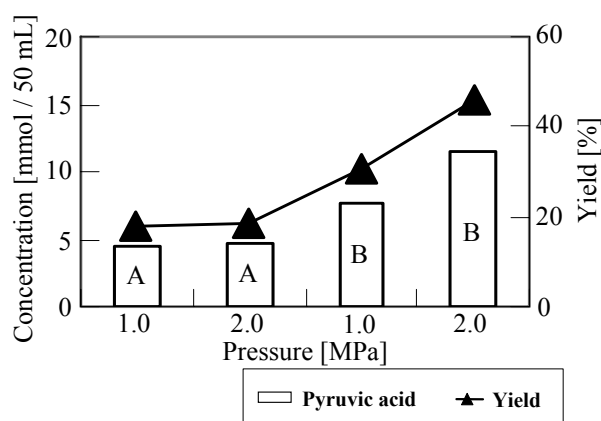


Fig. 2 Effects of solution volume in the reactor and pressure using 20% O₂ on the oxidative dehydrogenation of sodium lactate to pyruvate on Pd/C at 358 K; A and B: Solution volume = 50 and 25 mL, respectively

2.2 Oxidative dehydrogenation of sodium lactate using Pd/C doped with Te or Pb

Based on previous reports on the oxidative dehydrogenation of lactic acid (Tsuji *et al.*, 1992; Hayashi *et al.*, 1993, 1994), it is expected that the catalytic activity of Pd/C for the oxidative dehydrogenation of sodium lactate is also enhanced by doping with Te or Pb under pressurized oxygen. First, the catalytic activity of Pd/C doped with various amounts of Te was examined using 100% oxygen at 1.0 MPa (Figure 3). In this case, the effects of formalin reduction on the oxidative dehydrogenation were also examined using undoped Pd/C. The activity of previously reduced Pd/C (surface area: 918 m²/g) was greater than that using the unreduced catalyst (surface area: 946 m²/g). The activity was further improved by doping of Pd/C with Te, such that the maximal sodium pyruvate yield was 68.2% using the catalyst with Te/Pd = 0.03 (surface area: 878 m²/g). However additional Te doping decreased the sodium pyruvate yield (Figure 3). It should be noted that the advantage of Te loading observed in the present study was less than that observed for the oxidative dehydrogenation of lactic acid to pyruvic acid at pH 8 and atmospheric pressure (Tsuji *et al.*, 1992; Hayashi *et al.*, 1993, 1994). In order to check the reproducibility of the catalytic activity of the used catalyst, the catalyst with Te/Pd = 0.03 previously employed for obtaining the results shown in Figure 3 was again used for the reaction. Using the fresh catalyst, the yield of sodium pyruvate was 68.2% as shown in Figure 3. The catalyst was recovered and reused for the oxidative dehydrogenation, resulting in 63.0% yield of pyruvate.

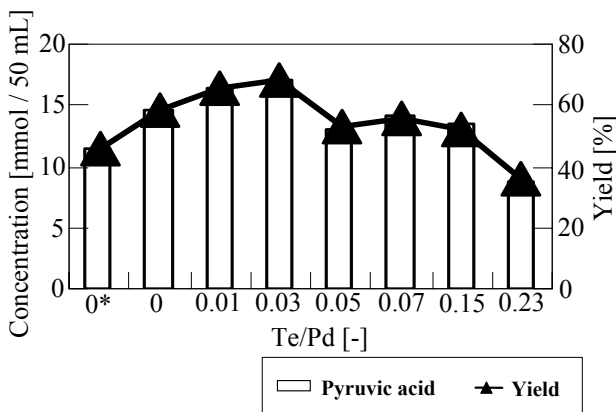


Fig. 3 The oxidative dehydrogenation of sodium lactate to pyruvate at 358 K and 1.0 MPa (100% O₂) using Pd/C doped with various amount of Te (solution volume = 50 mL); all catalysts except 0* had been previously reduced

In the oxidative dehydrogenation of lactic acid to pyruvic acid at pH 8 and atmospheric pressure, Pd/C loaded with Pb showed the greatest activity of the related catalysts tested; no activity was observed with Pd/C. However, Pb loading of Pd/C did not further

increase the activity for oxidative dehydrogenation at 1.0 MPa, as shown in Figure 4. During the oxidative dehydrogenation of lactic acid to pyruvic acid at pH 8 and atmospheric pressure, the amount of oxygen dissolved in the reaction solution is rather small. In this case, efficient use of dissolved oxygen by heavy metals, such as Te and Pb, might be possible. However, under pressurized oxygen, sufficient oxygen is dissolved in the reaction solution. Under this reaction condition, loading of Pd/C with heavy metals is no longer required. This conclusion conflicts with previous reports that considered the use of heavy-metal-doped catalysts for the oxidation of hydroxyl groups at the α -position, such as during the conversion of lactate to pyruvate, to be common sense.

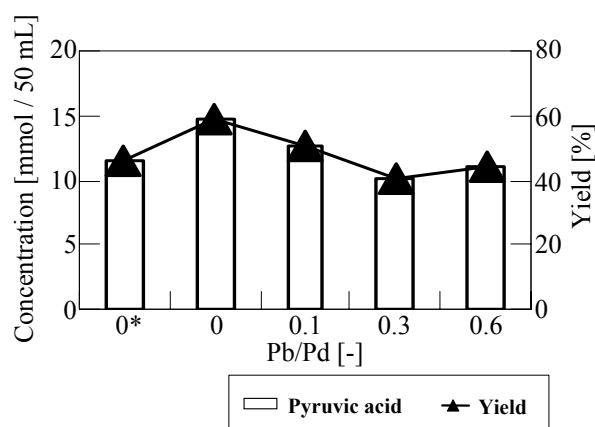


Fig. 4 The oxidative dehydrogenation of sodium lactate to pyruvate at 358 K and 1.0 MPa (100% O₂) using Pd/C doped with various amounts of Te (solution volume = 50 mL); all catalysts except 0* had been previously reduced

2.3 Kinetic study of the oxidative dehydrogenation of sodium lactate under pressurized oxygen

As described above, adequate volume for the gaseous oxidant (100% or 20% O₂) in the autoclave, rather than doping with heavy metals such as Te and Pb, was responsible for the enhanced catalysis of oxidative dehydrogenation of sodium lactate under pressurized oxygen. To examine the effect of the space volume on the reaction, a kinetic study was performed. The concentration of oxygen in the reaction solution was superabundant in comparison with that of sodium lactate because oxygen was continually supplied during the reaction. Therefore, the first-order kinetics of the concentration of sodium lactate for the reactions at 358, 368 or 378 K and 1.0 MPa (100% O₂) using 50 or 25 mL of the reaction solution were determined. The first-order rate-constant (k/min⁻¹) thus obtained was used to construct the Arrhenius plots in Figure 5. The activation energies obtained from Figure 5 were 20.2 and 56.0 kJ/mol using 50 or 25 mL of the reaction solution. Because the reaction conditions for the

oxidative dehydrogenation using 50 or 25 mL of the reaction solution were identical, the Arrhenius plots and the activation energy using 50 mL of the reaction solution should have been identical to those obtained using 25 mL of the solution. However, the Arrhenius plots and the activation energy obtained for the two volumes of reaction solution were different from each other. This result indicates that the rate-determining step in the present reaction system must be the dissolution step of gaseous O₂ in the solution. Sufficient space volume for gaseous oxygen in the autoclave was obtained by use of 25 mL of the reaction solution, which resulted in adequate dissolution of oxygen into the reaction solution and enhanced catalytic activity of undoped Pd/C.

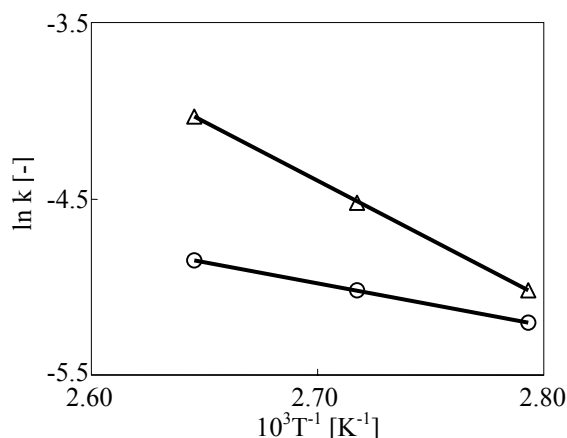


Fig. 5 Arrhenius plots for the oxidative dehydrogenation of sodium lactate by Pd/C at 1.0 MPa (100% O₂) using 50 (O) or 25 (Δ) mL of the reaction solution

2.4 Structural analysis of Pd/C before and after the oxidative dehydrogenation of sodium lactate

Since Pd/C exhibited high catalytic activity for the oxidative dehydrogenation of sodium lactate to pyruvate under pressurized oxygen, the conversion of palladium during the reaction is of interest. XRD patterns of Pd/C before and after the reaction are shown in **Figure 6**. Before the reaction, XRD peaks due to metallic Pd (JCPDS 461043) were evident (Figure 6 (a)), while broad and weak peaks were detected after the oxidative dehydrogenation of sodium lactate at 1.0 MPa and 358 K (Figure 6 (b)). Because Pd/C was kept under oxygen rich-conditions during the reaction, oxidation of metallic Pd to oxidized cationic Pd might have occurred. However, the broad and weak peaks shown in Figure 6 did not match the reference patterns of the palladium oxides. It is of interest to note that the lattice constant after the reaction (0.391 nm) was greater than that before the reaction (0.389 nm). This result suggests that another species might be incorporated into the metallic Pd during the reaction.

To detect fine structural changes in Pd/C during the reaction, EXAFS was analyzed near the Pd-K edges.

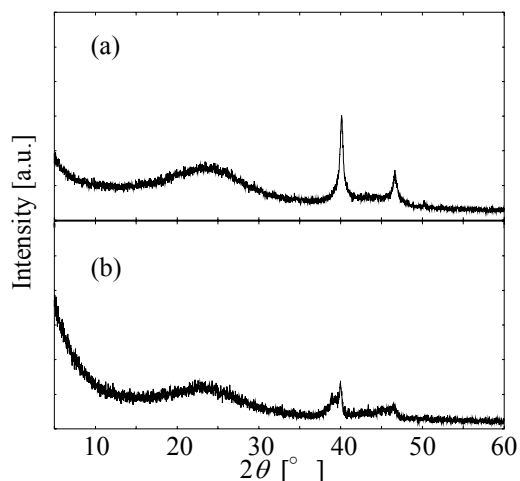


Fig. 6 XRD patterns of Pd/C before (a) and after (b) the oxidative dehydrogenation of sodium lactate at 358 K and 1.0 MPa (100% O₂)

The Pd K-edge XANES spectra (**Figure 7 (a)**) showed that the absorption edges due to Pd/C observed before (I) and after (II) the reaction of sodium lactate at 1.0 MPa and 358 K were essentially identical and were just like that due to Pd foil (III). The corresponding Fourier transformation near the Pd K-edge for these samples showed one signal characteristic of metallic Pd (**Figure 7 (b)**) (Shimizu *et al.*, 2004).

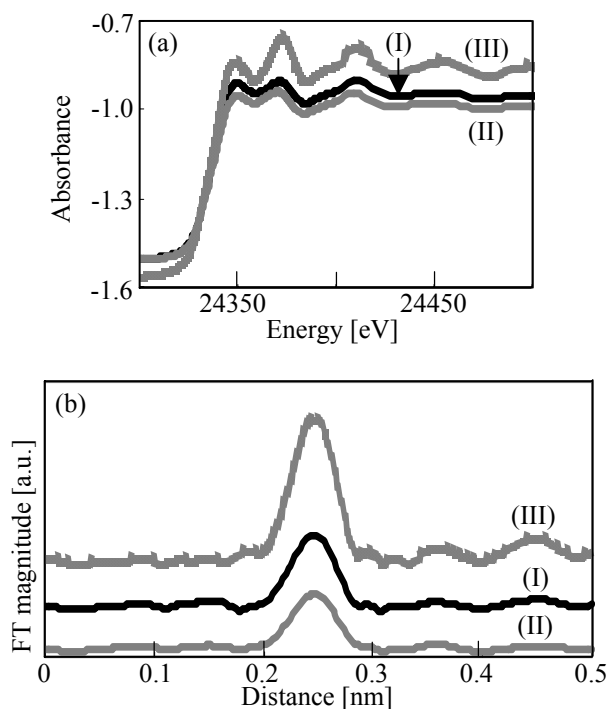


Fig. 7 Pd-K-edge spectra (a) and the corresponding Fourier transformation (b) of EXAFS of Pd/C before (I) and after (II) the oxidative dehydrogenation of sodium lactate at 358 K and 1.0 MPa (100% O₂) together those with Pd foil (III)

Therefore, it seems that the fine structural changes in Pd/C that occurred during the reaction were negligible. However, the nearest-neighbor distance to Pd obtained from the EXAFS analysis affords additional information on the fine structural changes that occurred during the reaction (**Table 2**). The nearest-neighbor distance around Pd was increased from 0.274 nm before the reaction to 0.276 nm after the reaction. By contrast, the coordination number around Pd decreased from 7.44 before the reaction to 7.32 after the reaction. This result can be explained by the incorporation of either hydrogen or carbon into the Pd bonds (Ziamecki *et al.*, 1985). Incorporation of hydrogen or carbon might lower the crystallinity of Pd/C during the reaction, which, in fact, was observed in the XRD experiment (Figure 6). Based on these results, the metallic nature of Pd was maintained even after the oxidative dehydrogenation of sodium lactate under pressurized oxygen and the contribution of cationic Pd were excluded.

Table 2 Results of curve-fitting analyses for Pd/C before (I) and after (II) the oxidative dehydrogenation of sodium lactate at 358 K and 1.0 MPa (100% O₂) together with those for Pd foil (III)

Sample	$r_{\text{Pd-Pd}}$ [nm ^a]	N^{b}	σ [nm ^c]	R^{d}
Pd/C (I)	0.274	7.44	0.0066	0.219
Pd/C (II)	0.276	7.32	0.0074	0.510
Pd foil (III)	0.274	12.1	0.0039	0.082

^a Nearest-neighbor distance around Pd; ^b Coordination number; ^c Debye—Waller (like) factor; ^d Reliability factor

Conclusions

Previous reports have indicated that both pH adjustment of the reaction solution and loading of Pd/C with a heavy metal were indispensable for the oxidative dehydrogenation of lactic acid to pyruvic acid using palladium-related catalysts. However, the results of the present study suggest that the employment of the sodium salt of lactate, instead of lactic acid, and high-pressure oxygen enhances the pyruvate yield from the oxidative dehydrogenation of sodium lactate using heavy-metal-free Pd/C catalysts. This result indicates that use of heavy metals is not required for the preparation of other related catalysts, which is relevant to green chemistry. Furthermore, this result suggests the potential use of heavy-metal-free Pd/C for other catalytic reactions. Dissolution of oxygen into the reaction solution at high pressure is critical for enhanced catalysis of oxidative dehydrogenation. The EXAFS analysis showed that metallic Pd, but not cationic Pd, in the Pd/C catalyst directly participates in the oxidative dehydrogenation.

Acknowledgements

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