[Regular Paper]

Direct Oxidative Esterification of Propionaldehyde to Methyl Propionate Using Heavy-metal-free Palladium Catalysts under Pressurized Oxygen

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The use of pressurized oxygen greatly enhanced catalytic activity for oxidative esterification of propionaldehyde to methyl propionate with methanol using heavy-metal-free Pd/C and Pd/Al$_2$O$_3$. For example, the conversion of propionaldehyde, the selectivity to methyl propionate, and the yield of the propionate using 5 % Pd/Al$_2$O$_3$ were 99.9, 62.7, and 62.6 %, respectively, at 1.5 MPa of oxygen gas and 333 K. This result demonstrated that Pb doping of Pd catalysts was not needed to achieve comparable activity, which runs contrary to previous reports, in which it had been suggested that loading of Pd catalysts using a heavy metal such as Pb was needed for the great activity such as 93.2, 76.8, and 71.6 % of the conversion of propionaldehyde, the selectivity to methyl propionate, and the yield of the propionate, respectively, at 0.3 MPa of oxygen gas and 353 K using 5 % Pd/Al$_2$O$_3$ doped with 5 % Pb.
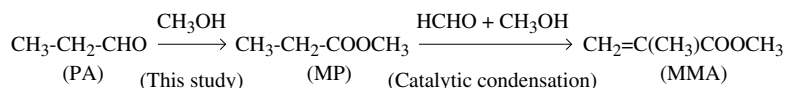
1. Introduction

Pd catalysts doped by heavy metals are known to be among the most important catalysts for a variety of catalytic reactions. Lindlar catalyst (Pb/Pd/CaCO$_3$) and Pb/Pd/SiO$_2$ for the selective hydrogenation of acetylene to olefins[1),2)] and Te/Pd/C for diacetoxylation of 1,3-butadiene[3)] are classic examples. Recently, Pd doped with a heavy metal, such as Te/Pd catalysts supported on various oxides and active carbon for the production of α,β-unsaturated carboxylic acid[4)], has attracted attention, particularly for industrial application. Although Pd catalysts doped by heavy metals such as Pb and Te are used widely in industry, green chemistry demands a clean process using a heavy-metal-free catalyst. In a previous study, a heavy-metal-free catalytic process for the production of pyruvic acid from the oxidative dehydrogenation of lactic acid in an aqueous phase has been developed. Pd/C doped with Pb or Te is reportedly an active catalyst for the reaction at pH=8, adjusted by aqueous NaOH, while no catalytic activity was observed using Pd/C under atmospheric pressure[5)~7)]. This has been further supported by previous results obtained from the catalytic oxidation of D-Gluconic acid using Pt/C doped and undoped with Pb[8)]. However, recent reports state that the use of pressurized O$_2$ resulted in great activity for the reaction of sodium lactate to sodium pyruvate using heavy-metal-free Pd/C, indicating that loading by heavy metals is not needed for the catalytic reaction[9),10)]. This result indicated that heavy metals are not required for the preparation of other related catalysts, which is important for green chemistry and suggests the potential use of heavy-metal-free Pd catalysts for other catalytic reactions. The direct oxidative esterification of propionaldehyde (PA) to methyl propionate (MP) in the liquid phase attracted attention in the present study (**Scheme 1**). Methyl propionate is an important intermediate for the production of methyl methacrylate (MMA)[11)~13)] (**Scheme 1**), which is used as a main raw ingredient for the production of acrylic resin. Earlier studies have established that the oxidative esterification of propionaldehyde to methyl propionate in the liquid phase occurs readily using Pd/Al$_2$O$_3$ doped with Pb in the presence of Mg(OH)$_2$ and NaOH in aqueous methanol at 353 K with 0.3 MPa of O$_2$ gas in a solution with pH of 6-8[14)]. In the present study, Pd/C and Pd/Al$_2$O$_3$ without heavy-metal doping were used for the direct oxidative esterification of propionaldehyde to methyl propionate in the liquid phase under

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$$\text{CH}_3\text{-CH}_2\text{-CHO} \xrightarrow[\text{(This study)}]{\text{CH}_3\text{OH}} \text{CH}_3\text{-CH}_2\text{-COOCH}_3 \xrightarrow[\text{(Catalytic condensation)}]{\text{HCHO + CH}_3\text{OH}} \text{CH}_2\text{=C(CH}_3\text{)COOCH}_3$$
$$\text{(PA)} \qquad\qquad\qquad \text{(MP)} \qquad\qquad\qquad\qquad \text{(MMA)}$$

Scheme 1 Reaction Scheme Related to the Present Study

pressurized O_2 to show that heavy-metal doping is unnecessary.

2. Experimental

Pd/C and Pd/Al$_2$O$_3$ (both with Pd of 5 % by weight) were purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan (Wako) and used as supplied. The BET surface areas of Pd/C and Pd/Al$_2$O$_3$ were 946 and 94.0 m^2/g, respectively. Pd/C catalyst doped with Te (Te/Pd/C) was prepared by impregnating the commercially available 5 % Pd/C with a given amount of H$_6$TeO$_6$ (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[15]. After 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 the atomic ratio of Te/Pd = 0.03 showed the greatest activity for oxidative dehydrogenation of sodium lactate to the 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 (85 mL) reactor[10] using the following procedures according to the previous study[14]. A given amount of the catalyst (Pd/C, Te/Pd/C or Pd/Al$_2$O$_3$) was added into a 25 mL methanol solution containing 75 mmol of propionaldehyde in the reactor. Then, 25 μL of aqueous 5 M (1 M = 1 mol·dm^{-3}) NaOH and 0.025 g of Mg(OH)$_2$ were added to keep the solution pH at 6-8. Reactions were carried out at 333 K and oxygen pressure of 0.1-2.0 MPa. The pressure in the autoclave was maintained by adding of 100 % O$_2$ to the autoclave during the reaction. It should be noted that the reaction temperature of 353 K and the pressure of 0.3 MPa was used in the previous study[14]. After the reaction, the solution was analyzed at least three times by FID-GC (GC-8AP, Shimadzu Corp.) with a 3 mm × 2 m stainless steel column (Gaskuropack 55). Data were obtained to be within 3 % of relative standard deviation. The conversion of propionaldehyde was calculated from the concentration of the aldehyde decreased during the reaction. The selectivity to methyl propionate was calculated from the conversion of propionaldehyde to methyl propionate on a mole basis. The yield of methyl propionate was calculated from the conversion of propionaldehyde and the selectivity to methyl propio-

nate (= conversion × selectivity/100). 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(311) 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 two polypropylene windows. The photon energy was scanned in the range of 24,080-25,600 eV for the Pd–K edge. Details of the calculation procedure have been previously reported[16]. Specific surface area was calculated from adsorption isotherms obtained with a conventional BET nitrogen adsorption apparatus (BELSORP-18SP, Bell Japan Inc.). In order to obtain information on a dispersion of Pd over the supports, CO adsorption was carried out using a CO-pulse experiment (BELCAT-A, Bell Japan Inc.). Before the CO adsorption to Al$_2$O$_3$-supported and C-supported catalysts, the supported catalysts were reduced at 673 and 393 K, respectively, for 15 min using H$_2$ (50 mL/min)[17]. Then a constant amount of CO (10 % CO/He) was pulse-injected into those reduced catalysts at 323 K[17].

3. Results and Discussion

The time-course of methyl propionate concentration and the yields for the oxidative esterification of propionaldehyde using 0.25 g of Pd/C or Te/Pd/C at 0.1 MPa are shown in **Fig. 1**. In the present reaction, methyl formate converted from methanol was detected without exception. It was evident that the initial rate for the esterification using Te/Pd/C was greater than that using Pd/C. However, the yield of methyl propionate showed a plateau when using Te/Pd/C, which was halved when using Pd/C after 6 h. This indicated that Pd/C not doped with heavy metals such as Te is effective for the present esterification. Therefore, the reminder of the present paper focuses on the effect of pressurized O$_2$ on the oxidative esterification of propionaldehyde using heavy-metal-free Pd/C. Although it had been reported that Mg(OH)$_2$ was added in the reaction solution in the previous study[14], it should be noted that the yield of methyl propionate in the presence of
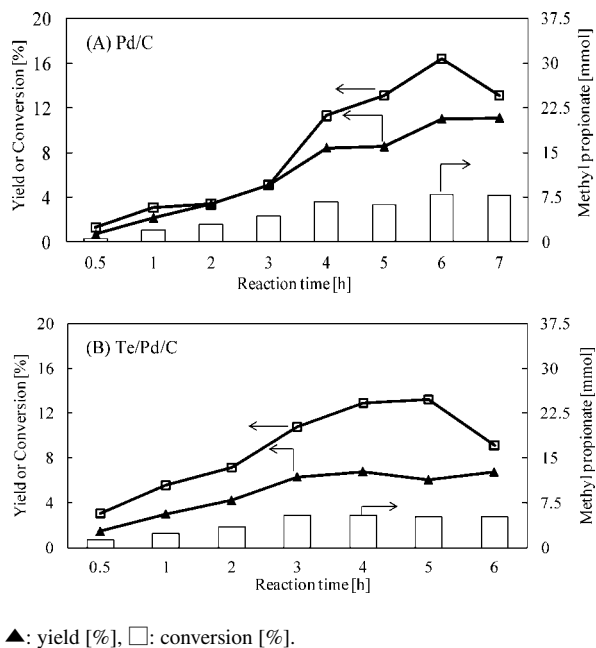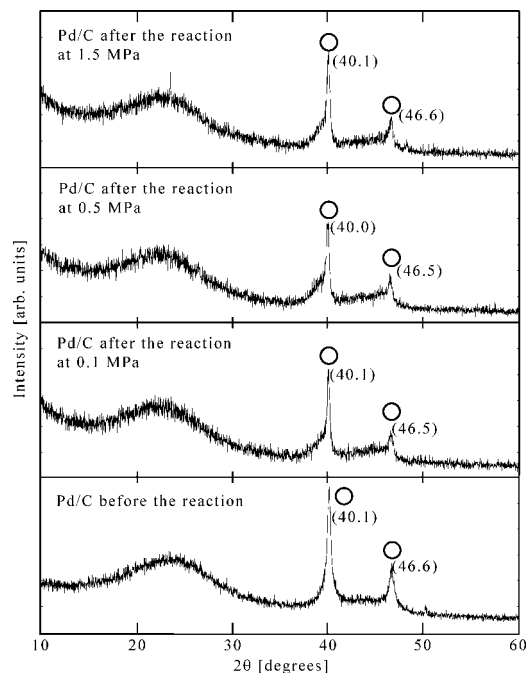
Fig. 1 Time-course of the Oxidative Esterification of Propionaldehyde at 333 K under Atmospheric Pressure Using Pd/C and Te/Pd/C
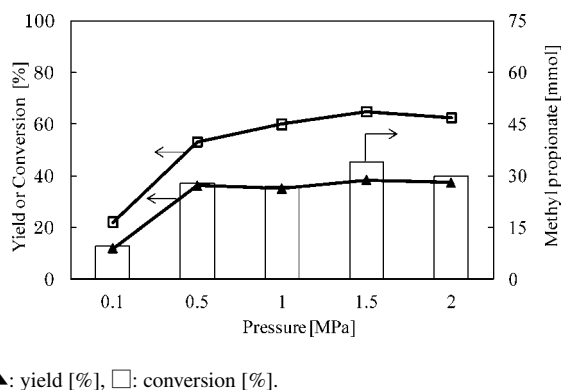
▲: yield [%], □: conversion [%].

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Fig. 2 The Effect of the Pressure of O_2 on the Oxidative Esterification of Propionaldehyde for 6 h at 333 K Using Pd/C

Values in parenthesis indicate diffraction angle.
○: Metallic Pd (JCPDS 461043).

Fig. 3 XRD Patterns of Pd/C before and after the Oxidative Esterification of Propionaldehyde at Various Pressures

$Mg(OH)_2$ was essentially identical to that in the absence of $Mg(OH)_2$. Therefore the solution pH seems to be adjusted with NaOH. As shown in **Fig. 2**, using 1.0 g of the catalyst with a reaction time of 6 h dramatically improved the yield of methyl propionate from 11.9 % at 0.1 MPa to 36.2 % at 0.5 MPa and was kept nearly constant by 2.0 MPa. The highest yield was 38.5 % at 1.5 MPa, in which the conversion of propionaldehyde and the selectivity to methyl propionate were 64.7 and 59.5 %, respectively. Since Pd/C exhibited high catalytic activity for the oxidative esterification of propionaldehyde under pressurized O_2, the conversion of Pd species during reaction under high pressure was of interest. XRD patterns of some Pd/C that was previously used for obtaining the results shown in **Fig. 2** are de-

scribed in **Fig. 3**. Before the reaction, XRD peaks due to metallic Pd (JCPDS 461043) were evident at $2\theta = 40.1$ and 46.6° together with a broad signal between approximately 15 and 31° which was characteristic to amorphous active carbon support. After the reaction under pressurized O_2, broad and small peaks at approximately 39° were detected along with a broad shoulder while main peaks were essentially due to metallic Pd. It should be noted that these XRD results were in contrast to those obtained from Pd/C used for the oxidative dehydrogenation of sodium lactate, in which the peaks due to metallic Pd in Pd/C catalyst almost disappeared after the reaction under pressurized O_2[10]. Since Pd/C was kept under O_2-rich conditions during the reaction, oxidation of metallic Pd to the oxidized cationic Pd species might have occurred. However, the shoulder detected with the peaks due to metallic Pd did not match the reference patterns of the Pd oxides. It should be noted that the weak diffraction lines at $2\theta = ca.$ 24 and 48° in the pattern of Pd/C after the reaction at 1.5 MPa were not assignable to Pd oxides phases (JCPDS 41107 for PdO and 520752 for PdO_2). As shown in **Fig. 3**, XRD patterns of the catalysts used at 0.1, 0.5 and 1.5 MPa were rather similar, while the dramatic enhancement of the activity was observed using the catalyst at 0.5 MPa. As described in our previous paper[10], the solubility of oxygen gas into a solution was increased with increase of the partial
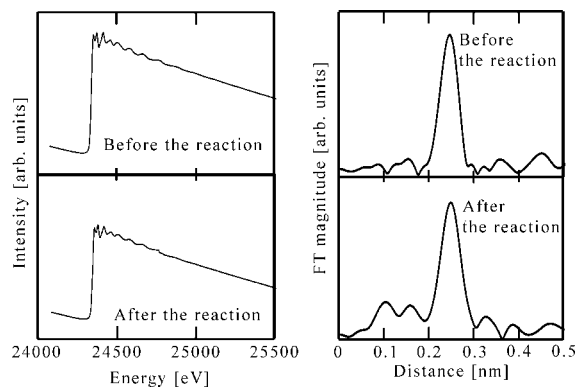
Fig. 4 Pd K-edge Spectra (left column) and the Corresponding Fourier Transformation (right column) of Pd/C before and after the Oxidative Esterification of Propionaldehyde at 1.5 MPa for 6 h

Table 1 Dispersion of Pd over Pd/C and Pd/Al₂O₃

Catalyst	CO adsorption [cm³/g]	Pd dispersion [%]	Particle size [nm]
Pd/C	1.46	13.89	8.06
Pd/Al₂O₃	1.85	17.61	6.37

pressure of gaseous oxygen. Therefore oxygen dissolved into the reaction solution at 0.5 MPa of gaseous oxygen may be sufficient for the present reaction system while more dissolved oxygen in the solution may not be needed, resulting in the similar yield of methyl propionate from 0.5 to 2.0 MPa (**Fig. 2**). The lattice constant after the reaction at 0.1, 0.5 and 1.5 MPa (0.390 nm, respectively) was greater than that before the reaction (0.389 nm), indicating that another species such as hydrogen or carbon might be incorporated into the metallic Pd during the reaction[18]. To detect such fine structure changes in the Pd/C during the reaction, EXAFS was analyzed near the Pd–K edges using the samples previously used for obtaining the results shown in **Fig. 2** before and after the reaction at 1.5 MPa (**Fig. 4**). The Pd–K edge EXAFS spectra (left column in **Fig. 4**) showed that the absorption due to Pd/C before and after the reaction at 1.5 MPa were essentially identical, which was due to metallic Pd[10]. The corresponding Fourier transformation near the Pd–K edge for these samples showed one signal characteristic metallic Pd[10),19]; weak or noise-level signals were also detected from Pd/C after the reaction while these signals were not assignable to those of PdO[19]. The nearest-neighbor distance around the Pd increased from 0.274 nm before the reaction to 0.278 nm after the reaction. Furthermore the coordination number increased from 8.18 before the reaction to 9.08 after the reaction. These results may be again explained by the incorporation of either hydrogen or carbon into Pd bonds[18]. Incorporation of these species might lower the crystallinity of Pd/C during the reaction, which was observed in the XRD (**Fig. 3**). Based on these results, it should be emphasized that the metallic nature of Pd was maintained even after the oxidative esterification of propionaldehyde under pressurized O₂.

Although the use of pressurized O₂ resulted in a great enhancement of the catalytic activity for the oxidative esterification of propionaldehyde using Pd/C, the advantages are rather insufficient. Since alumina support rather than active carbon support is generally used for similar reactions[14], Pd/Al₂O₃ was used as a catalyst for the reaction in the present study. When the oxidative esterification of propionaldehyde using Pd/Al₂O₃ (1.0 g) at 1.5 MPa and 333 K for 6 h was carried out, the conversion of propionaldehyde and the selectivity to methyl propionate were 99.9 and 62.7(±0.8) %, respectively, resulting in a yield of 62.6(±0.8) %. Therefore the yield of methyl propionate was improved from 38.5 % using Pd/C to 62.7 % using Pd/Al₂O₃. Although the present yield was a bit lower than that previously reported (71.6 %) for Pd/Al₂O₃ doped with Pb[14], doping of the Pd catalyst with heavy metal may not be needed for the present reaction system. Since the catalytic activity using Pd/C is evidently different from that using Pd/Al₂O₃, the effect of these supports on the dispersion of Pd was examined using a CO-pulse technique. Although the surface area of Pd/C (946 m²/g) was considerably greater than that of Pd/Al₂O₃ (94.0 m²/g), Pd-dispersion of Pd/Al₂O₃ were slightly greater than that of Pd/C, resulting in the particle size of Pd for Pd/Al₂O₃ being smaller than that for Pd/C (**Table 1**). Therefore the interaction between the support and the substrate may contribute to the evident enhancement of the catalytic activity when using Pd/Al₂O₃.

4. Conclusion

A previous report indicated that the loading of Pd/Al₂O₃ with a heavy metal was required for the effective reaction of oxidative esterification of propionaldehyde[14]. However the results of the present study suggest that the use of pressurized O₂ enhances the yield of methyl propionate using heavy-metal-free Pd/Al₂O₃, as anticipated in our previous report, in which the potential use of heavy-metal-free Pd catalyst for various catalytic reactions was suggested[10].

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酸素加圧下重金属非修飾パラジウム触媒によるプロピオンアルデヒドから
プロピオン酸メチルへの酸化的エステル化反応

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　プロピオンアルデヒドからプロピオン酸メチルへの酸化的エステル化は，鉛などの重金属で修飾した活性炭担持もしくはアルミナ担持パラジウム触媒で行うと良好に進む，と従来報告されていた。たとえば，5％の鉛で修飾した5％ Pd/Al₂O₃触媒を用いると，酸素加圧0.3 MPa，反応温度353 Kにおいて，93.2％のプロピオンアルデヒド変化率，76.8％のプロピオン酸メチルの選択率が報告されていた。しかし，酸素加圧下（1.5 MPa），重金属で修飾していない5％ Pd/C を用いて反応温度333 Kで本反応を行うと，99.9％のプロピオンアルデヒド変化率において，62.7％のプロピオン酸メチル選択率という従来の報告に匹敵する活性が得られ，鉛などの重金属で修飾したパラジウム触媒を用いる必要がないことが明らかになった。

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