The Oxidative Esterification of Propionaldehyde to Methyl Propionate in the Liquid-Phase Using a Heterogeneous Palladium Catalyst

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The optimization of the oxidative esterification of propionaldehyde to methyl propionate using a supported palladium catalyst in methanol under heavy-metal-free and pressurized-oxygen conditions, which we recently reported in a previous paper, were carried out together with a study of the reaction route, the nature of the catalytic active sites, and the effect of the support. In our previous paper, we reported significantly improved activity for oxidative esterification using commercially available 5%Pd/Al_2O_3 at 1.5 MPa of O_2 gas and 333 K and emphasized that the doping of 5%Pd/Al_2O_3 with lead was not needed for the reaction system, but we could not improve the activity that was reported when using 5%Pd/γ-Al_2O_3 doped with 5% Pb (a 93.2% conversion of propionaldehyde, 76.8% selectivity for methyl propionate and a 71.6% yield of methyl propionate) at 0.3 MPa of O_2 gas and 353 K, as reported by another laboratory. In the present study, however, we exceeded those values and obtained a 98.3% conversion of propionaldehyde, 75.3% selectivity for methyl propionate and a 74.0% yield of methyl propionate using 5%Pd/γ-Al_2O_3 undoped with Pb at 1.5 MPa of O_2 gas and 333 K. It should be noted that, in the preparation of the present 5%Pd/γ-Al_2O_3, Pd was doped onto Al_2O_3 that had been previously treated with aqueous NaOH. Another active alumina support, η-Al_2O_3, prepared from boehmite, afforded activity that was substantially lower than that of γ-Al_2O_3 and depended on the calcination temperature of boehmite to η-Al_2O_3. When using various concentrations of CH_3OH in the aqueous reaction solution, the oxidative esterification proceeded through the formation of propionic acid. To determine why the Al_2O_3 support afforded better activity than the active carbon support, Pd/Al_2O_3 and Pd/C catalysts were examined by XAFS (X-ray absorption fine structure). XAFS revealed that Pd on Al_2O_3 shows a better redox nature than Pd on C, which resulted in activity on Pd/Al_2O_3 that was better than that on Pd/C.

Introduction

A combination of noble metals and heavy metals is sometimes used as a catalyst. With these combined systems, two effects are tentatively expected: the first is the preparation of a new catalytic site, and the second is the enhancement of activity that reduces the amount of the noble metal. For the first effect, the combination of noble metal and a heavy metal is undoubtedly needed. However, for the second effect, the combination may not always be needed, because the combination of a noble catalyst together with the reactor or with various reaction conditions, may compensate the activity of the combined catalysts. Since green chemistry demands a clean process when using a heavy-metal-free catalyst, we recently focused on the second effect. The first example from our group was the oxidative dehydrogenation of lactic acid to pyruvic acid in an aqueous phase. It was first reported that Pd/C doped with Pb and Te for the reaction was one of the best catalysts under atmospheric pressure (Tsujino *et al*., 1992; Hayashi *et al.*, 1993, 1994). However, the use of pressurized oxygen resulted in great activity for a reaction using heavy-metal-free Pd/C, indicating that doping by a heavy metal is unnecessary for the reaction (Sugiyama *et al*., 2009, 2010). A subsequent example was the liquid-phase oxidation of propylene glycol in the presence of NaOH to pyruvic acid. At first, it had been reported that Pd/C showed activity for the production of pyruvic acid through hydroxyl acetone, while Pd/C doped with heavy metals has shown activity for the production of pyruvic acid through lactic acid under atmospheric pressure (Tsujino *et al*., 1992). However, a recent study under pressurized oxygen revealed that the catalytic activity is not dependent on doping with heavy metals, but is instead dependent on

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the molar ratio of the NaOH that is added to the reaction solution against propylene glycol, again indicating that the doping of Pd/C with heavy metals is unnecessary under pressurized oxygen (Sugiyama *et al*., 2013). A third example was the direct oxidative esterification of propionaldehyde to methyl propionate using Pd/Al$_2$O$_3$ in a methanol solution. For the present study, Diao *et al*. (2009) had reported that Pd/Al$_2$O$_3$ doped with Pb showed activity as great as 93.2% for the conversion of propionaldehyde, 76.8% of the selectivity for methyl propionate, and a 71.6% yield of methyl propionate at 0.3 MPa of O$_2$ and 353 K. However, our most recent study using heavy-metal-free Pd/Al$_2$O$_3$ showed comparable activity that included a 99.9% conversion of propionaldehyde, 62.7% selectivity to methyl propionate, and a 62.6% yield of methyl propionate obtained at 1.5 MPa of O$_2$ and 333 K, indicating potential for the use of a heavy-metal-free Pd catalyst in various catalytic reactions (Sugiyama *et al*., 2011).

Methyl propionate (MP) is an important intermediate for the production of methyl methacrylate (MMA) (**Figure 1**) (Albanesi and Moggi, 1983; Jackson, 2002; So, 2010), which is used as a main raw ingredient for the production of acrylic resin. However, in our previous paper on the direct oxidative esterification of propionaldehyde (PA) to MP using Pd/Al$_2$O$_3$ in a liquid phase under pressurized oxygen, we did not present the reaction data that exceeded that using Pd/Al$_2$O$_3$ doped with Pb. That paper also did not provide information on the nature of Pd together with the reaction route. Therefore, in the present study, the direct oxidative esterification of PA to MP using Pd/Al$_2$O$_3$ in a liquid phase under pressurized oxygen was examined in detail.
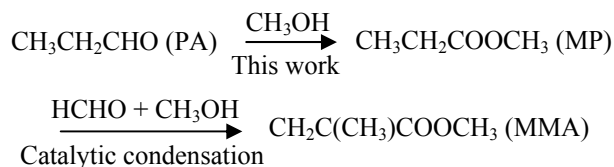
$$CH_3CH_2CHO \text{ (PA)} \xrightarrow[\text{This work}]{CH_3OH} CH_3CH_2COOCH_3 \text{ (MP)}$$

$$\xrightarrow[\text{Catalytic condensation}]{HCHO + CH_3OH} CH_2C(CH_3)COOCH_3 \text{ (MMA)}$$

Fig. 1 Reaction scheme in the present study

1. Experimental

As a standard catalyst, Pd/C and Pd/Al$_2$O$_3$ (both with Pd of 5% by weight) were purchased from Wako Pure Chemical Industries, Ltd., (Wako) and Sigma-Aldrich Co. LLC, respectively, and used as supplied. In the present study, alumina-supported Pd catalysts were also prepared from various combinations of Al$_2$O$_3$ using the following procedure. It should be noted that the commercially available catalysts were Pd/C and Pd/Al$_2$O$_3$, while Pd/α-Al$_2$O$_3$, Pd/γ-Al$_2$O$_3$, and Pd/η-Al$_2$O$_3$ were the prepared palladium catalysts. For an Al$_2$O$_3$ support without pretreatment, Pd/Al$_2$O$_3$ was prepared from α-Al$_2$O$_3$ (Wako), γ-Al$_2$O$_3$ (Wako), and η-

Al$_2$O$_3$; the latter of which was prepared from the calcination of boehmite (Hasegawa *et al*., 2002) by impregnation with an aqueous Pd(NO$_3$)$_2$ solution (24.41% by weight, N.E. Chemcat Corporation, Tokyo, Japan). The palladium-supported catalysts then were reduced by aqueous formalin (37%, Kanto Chemical Co., INC. (Kanto)) at 343 K for 2 h or by NaBH$_4$ (Wako) at 363 K for 1 h. For the pretreated Al$_2$O$_3$ support, γ-Al$_2$O$_3$ (Wako) was pretreated with aqueous NaOH (Hodoshima *et al*., 2001) and palladium was loaded by impregnation with an aqueous solution of K$_2$PdCl$_4$ (Kanto), followed by reduction with NaBH$_4$. The loading of Pb was adjusted to 5% by weight for all catalysts. Any leaching of Pd from the catalyst during the preparation was not detected. Catalytic activity was tested in a magnetically-stirred stainless steel autoclave (85 mL) reactor (Sugiyama *et al*., 2011) using the following procedures according to the results from a previous study (Diao *et al*., 2009). A given amount of the catalyst (1.0 or 0.5 g) was added to the reactor along with a 25 mL methanol solution containing 75 or 37.5 mmol of propionaldehyde. Then, 25 µL of aqueous 5 M 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 under an oxygen pressure of 1.5 MPa. The pressure in the autoclave was maintained by the addition of 100% O$_2$ to the autoclave during the reaction. After the reaction, the solution was analyzed by FID-GC (GC-8AP, Shimadzu Corp.) with a 3 mm × 2 m stainless steel column (Gaskuropack 55). The yield of the methyl propionate was calculated from the conversion of propionaldehyde and from the selectivity to methyl propionate (= 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 the EXAFS near the Pd K-edge was carried out at the High Energy Accelerator Research Organization using 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 into a disk with diluents, the catalysts were carefully placed into a handmade sample holder with two polypropylene windows. The photon energy was scanned ranging from 24,080–25,600 eV along the Pd K-edge. The details of the calculation procedure were previously reported (Sugiyama *et al*., 2008). The specific surface area was calculated from adsorption isotherms obtained using 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 Pd-supported catalysts, the supported catalysts were reduced at 673

and 393 K, respectively, for 15 min using H_2 (50 mL/min). Then, a constant amount of CO (10% CO/He) was pulse-injected into those reduced catalysts at 323 K.

2. Results and Discussion

2.1 Oxidative esterification of propionaldehyde using various Pd/Al₂O₃ catalysts

In our previous paper (Sugiyama *et al.*, 2011), catalysis using Pd/C under atmospheric pressure showed that the doping of Pd/C with heavy metal (tellurium) was unnecessary, while that using Pd/Al₂O₃ (62.6% of the yield of MP at 1.5 MPa of O_2 and 333 K after 6 h), which was evidently greater than when Pd/C (38.5% of the yield of MP under the same reaction conditions) was used, was briefly described. Therefore, the time-course of the esterification using 1.0 g of Pd/Al₂O₃ and 75.0 mmol of PA at 1.5 MPa of O_2 and 333 K was again examined. In the present study, methyl formate converted from methanol was detected without exception.
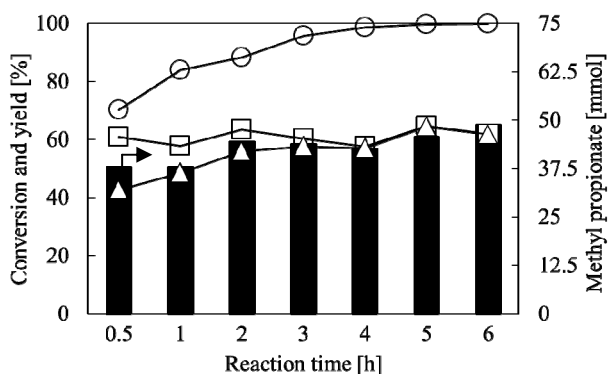

Fig. 2 The oxidative esterification of propionaldehyde at 333 K and 1.5 MPa of O_2 using Pd/Al₂O₃. Symbols: ○, the conversion of PA; □, the selectivity to MP; △, the yield of MP; and closed bar, the MP

As shown in **Figure 2**, the conversion of PA increased with the reaction time while the selectivity to MP was essentially constant regardless of the reaction time, which resulted in an increase in the yield of MP. During the conversion of PA, the selectivity to MP, and the yield of MP after 6 h were 99.9, 61.9 and 61.8%, respectively, which was essentially identical to the activity reported under the same conditions (99.9, 62.7 and 62.6%, respectively) in our previous paper (Sugiyama *et al*., 2011). This data was evidently lower than that (93.2, 76.8 and 71.6%, respectively) reported by Diao *et al.* (2009) at 0.3 MPa of O_2 and 353 K after 2 h, although the reaction temperature in the present reaction was 20 K lower than that reported by Diao *et al*. (2009), and the weight of the catalyst (1.0 g) was four-fold greater than that reported by Diao *et al*.

(2009). Therefore, various Pd/Al₂O₃ catalysts were examined in the present study to determine more active catalyst systems under pressurized oxygen.

Table 1 Comparison of catalytic activity for the oxidative esterification of propionaldehyde using various Pd/Al₂O₃ at 333 K and 1.5 MPa of O_2

	T [h][e]	PA Con [%][f]	MP Sel [%][g]	MP Y [%][h]	SA [m²/g][i]	Pd Disp. [%][j]
Pd/Al₂O₃	2	88.3	63.4	56.0	94.0	17.6
	4	98.7	57.6	56.9		
Pd/α-Al₂O₃	4	49.4	55.6	27.4	3.6	0.87
Pd/γ-Al₂O₃ untreated[a]	2	83.9	66.9	56.1	193	9.9
	4	88.5	63.6	56.3		
Pd/γ-Al₂O₃ pretreated[b]	2	98.3	75.3	74.0	229	17.7
	4	98.8	62.9	62.1		
Pd/η-Al₂O₃ (673 K)[c]	2	90.0	57.4	51.7	263	15.3
	4	89.8	63.4	56.9		
Pd/η-Al₂O₃ (873 K)[d]	2	85.6	61.1	52.2	210	11.0
	4	92.2	54.4	50.2		

a: Untreated; b: Pretreated with aq. NaOH; c: Obtained by the calcination of boehmite at 673 K for 3 h; d: Obtained by the calcination of boehmite at 873 K for 3 h; e: Reaction time; f: Conversion of PA; g: Selectivity to MP; h: Yield of MP; i: Specific surface area; j: Pd dispersion

Table 1 compares catalytic activity using various Pd/Al₂O₃ catalysts. The catalytic activity of Pd/α-Al₂O₃ (1.0 g) for the oxidative esterification of PA (75.0 mmol) was lower than that of commercially available Pd/Al₂O₃ under the same reaction conditions due to the small surface area and dispersivity of the Pd metal. However, the use of active forms of alumina such as γ-Al₂O₃, and η-Al₂O₃ as a support resulted in an enhancement of the activity due to a markedly wider surface area and a better dispersion of the Pd metal. The results shown in Table 1 for Pd/γ-Al₂O₃, and Pd/η-Al₂O₃ were obtained using 0.5 g of the catalysts and 37.5 mmol of PA. The best activity among those catalysts, which finally exceeded the activity reported by Diao *et al.* (2009), was obtained from Pd/γ-Al₂O₃ with a support that had been pretreated with an aqueous NaOH solution. Previous reports have shown that cationic Pd species can be ion-exchanged with Na^+ on a support that has been introduced on a surface pore during pretreatment with NaOH (Hodoshima *et al*., 2001). When the cationic Pd species was reduced with NaBH₄, a much greater dispersion of metallic Pd was formed. The combination of a greater dispersion of Pd and a wider surface area in the case of γ-Al₂O₃ resulted in the best activity among those catalysts, as shown in Table 1. Although η-Al₂O₃ obtained with the calcination of boehmite at 673 K for 3 h possessed the

widest surface area, the activity was evidently lower than when using a γ-Al$_2$O$_3$ support, due to a lower dispersion of Pd metal. The lower calcination temperature resulted in an incomplete conversion of boehmite, while a higher calcination temperature such as 873 K resulted in a decrease in both the surface area and the dispersion of Pd metal, and, as expected, a lower activity was observed as shown in Table 1.

2.2 Reaction route of the oxidative esterification of propionaldehyde using Pd/Al$_2$O$_3$

For the oxidative esterification of PA to MP in a methanol solution using Pd/Al$_2$O$_3$, the reaction using propionic acid (PAC) may be the most suitable candidate for a reaction route (**Figure 3**).

$$CH_3CH_2CHO \text{ (PA)} \xrightarrow{O_2} CH_3CH_2COOH \text{ (PAC)}$$
$$\xrightarrow{CH_3OH} CH_3CH_2COOCH_3 \text{ (MP)}$$

Fig. 3 Reaction route for the present reaction

In order to check the reaction route, the oxidative esterification of PA using Pd/Al$_2$O$_3$ was examined in a solution consisting of methanol and H$_2$O. **Figure 4** describes the results obtained from the oxidative esterification of PA (37.5 mmol) in a reaction solution (25 mL) consisting of various concentrations of methanol using Pd/Al$_2$O$_3$ (0.5 g) at 1.5 MPa of O$_2$ and 333 K after 2 h. In that figure, 0 and 562.5 mmol/25 mL of the concentration of methanol corresponded to the reaction solution consisting only of H$_2$O and methanol, respectively.

Fig. 4 The oxidative esterification of propionaldehyde at 333 K and 1.5 MPa of O$_2$ using Pd/Al$_2$O$_3$. Symbols: ○, the conversion of PA; □, the selectivity to MP; ◇, the selectivity to PAC; open bar, the PAC; closed bar, the MP

As shown in Figure 4, PAC was only formed in the absence of methanol in the reaction solution (94.2% of the selectivity) and the minimum selectivity to PAC was

detected at 75.0 mmol of methanol in the reaction solution. Meanwhile, the minimum selectivity to MP was detected at 37.5 mmol of methanol in the reaction solution. The selectivity to MP increased as methanol concentration reached 51.4%. It is interesting to note that the minimum value for the conversion of PA was detected at 187.5 mmol of methanol in the reaction solution. A lowering of the selectivity occurred at this point. Much better selectivity to PAC and/or MP at 0 and 562.5 mmol/L of methanol concentration (94.2% (PAC) and 64.0% (MP (51.4%) + PAC (12.6%))), respectively) were observed, while 16.1% of the selectivity to MP (5.2%) and PAC (10.9%) was observed at 75.0 mmol/L. At 0 mmol/L of methanol concentration, the conversion of PA to PAC proceeded favorably due to the great solubility of O$_2$ in H$_2$O. With increasing methanol concentration, the solubility of O$_2$ in the solution was decreased due to the rather lower solubility of O$_2$ into methanol, resulting in a decrease in the conversion of PA and in the selectivity to PAC as shown in Figure 4. In contrast, at 562.5 mmol/L of methanol concentration, the esterification of PA to MP through PAC proceeded favorably due to the great concentration of methanol in the reaction solution. By decreasing the methanol concentration in the solution, it is reasonable to expect a decrease in esterification due to a lack of methanol. These two factors resulted in minimum activity at around 75.0 and 187.5 mol/L of methanol concentration, as shown in Figure 4. Furthermore, the formation of by-products, with the exception of PAC and MP, may have contributed to the lower conversion of PA. Unfortunately, other species rather than MP and PAC could not be detected in the present study.

2.3 XAFS analysis of the Pd species on Pd/C and Pd/Al$_2$O$_3$

As pointed out in Section 2.1., the surface area and dispersion of the Pd metal contributed to the catalytic activity. However, as shown in our previous paper (Sugiyama *et al.*, 2011), the activity of Pd/C, with a greater surface area (946 m^2/g) and a greater dispersion of Pd (13.9%), was evidently lower than that using Pd/Al$_2$O$_3$. This indicated that the nature of the influence of Pd over the supports, C and Al$_2$O$_3$, might have differed.

XRD analysis of Pd/C before and after the oxidative esterification showed two peaks at $2\theta = 40.1$ and 46.6 degrees due to the metallic Pd (JCPDS 461043) and to the intensity of the Pd peaks being weaker after esterification (Sugiyama *et al.*, 2011). However, in the XRD of Pd/Al$_2$O$_3$, the peaks due to the metallic Pd overlapped the broader peaks due to Al$_2$O$_3$, and information on the Pd species could not be obtained using XRD, while the peak intensity at approximately

40 and 46 degrees seemed to be greater after esterification (**Figure 5**).
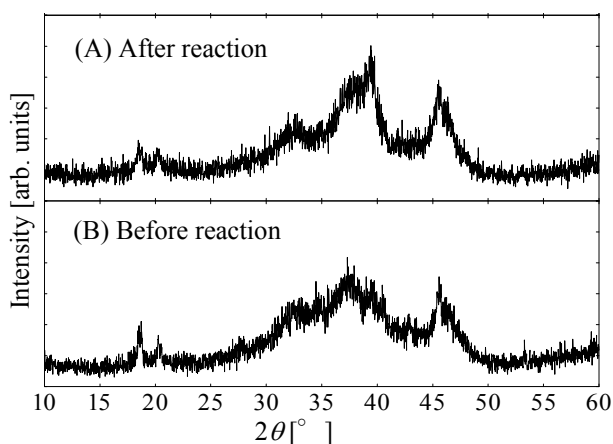

Fig. 5 XRD patterns of Pd/Al$_2$O$_3$ before and after the oxidative esterification of propionaldehyde. Sample (A): Pd/Al$_2$O$_3$ used for obtaining the results shown in Figure 2, albeit after 4 h

To detect the differing nature of Pd on Pd/C and Pd/Al$_2$O$_3$, EXAFS was analyzed near the Pd K-edge using those catalysts before and after the oxidative esterification at 333 K and 1.5 MPa of O$_2$ for 4 h.
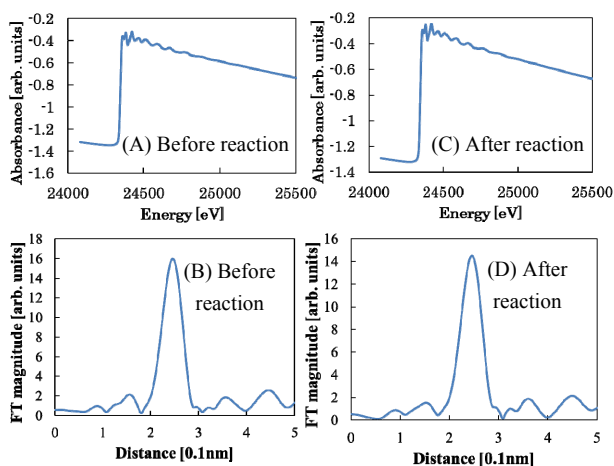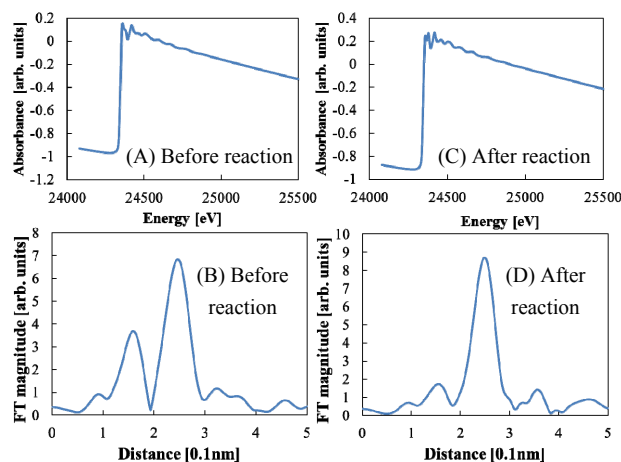

Fig. 6 Pd K-edge spectra (upper row) and the corresponding Fourier transformation (lower row) of Pd/C before and after the oxidative esterification of propionaldehyde at 333 K and 1.5 MPa of O$_2$ for 4 h

The Pd K-edge EXAFS spectra of Pd/C before and after the reaction (**Figures 6 (A)** and **(C)**, respectively) showed that the absorption due to the Pd species were essentially identical, which was due to the metallic Pd (Sugiyama *et al*., 2010). The corresponding Fourier transformation near the Pd K-edge for those catalysts showed one signal (**Figures 6 (B)** and **(D)**, respectively), which was characteristic to metallic Pd (Shimizu *et al*., 2004; Sugiyama *et al*., 2010).

In contrast, the Pd K-edge EXAFS spectra of Pd/Al$_2$O$_3$ before and after the reaction showed that the absorption due to the Pd species from the catalyst before the reaction (**Figure 7 (A)**) was evidently different from that after the reaction (**Figure 7 (C)**), the latter of which was an analogue of those obtained from Pd/C before and after the reaction. The Fourier transformation near the Pd K-edge for Pd/Al$_2$O$_3$ before the reaction showed two signals (**Figure 7 (B)**): small and great signal characteristics to Pd-oxide and metallic Pd, respectively. From the Fourier transformation for Pd/Al$_2$O$_3$ after the reaction, only one signal characteristic to metallic Pd was detected (**Figure 7 (D)**). Therefore, we suggest that the suitability of the redox nature of the Pd species over Al$_2$O$_3$, rather than that over C, may have contributed to the enhancement of the catalytic activity of Pd/Al$_2$O$_3$.

Fig. 7 Pd K-edge spectra (upper row) and the corresponding Fourier transformation (lower row) of Pd/Al$_2$O$_3$ before and after the oxidative esterification of propionaldehyde at 333 K and 1.5 MPa of O$_2$ for 4 h

It is interesting to note that the nearest neighbor of the Pd-Pd atoms and the coordination number around Pd were estimated from the curve-fitting analyses for Pd/C and Pd/Al$_2$O$_3$ before and after, respectively, the oxidative esterification of propionaldehyde (**Table 2**).

Table 2 Results of the curve-fitting analyses for Pd/C and Pd/Al$_2$O$_3$ before and after the oxidative esterification of propionaldehyde

Sample	Conditions	r_{Pd-Pd}[a]	N[b]
Pd/C	Before reaction	0.274	7.61
	After reaction	0.275	7.63
Pd/Al$_2$O$_3$	Before reaction	0.274	4.46
	After reaction	0.277	6.77

[a] Nearest-neighbor distance around Pd [nm];
[b] Coordination number

As shown in Table 2, the nearest-neighbor distance and the coordination number around metallic Pd increased after the reaction using Pd/C and Pd/Al$_2$O$_3$, indicating the incorporation of either hydrogen or carbon into the Pd bonds (Ziemecki *et al.*, 1985).

In order to examine the effect of Pd-oxide species on the oxidative esterification of propionaldehyde using Pd/Al$_2$O$_3$, the effect of the treatment of O$_2$ for Pd/Al$_2$O$_3$ and Pd/γ-Al$_2$O$_3$, the latter of which was prepared using γ-Al$_2$O$_3$ with no pretreatment, was examined together with the reaction using PdO/γ-Al$_2$O$_3$. For the oxygen treatment, oxygen gas was continuously introduced into a methanol solution consisting of the supported Pd catalysts (0.5 g) at 298 K for 1 h and then the reactant, the given amounts of Mg(OH)$_2$ and aqueous NaOH solution were added into the solution to start the oxidative esterification at 333 K and 1.5 MPa of O$_2$ for 2 h. The yields of MP using Pd/Al$_2$O$_3$ un-treated and treated were 57.0 and 55.9%, respectively, while the yields were 56.1 and 58.5% from Pd/γ-Al$_2$O$_3$ that was un-treated and treated, respectively, indicating that there was no advantageous effect from oxygen treatment. Furthermore, PdO/γ-Al$_2$O$_3$ showed quite low activity (1.2% of the yield of MP). Therefore, the redox nature produced from the interaction between Al$_2$O$_3$ and metallic Pd, rather than the contribution of the Pd-oxide itself, seemed necessary for oxidative esterification.

Finally, it is worthwhile to mention that the redox nature of Pd on Pd/Al$_2$O$_3$ reflects the reuse of Pd/Al$_2$O$_3$ as a catalyst for the esterification of PA. When Pd/Al$_2$O$_3$ (0.5 g) was reused three times for the conversion of PA at 333 K and 1.5 MPa of O$_2$ for 4 h using a 25 mL methanol solution containing 37.5 mmol of PA, turn over frequency, which is defined as a ratio of molar number of PA converted versus molar number of Pd in the catalyst, increased from 159 in the first run to 192 in the second run and to 251 in the third run. As shown above, Pd maintained its cationic properties in the first run, while the cationic properties decreased with reuse, resulting in an increase in the turn over frequency.

Conclusions

The present study was focused on the factors that contribute to the oxidative esterification of propionaldehyde under pressurized oxygen using Pd/Al$_2$O$_3$ catalysts, along with the reaction route. Esterification was shown to begin through the formation of propionic acid with the oxidation of propionaldehyde, followed by esterification with methanol to methyl propionate. Together with the combination of the great surface area of the catalyst and the dispersion of Pd over the catalyst, the suitable redox nature of Pd, which was produced from the interaction of Al$_2$O$_3$ and metallic Pd, was necessary for the enhanced activity during the oxidative esterification of propionaldehyde under

pressurized oxygen using Pd/Al$_2$O$_3$ catalysts. In our previous study, the activity using Pd/Al$_2$O$_3$ under pressurized oxygen did not exceed that produced by another laboratory using Pd/Al$_2$O$_3$ doped with Pb. In the present study, however, the activity using Pd/Al$_2$O$_3$ finally exceeded the activity using Pb-doped Pd/Al$_2$O$_3$, indicating that the doping of Pd/Al$_2$O$_3$ with a heavy metal such as lead is unnecessary for esterification under pressurized oxygen.

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