Allylic C–H acetoxylation of terminal alkenes over TiO₂ supported palladium nanoparticles using molecular oxygen as the oxidant

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Abstract

A method for synthesizing linear allylic acetates from terminal alkenes over TiO₂ supported Pd nanoparticles has been developed, in which O₂ serves as the sole oxidant. Good catalytic activity was performed when using allylbenzene as a substrate and the catalyst can be reused at least five times without activity losing. The catalytic system has a broad substrate scope including transformation of 1,3-butadiene into 1,4-diacetoxy-2-butene, which is an important industrial intermediate for production of 1,4-butanediol. In contrast to previous reports that the Pd-catalyzed allylic acetoxylation is generally promoted by Pd^{II} species, the XAFS measurements suggest that this reaction is catalyzed over Pd⁰ NPs. Additionally, XPS analysis of the catalyst confirm that the interaction between Pd and TiO₂, which probably promote the initial catalytic procedure.

Keywords: acetoxylation, heterogeneous catalyst, terminal alkenes, linear allylic acetates

1. Introduction

Palladium-catalyzed selective allylic oxidation is an attractive and efficient methodology to construct the valuable molecules via a C–H bond cleavage and functionalization process [1–2]. For example, selective allylic C–H acetoxylation of terminal alkenes into linear allylic acetates has a potential to prepare primary alcohols through further hydrogenation and hydrolysis [3–4]. In the previous studies, the allylic C–H acetoxylation was carried out over a Pd^{II} catalytic system combined with stoichiometric organic or inorganic oxidants [5–16]. In the vast majority of these works, benzoquinone (BQ) has been predominantly employed as a highly effective oxidizing reagent. These oxidants promote the nucleophilic attack of acetate to a π -allyl-Pd^{II} intermediate and the re-oxidation of the Pd⁰ to Pd^{II} during the reaction

cycle [7–8]. However, from the point of view of green chemistry, replacement of stoichiometric oxidants with clean and inexpensive molecular oxygen would be a significant advance [17]. Stahl and co-workers have developed a catalytic system using $\text{Pd}(\text{OAc})_2$ with a nitrogenous ligand for transformation of allylbenzenes into cinnamyl acetate and its derivatives. Although BQ was successfully replaced with O_2 in their work, the catalytic system still has some drawbacks such as using expensive additives and a non-recyclable catalyst [3]. Kaneda et al. also reported the combination of PdCl_2 and dimethylacetamide (DMA) allowed oxygenation of the allylic site of terminal alkenes in the absence of BQ or other organic oxidants to prepare linear allylic acetates, but high pressure of O_2 (6 atm) was required due to the fact that re-oxidation of Pd^0 as the rate-determining step was generally difficult to achieve [4].

On the other hand, allylic C–H acetoxylation is also a fundamental and essential process in chemical industry. Heterogeneous catalytic systems have been widely applied in this area based on several advantages such as easy separation and recyclability. Showa Denko Corporation has commercialized the aerobic acetoxylation of propene to allyl acetate over supported Pd catalysts, and allyl acetate is converted to allyl alcohol after the hydrolysis process [18]. Moreover, Mitsubishi Chemical Corporation developed a supported Pd–Te catalyzed allylic C–H acetoxylation process for a production of 1,4-butanediol from 1,3-butadiene as the initial step [19–21]. However, only these two gas phase substrates have been applied to this reaction and the substrates scope was never explored with heterogeneous catalysts. Recently, we reported that metal oxide supported $\text{Pd}(\text{OH})_2$ or Pd^0 catalysts exhibited outstanding performance in C–H activation processes such as oxidative intramolecular C–C bond formation and oxidative dehydrogenation reactions [22–23]. This feature inspired us to explore other environmentally friendly and efficient selective oxidations using O_2 as the sole oxidant. In this work, we report that TiO_2 supported Pd catalyzed the aerobic allylic C–H acetoxylation of terminal alkenes to selectively give various linear allylic acetate products. The reaction can be performed under 1 atm of O_2 , and the catalyst exhibits good recyclability.

2. Experimental

2.1 Material and measurements

Palladium on activated carbon (Pd/C) and Palladium nitrate were supplied by Wako Pure Chemical Industries Co., Ltd. TiO_2 (ST111), $\gamma\text{-Al}_2\text{O}_3$ (AKP-G015) and ZrO_2 (RC-100) were supplied from Titan Kogyo, Sumitomo Chemical Co., Ltd. and Daiichi Kigenso Kagaku Kogyo Co., Ltd., respectively. All other reagents were used in commercial grade. The authentic samples of allylic acetates were purchased from Wako Pure Chemical Industries Co., Ltd., Tokyo Chemical Industry Co., Ltd. and Sigma-aldrich, Inc. High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) observations were performed using a JEOL JEM-ARM200F. X-ray powder diffraction (XRD) patterns were obtained on a Rigaku MiniFlex600 with a high-intensity Cu $K\alpha$ radiation source ($\lambda = 0.154178$ nm) at a scanning rate of $20^\circ/\text{min}$. X-ray absorption fine structure (XAFS) measurements were performed at BL14B2 beam line of SPring-8 (Hyogo, Japan) with Si (311) double crystal monochromator [24–25]. The XAFS spectra were recorded in the transmission mode using ionization chambers. The spectral analysis was performed using the XAFS analysis software, Athena [26]. XPS of the samples was collected using a Shimadzu AXIS-165 spectrometer equipped

with a Al K α anode. The calibration peak is C1s at 283.6 eV. Palladium loading of the catalysts were analyzed by microwave plasma-atomic emission spectrometry (MP-AES) by Agilent, 4100 MP-AES. To analyze the leaching of Pd during the reaction, the solid catalyst was filtered from the reaction mixture after reaction and dried at 70 °C overnight, and then, dissolved in amount of aqua regia for analysis. Conversions and product yields were analyzed by gas chromatography (GC) using Agilent GC 6850 Series II equipped with FID and a J&W HP-1 column (0.25 μ m thickness, 0.25 mm I.D., 30 m). ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 spectrometer at 400 and 100 MHz, respectively. ^1H assignment abbreviations are the following: singlet (s), doublet (d), triplet (t), double of doublet (dd), double of triplet (dt), and multiplet (m).

2.2 Preparation of catalysts

Pd/metal oxide catalysts were prepared by an impregnation (IMP) method. Palladium loading was adjusted to 5 wt%. Palladium nitrate (0.114 g) was dissolved in a small portion of water. Support (1.0 g), such as TiO_2 , was added to the aqueous solution and stirred at room temperature for 30 min. After impregnation, H_2O was removed by vacuum-freeze drying or evaporation. The obtained catalyst was calcined at 300 °C for 4 h to obtain PdO/TiO_2 . Then, PdO/TiO_2 was reduced in a flow of pure H_2 (20 mL/min) at 200 °C for 3 h to obtain Pd/TiO_2 .

2.3 Catalytic activity test

A typical procedure for catalytic reactions: a glass tube was charged with a stirring bar, allylbenzene (1 mmol), catalyst (Pd 5 mol%), NaOAc (1 mmol), solvent (total amount of AcOH and DMSO was 2.0 mL), and sealed with an O_2 balloon. The reaction was conducted at 90 °C for 28 h. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was analyzed by GC using tridecane as an internal standard.

A typical procedure for acetoxylation of 1,3-butadiene: the reaction was performed in an autoclave which was charged with Pd/TiO_2 (Pd 5 mmol), AcOH/DMSO (10/1 v/v, total amount was 2.0 mL), NaOAc (1 mmol) and a stirring bar. The autoclave was cooled below 0 °C by liquid N_2 , then, 1,3-butadiene was introduced as a liquid, and O_2 was introduced until the pressure reached 2.5 atm. The reaction was conducted at 50 °C for 24 h. After cooling to room temperature, the reaction mixture was analyzed by GC.

3. Result and discussion

3.1 Characterization

HAADF-STEM observation revealed that Pd nanoparticles (NPs) were highly dispersed on TiO_2 (supplementary information, Figure S1). The mean diameter was calculated to be 4.6 ± 1.5 nm. In addition, the mean diameters of Pd NPs were 3.6 ± 1.1 nm for $\text{Pd/Al}_2\text{O}_3$ and 2.4 ± 1.0 nm for Pd/ZrO_2 , respectively (Figure S2 and S3). The XRD pattern of Pd/TiO_2 was compared with those of TiO_2 and PdO/TiO_2 (Figure S4). The diffraction peaks of Pd/TiO_2 at 40, 46, and 68° were assigned to (111), (200), and (220) crystalline planes of the face-centered cubic (*fcc*) lattice of Pd (PDF-2

Database, No. 01-087-0645) (Figure S4b). In contrast, only weak broad peaks of PdO were observed in the XRD patterns of PdO/TiO₂, probably due to the small size of PdO and overlapping with TiO₂.

3.2 Synthesis of cinnamyl acetate from allylbenzene

Initially, several organic solvents mixed with AcOH were investigated for allylic C–H acetoxylation of allylbenzene (**1a**) over Pd/C (Table 1). Cinnamyl acetate (**2a**) was determined as the major product and no branched product was formed under these reaction conditions. Higher yield was obtained when the reaction was performed in AcOH/DMSO than those obtained in AcOH mixed with 1,4-dioxane or DMA (entries 1–3). The selectivity of **2a** was slightly decreased when only AcOH was used probably due to the homocoupling of allylbenzene (entry 4). The ratio of AcOH and DMSO was adjusted to 10:1 that enabled a better result than using AcOH/DMSO at 1:1 (entry 5). In entry 6, the product yield was maintained even when the reaction was performed under 1 atm of O₂. Furthermore, the reaction temperature and time were discussed, and the reaction proceeded well at 90 °C for 28 h (entry 7). The yield was decreased in the absence of sodium acetate (entry 8), which was in accordance with Szabó's result that carboxylate salt efficiently promoted the allylic C–H acetoxylation process [6]. In this work, we confirmed that 1 equivalent of sodium acetate was optimum (entry 9). Next, several metal oxide supported Pd catalysts were screened for this process. Among these catalysts, Pd/ZrO₂ showed a poor activity (entry 10). Al₂O₃ supported Pd exhibited good catalytic activity and gave the product in a moderate yield (entry 11). In entry 12, 97% allylbenzene was converted over Pd/TiO₂ catalyst, and cinnamyl acetate was afforded in 81% yield. Several byproducts were determined including β -methyl-styrene (3%) as a substrate isomer, 1-phenylallyl acetate (2%) as a branch selective product, cinnamaldehyde (3%) which was formed by over oxidation, and homo-coupling byproducts (5%) of allylbenzene. TiO₂ supported PdO was also tested, but the yield was significantly decreased (entry 13). Thus, entry 12 was selected as the optimized reaction conditions for further studies.

Table 1. Optimization of reaction conditions for synthesis of cinnamyl acetate from allylbenzene.

Reaction scheme: Allylbenzene (**1a**, 1 mmol) reacts with Catalyst (Pd: 5 mol%), NaOAc (1 equiv.) in Solvent (2.0 mL), O₂ (atm) at 80 °C, 20 h to form Cinnamyl acetate (**2a**).

Entry	Catalyst	Solvent	O ₂ (atm)	Temp. (°C)	Conv. (%) ^a	Yield (%) ^a
1	Pd/C	AcOH: 1,4-dioxane (1:1)	2.5	80	55	19
2	Pd/C	AcOH: DMA (1:1)	2.5	80	64	24
3	Pd/C	AcOH: DMSO (1:1)	2.5	80	73	31
4	Pd/C	AcOH	2.5	80	88	13
5	Pd/C	AcOH: DMSO (10:1)	2.5	80	88	42
6	Pd/C	AcOH: DMSO (10:1)	balloon	80	82	49
7 ^b	Pd/C	AcOH: DMSO (10:1)	balloon	90	95	58
8 ^c	Pd/C	AcOH: DMSO (10:1)	balloon	90	63	34

9 ^d	Pd/C	AcOH: DMSO (10:1)	balloon	90	91	50
10	Pd/ZrO ₂	AcOH: DMSO (10:1)	balloon	90	26	24
11	Pd/Al ₂ O ₃	AcOH: DMSO (10:1)	balloon	90	85	69
12	Pd/TiO ₂	AcOH: DMSO (10:1)	balloon	90	97	81
13	PdO/TiO ₂	AcOH: DMSO (10:1)	balloon	90	23	11

^a The conversion and yield were calculated by GC analysis using tridecane as an internal standard. ^b Reacted for 28 h. ^c Without NaOAc. ^d KOAc was used instead of NaOAc.

3.3 Scope of substrates

To examine the substrate scope of allylic C–H acetoxylation over Pd/TiO₂, several electron-donating or withdrawing group substituted allylbenzenes were tested (Table 2). Methyl and methoxy group substituted substrates tend to be transformed smoothly into the corresponding allylic acetate derivatives (entries 1 and 2). However, when the methoxy group was substituted on the *para* position of allylbenzene, the product selectivity was decreased (entry 3). Several 4-allylanisole dimers were detected in this reaction, indicating that the C–H bonds next to methoxy group are easy to be activated over Pd/TiO₂ and go through an intermolecular cross-coupling process. Fluorine substituted allylbenzene was examined as an electron-withdrawing substrate, and the corresponding allylic acetate was obtained in good yield (entry 4). The catalytic system was also found to be applicable for acetoxylation of aliphatic alkenes, affording the allylic acetates with a small amount of branched products (<1%), although the yield of **2f** was fairly poor (entry 5). Moreover, 1,3-butadiene was used as a substrate for the synthesis of 1,4-diacetoxy-2-butene (**2g**), which is a crucial intermediate for a production of 1,4-butanediol in chemical industry. The product yield was calculated based on O₂, because a large excess amount of 1,3-butadiene and AcOH to O₂ was added. After optimization of the conditions, the reaction proceeded well in an autoclave to give 1,4-diacetoxy-2-butene in 61% and 3,4-diacetoxy-1-butene in 4% yield, respectively (entry 6). This process probably become an alternative method to improve the current 1,4-butanediol synthetic process, because of good selectivity for the linear allylic acetate [21]. In addition, β -methyl styrene, which was detected as an isomer of allylbenzene, exhibited good reactivity to give cinnamyl acetate as well (entry 7). Other internal alkene such as *trans*-2-octene was also tested, while only trace amount of the product was generated (entry 8).

Table 2. Scope of substrates.

$ \begin{array}{c} \text{R}-\text{CH}=\text{CH}_2 \\ (1 \text{ mmol}) \end{array} \xrightarrow[\text{O}_2 \text{ balloon, } 90^\circ\text{C, } 28 \text{ h}]{\begin{array}{c} \text{Pd/TiO}_2 \text{ (Pd 5 mol\%)} \\ \text{NaOAc (1 equiv.)} \\ \text{AcOH:DMSO} = 10:1 \text{ (2.0 mL)} \end{array}} \begin{array}{c} \text{R}-\text{CH}=\text{CH}-\text{CH}_2\text{OAc} \end{array} $			
Entry	Substrates	Products	Yield (%) ^a
1	1b	2b	73

2	1c	2c	68
3	1d	2d	35
4	1e	2e	66
5	1f	2f	12
6 ^b	1g	2g	61 ^c
7	1h	2a	77
8	1i	2f	<1

^a Isolated yield. ^b Reaction conditions: 1,3-butadiene, Pd/TiO₂ (Pd 5 mmol), AcOH/DMSO (2.0 mL, the ratio is 10 : 1), NaOAc (1 mmol), O₂ (2.5 atm), 50 °C for 24 h. ^c The yield was calculated based on O₂, and 4% yield of 3,4-diacetoxy-1-butene was determined as a byproduct.

3.4 Recyclability of Pd/TiO₂

Pd leaching and recyclability of the catalyst were assessed by MP-AES analysis, which indicated that Pd loading was 4.98 wt% in the fresh catalyst and 4.66 wt% in the catalyst after reaction, respectively. Moreover, after removal of the catalyst at 12 h, the yield was determined at 22% and increased to 29% at 24 h. In contrast, the yield could reach to 59% at 24 h without filtration of the catalyst (Figure S5). These results suggested that a small amount of Pd was dissolved in the organic solvent.

Next, the recyclability of Pd/TiO₂ was tested for the transformation of allylbenzene into cinnamyl acetate. The catalyst was filtrated from the reaction mixture, washed with MeOH and CH₂Cl₂ for several times, dried in air at 70 °C overnight, and then used for the next run. Figure 1 demonstrates that the catalyst could be used at least five times without obvious deactivation.

Figure 1. Recyclability of Pd/TiO₂ in the synthesis of cinnmyl acetate from allylbenzene. Reaction conditions: allylbenzene (1 mmol), Pd/TiO₂ (Pd 5 mol%), NaOAc (1 mmol), AcOH/DMSO (10/1, v/v, total 2.0 mL), O₂ balloon, 90 °C, 28 h.

3.5 Mechanism studies

In order to investigate the change of chemical state of Pd during the allylic C–H acetoxylation, Pd K-edge XAFS of the catalysts were measured before and after the reaction. In the X-ray absorption near edge structure (XANES) spectra, compared with Pd foil and PdO, the chemical state of Pd in both fresh and recycled Pd/TiO₂ could be confirmed as Pd⁰ (Figure 2A). Although Shi and co-workers have reported an allylic C–H oxidation process using Pd₂(dba)₃, Pd⁰ should react with di-*tert*-butyldiaziridinone to generate the Pd^{II} complex which was recognized as the active species for further oxidation [27]. In the radial structure functions (RSF), the peaks discernible at 2.0–2.8 Å, which corresponds to the scattering of photoelectrons ejected from Pd atoms as observed in Pd foil, were observed in both fresh and recycled Pd/TiO₂ with similar magnitudes. The interaction of Pd–O or Pd–O–Pd was not detected in Pd/TiO₂ (Figure 2B). These results explained that the chemical state and the particle size did not change after the reaction.

Figure 2. Pd K-edge XANES spectra (A) and Radial structure functions (B) of Pd foil (a), PdO (b), fresh Pd/TiO₂ catalyst (c), the catalyst after allylic C–H acetoxylation reaction (d).

XPS analysis was carried out to investigate the interaction between Pd and TiO₂. As shown in Figure 3, two main peaks were observed from the Pd3d spectrum, and the binding energy values were confirmed at 335.4 eV for Pd3d_{5/2} and 340.8 eV for Pd3d_{3/2}. In contrast to the literature reporting that BE values of Pd⁰ were 335.2 and 340.5 eV for Pd3d_{5/2} and Pd3d_{3/2}, respectively [28], the peaks on Pd/TiO₂ catalyst shifted to higher BE by approximately 0.2 eV. This result indicated that an interaction exists between Pd and TiO₂, and Pd is positively charged on the TiO₂ support. As acetic acid is used as the nucleophilic reagent to react with terminal alkenes, positively charged Pd NPs benefit the adsorption of these organic compounds on the catalyst surface, where the initial step of allylic C–H bond activation is promoted.

Figure 3. XPS spectra of 5 wt% Pd/TiO₂.

Based on several experimental results, we suggest that the allylic acetate products are generated from a π -allyl-Pd intermediate for three reasons. Firstly, cinnamyl acetate was produced as the major product, and 1-phenylallyl acetate was also detected. These compounds could be formed as a result of the nucleophilic attack at the different position of π -allyl-Pd intermediate by AcOH. Also, as discussed in Table 1, β -methyl styrene could be converted into cinnamyl acetate as well, suggesting that the reaction was initially started by activation of allylic C–H bond, and the activity of allylic C–H bond of the substrates affected their reactivity. In addition, 1-phenylpropan-2-one and 1-phenylpropan-1-one, which are recognized as the Wacker oxidation-type products from allylbenzene or β -methyl styrene, were not detected in this reaction. Therefore, the reaction pathway was speculated as follows: (I) positively charged Pd NPs on TiO₂ were oxidized by AcOH and O₂ to form the intermediate **B**; (II) allylic C–H bond of alkenes was activated by the absorbed acetate group to produce the intermediate **C**; through the concerted metalation-deprotonation (CMD) pathway, (III) π -allyl-Pd intermediate was generated after cleavage of C–H bond, and (IV) another molecule of AcOH was served as a nucleophile to attack the terminal position of π -allyl-Pd intermediate, and the absorbed acetate group was

desorbed from the catalyst simultaneously as AcOH; (V) the product was generated after leaving the catalyst surface (Figure 4). Alternatively, due to the difficulty to observe the intermediates in a heterogeneous catalytic system and large size of Pd NPs expressed good catalytic activity, the direct activation of allylic C–H bond of terminal alkenes could not be fully excluded (Figure S5).

Figure 4. Suggested reaction pathway for allylic C–H acetoxylation.

4. Conclusion

The allylic C–H bond acetoxylation of terminal alkenes to synthesize cinnamyl acetates has been developed over a heterogeneous Pd catalytic system with O₂ as the sole oxidant. Using transformation of allylbenzene into cinnamyl acetate as a model reaction, TiO₂ supported Pd NPs gave selectively the corresponding linear allylic acetates up to 81% yield with good catalyst recyclability. Moreover, this synthetic protocol enabled acetoxylation of several terminal alkenes, in particular for 1,3-butadiene, which is a crucial material in petrochemical industry. For the mechanistic studies, XPS analysis confirmed that Pd NPs were positively charged on TiO₂, and XAFS measurements proved that the oxidation process was catalyzed by Pd⁰ NPs. This work is expected to be a good initiation to enlarge the applications of supported transition metal catalysts in oxidation reactions under environmentally friendly conditions.

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References

- [1] A. N. Campbell, S. S. Stahl, *Acc. Chem. Res.*, 45 (2012) 851–863.
- [2] J.-Q. Yu, Z. Shi, *Topics in Current Chemistry: C-H activation*, Springer-Verlag Berlin Heidelberg 2010.
- [3] A. N. Campbell, P. B. White, I. A. Guzei, S. S. Stahl, *J. Am. Chem. Soc.*, 132 (2010) 15116–15119.
- [4] T. Mitsudome, T. Umetani, N. Nosaka, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *Angew. Chem. Int. Ed.* 45 (2006) 481–485.
- [5] M. S. Chen, M. C. White, *J. Am. Chem. Soc.*, 126 (2004) 1346–1347.
- [6] L. T. Pilarski, N. Selander, D. Böse, K. J. Szabó, *Org. Lett.*, 11 (2009) 5518–5521.
- [7] H. Grennberg, A. Gogoll, J. E. Bäckvall, *J. Org. Chem.*, 56 (1991) 5808–5811.
- [8] T. Diao, S. S. Stahl, *Polyhedron*, 84 (2014) 96–102.
- [9] W. H. Henderson, C. T. Check, N. Proust, J. P. Stambuli, *Org. Lett.*, 12 (2010) 824–827.
- [10] J. E. Bercaw, N. Hazari, J. A. Labinger, P. F. Oblad, *Angew. Chem. Int. Ed.*, 47 (2008) 9941–9943.
- [11] B. L. Lin, J. A. Labinger, J. E. Bercaw, *Can. J. Chem.*, 87 (2009) 264–271.
- [12] R. C. Larock, T. R. Hightower, L. A. Hasvold, K. P. Peterson, *J. Org. Chem.*, 61 (1996) 3584–3585.
- [13] H. Grennberg, J. E. Bäckvall, *Chem. Eur. J.*, 4 (1998) 1083–1089.
- [14] C. Jia, P. Müller, H. Mimoun, *J. Mol. Catal. A: Chem.*, 101 (1995) 127–136.
- [15] S. Hansson, A. Heumann, T. Rein, B. Åkermark, *J. Org. Chem.*, 55 (1990) 975–984.
- [16] R. Alam, L. T. Pilarski, E. Pershagen, K. J. Szabó, *J. Am. Chem. Soc.*, 134 (2012) 8778–8781.
- [17] C. P. Vinod, K. Wilson, A. F. Lee, *J. Chem. Technol. Biotechnol.*, 86 (2011) 167–171.
- [18] J. Tsuji, *Synthesis*, (1990) 739–749.
- [19] R. D. Ashford, *Ashford's dictionary of industrial chemicals*, 3rd Ed., Wavelength: London, 2011.
- [20] Mitsubishi Kasei Corporation, *Chemtech*, (1988) 759
- [21] N. I. Kuznetsova, V. N. Zudin, L. I. Kuznetsova, V. I. Zaikovskii, H. Kajitani, M. Utsunomiya, K. Takahashi, *Appl. Catal. A: Gen.*, 513 (2016) 30–38.
- [22] T. Ishida, R. Tsunoda, Z. Zhang, A. Hamasaki, T. Honma, H. Ohashi, T. Yokoyama, M. Tokunaga, *Appl. Catal. B: Environ.*, 150–151 (2014) 523–531.
- [23] Z. Zhang, T. Hashiguchi, T. Ishida, A. Hamasaki, T. Honma, H. Ohashi, T. Yokoyama, M. Tokunaga, *Org. Chem. Front.*, 2 (2015) 654–660.
- [24] T. Honma, H. Oji, S. Hirayama, Y. Taniguchi, H. Ofuchi, M. Takagaki, *AIP Conf. Proc.*, 1234 (2010) 13–16.
- [25] H. Oji, Y. Taniguchi, S. Hirayama, H. Ofuchi, M. Takagaki, T. Honma, *J. Synchrotron Rad.*, 19 (2012) 54–59.
- [26] B. Ravel, M. Newville, *J. Synchrotron Rad.*, 12 (2005) 537–541.
- [27] B. Wang, H. Du, Y. Shi, *Angew. Chem. Int. Ed.*, 47 (2008) 8224–8227.
- [28] Y. He, J. Fan, J. Feng, C. Luo, P. Yang, D. Li, *J. Catal.*, 331 (2015) 118–127.

Table 1. Optimization of reaction conditions for synthesis of cinnamyl acetate from allylbenzene.

Entry	Catalyst	Solvent	O ₂ (atm)	Temp. (°C)	Conv. (%) ^a	Yield (%) ^a
1	Pd/C	AcOH: 1,4-dioxane (1:1)	2.5	80	55	19
2	Pd/C	AcOH: DMA (1:1)	2.5	80	64	24
3	Pd/C	AcOH: DMSO (1:1)	2.5	80	73	31
4	Pd/C	AcOH	2.5	80	88	13
5	Pd/C	AcOH: DMSO (10:1)	2.5	80	88	42
6	Pd/C	AcOH: DMSO (10:1)	balloon	80	82	49
7 ^b	Pd/C	AcOH: DMSO (10:1)	balloon	90	95	58
8 ^c	Pd/C	AcOH: DMSO (10:1)	balloon	90	63	34
9 ^d	Pd/C	AcOH: DMSO (10:1)	balloon	90	91	50
10	Pd/ZrO ₂	AcOH: DMSO (10:1)	balloon	90	26	24
11	Pd/Al ₂ O ₃	AcOH: DMSO (10:1)	balloon	90	85	69
12	Pd/TiO ₂	AcOH: DMSO (10:1)	balloon	90	97	81
13	PdO/TiO ₂	AcOH: DMSO (10:1)	balloon	90	23	11

^a The conversion and yield were calculated by GC analysis using tridecane as an internal standard. ^b Reacted for 28 h. ^c Without NaOAc. ^d KOAc was used instead of NaOAc.

Table 2. Scope of substrates.

$ \begin{array}{c} \text{Pd/TiO}_2 \text{ (Pd 5 mol\%)} \\ \text{NaOAc (1 equiv.)} \\ \text{AcOH:DMSO = 10:1 (2.0 mL)} \\ \text{O}_2 \text{ balloon} \\ 90^\circ\text{C, 28 h} \end{array} \xrightarrow{\hspace{1cm}} $			
Entry	Substrates	Products	Yield (%) ^a
1	1b	2b	73
2	1c	2c	68
3	1d	2d	35
4	1e	2e	66
5	1f	2f	12
6 ^b	1g	2g	61 ^c
7	1h	2a	77
8	1i	2f	<1

^a Isolated yield. ^b Reaction conditions: 1,3-butadiene, Pd/TiO₂ (Pd 5 mmol), AcOH/DMSO (2.0 mL, the ratio is 10 : 1), NaOAc (1 mmol), O₂ (2.5 atm), 50 °C for 24 h. ^c The yield was calculated based on O₂, and 4% yield of 3,4-diacetoxy-1-butene was determined as a byproduct.

Figure 1. Recyclability of Pd/TiO₂ in the synthesis of cinnmyl acetate from allylbenzene. Reaction conditions: allylbenzene (1 mmol), Pd/TiO₂ (Pd 5 mol%), NaOAc (1 mmol), AcOH/DMSO (10/1, v/v, total 2.0 mL), O₂ balloon, 90 °C, 28 h.

Figure 2. Pd K-edge XANES spectra (A) and Radial structure functions (B) of Pd foil (a), PdO (b), fresh Pd/TiO₂ catalyst (c), the catalyst after allylic C–H acetoxylation reaction (d).

Figure 3. XPS spectra of 5 wt% Pd/TiO₂.

Figure 4. Suggested reaction pathway for allylic C-H acetoxylation.