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Short communication

Allylic C–H acetoxylation of terminal alkenes over TiO_2 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 TiO_2 supported Pd nanoparticles (NPs) has been developed, in which O_2 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 Pd^0 NPs. Additionally, XPS analysis of the catalyst confirms the interaction between Pd and TiO_2, which probably promote the initial catalytic procedure.

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 Pd^0 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 $Pd(OAc)_2$ 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 $Pd(OH)_2$ 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

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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), γ-Al_2O_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 used were 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 Kα radiation source ($\lambda = 0.154178$ nm) at a scanning rate of 20°/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 Kα anode. The calibration peak is C1s at 283.6 eV. Palladium loading of the catalysts was 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 μm 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

2.3.1. 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.

2.3.2. 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

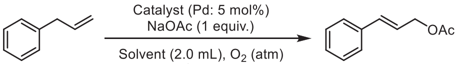
3.1. Characterization

HAADF-STEM observation revealed that Pd nanoparticles (NPs) were highly dispersed on TiO_2 (supplementary information, Fig. 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 Pd/Al_2O_3 and 2.4 ± 1.0 nm for Pd/ZrO_2, respectively (Figs. S2 and S3). The XRD pattern of Pd/TiO_2 was compared with those of TiO_2 and PdO/TiO_2 (Fig. 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) (Fig. S4b). In contrast, only weak broad peaks of PdO were observed in the XRD patterns of PdO/TiO_2, probably due to the small size of PdO and overlapping with TiO_2.

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), and cinnamyl acetate (**2a**) was determined as the major product. 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 gave 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 O_2. 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/ZrO_2 showed a

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



1a (1 mmol) **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_2O_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.