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Palladium(II) Supported by Hydrotalcite[Pd(II)-Hydrotalcite]-Catalyzed Selective Oxidation of Alcohols Using Molecular Oxygen

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Novel heterogenized Pd catalyst, palladium supported by hydrotalcite[Pd(II)-hydrotalcite], has been synthesized. The catalyst is found to be effective for the oxidation of a wide range of alcohols using molecular oxygen as a sole oxidant. In this catalytic system, various alcohols are readily converted to the corresponding aldehydes or ketones selectively in high to excellent yields. It is noteworthy that the catalyst is also applicable to the oxidation of unsaturated alcohols such as geraniol and nerol without any isomerization of an alkenic part. Another characteristic property of this heterogeneous catalyst is that a shape selectivity depending on the structure of alcohols is observed in some extent. The catalyst has also advantages such as ease of handling, easy preparation, and reusability for several times without appreciable loss of the catalytic activity.

Introduction

The increasing environmental and economical concerns let chemists to develop the clean and high-performance catalytic reaction. Especially, much attention has been paid for the heterogeneous or heterogenized catalysts [1,2] because of their unique properties such as reusability and molecular recognition effect. For example, the application of these catalysts for aerobic oxidation of alcohols is an interesting target for many chemists. Immobilization of transition metal salts to various kinds of supports such as activated carbon, alumina, silica, clays and polymers is an important method to produce such effective heterogeneous catalysts. For recent examples, the aerobic oxidation of alcohols was successfully carried out using heterogenized catalysts such as polymer- or mesoporous solid MCM-41-supported TPAP (tetrapropylammonium perruthenate) [3,4] and TiO_2-supported palladium cluster [5b,c]. Ruthenium doped hydrotalcites (layered basic clay minerals) were also reported as efficient heterogeneous catalysts for the oxidation of alcohols under O_2[6]. Recently, we reported the oxidation of alcohols using a homogeneous palladium catalyst under atmospheric pressure of oxygen [7], and also succeeded in the immobilization of the homogeneous palladium catalyst on hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$) and its application for aerobic oxidation of alcohols [8]. In this paper we describe details of this aerobic oxidation using Pd(II)-hydrotalcite as catalyst [9].

Results and Discussion

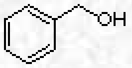
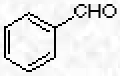
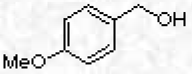
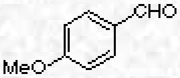
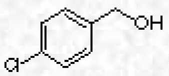
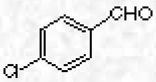
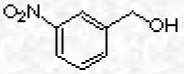
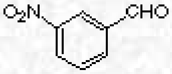
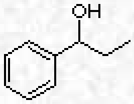
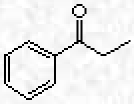
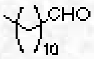
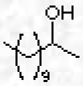
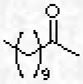
Preparation and Characterization of Pd(II)-Hydrotalcite.

Pd(II)-hydrotalcite was prepared by mixing $Pd(OAc)_2$ (1.67 mmol), pyridine (4.18 mmol) and hydrotalcite (10.0 g) in toluene (100 mL) at 80°C for 1 h, followed by filtration, washing, and drying under vacuum at room temperature. In this process $Pd(OAc)_2 \cdot (py)_2$ complex [10] was initially formed and then it was adsorbed on the hydrotalcite support. The Pd content in the Pd(II)-hydrotalcite was 0.16 mmol g^{-1} estimated by inductively coupled plasma (ICP) atomic emission spectrometry. Hydrotalcite has a layered structure consisting of positively charged brucite-like layers and negatively charged counter ions and water molecules located in the interlayers [11]. Thus, we first investigated the spacing between layers of newly prepared Pd(II)-hydrotalcite. Spacing (d_{003}) of both commercially available hydrotalcite and the Pd(II)-hydrotalcite was estimated to be almost the same by X-ray diffraction (XRD) analysis. These results suggest that the palladium salt does not exist between brucite layers by an anion exchange. The possibility of the substitution of any cations in brucite layers by the palladium salt is also low because of a stable structure of the brucite. So, we postulated that the palladium salt is located on the external surface of thin plates-like crystals of hydrotalcite (not between layers). For the purpose of confirming our assumption and disclosing the dispersion state of the palladium salt, the Pd(II)-hydrotalcite was analyzed by transmission electron microscopy (TEM). At low magnification, a number of small particles were observed on the plates-like crystals of the hydrotalcite. However, because of severe dehydration of hydrotalcite by irradiation of electron beam, the high magnification image of surface morphology of Pd(II)-hydrotalcite could not be obtained. Next, we attempted to investigate the presence of pyridine in Pd(II)-hydrotalcite. Elemental analysis showed that 0.35% of N atom was contained in Pd(II)-hydrotalcite, which was quite close to a theoretical percentage of nitrogen (0.45% calculated from the result of ICP atomic emission analysis, assuming that Pd atoms exist in the $Pd(OAc)_2 \cdot (py)_2$ form in Pd(II)-hydrotalcite). Further evidence of the existence of pyridine in Pd(II)-hydrotalcite was obtained by thermogravimetry / mass spectrometry (TG/MS) analysis. MS peak of pyridine ($m/z = 79$) desorbed from Pd(II)-hydrotalcite was observed at around 160°C [12]. We also carried out control experiments to rule out the possibility of adsorption of pyridine on hydrotalcite; that is, another sample was prepared by treating hydrotalcite only with pyridine in toluene and by washing the resultant solid in the same way as in the preparation of Pd(II)-hydrotalcite. In this sample, pyridine was not detected by elemental analysis and TG/MS. These results suggest that pyridine exists as a ligand on palladium in Pd(II)-hydrotalcite. Thus, we concluded that the palladium-pyridine complex was immobilized on the external surface of brucite layers of Pd(II)-hydrotalcite [13].

Pd(II)-Hydrotalcite-Catalyzed Oxidation of Alcohols.

The oxidation of alcohols was performed as follows: Pd(II)-hydrotalcite (300 mg, Pd: ca. 5 mol%), alcohol (1.0 mmol) and pyridine (0.2 mmol) were mixed in toluene and the mixture was stirred at 80°C under atmospheric pressure of oxygen [14]. The results of the oxidation of primary and secondary alcohols were shown in Table 1. In the oxidation of primary benzylic alcohols, substrates were consumed within 2 h to afford the corresponding aldehydes in high yields (Table 1, Entries 1-3), irrespective of the presence of either an electron-donating substituent (entry 2) or an electron-withdrawing substituent (entry 3). However, 3-nitrobenzyl alcohol yielded the corresponding aldehyde in a slightly lower yield (69%) in spite of high conversion of the alcohol. Secondary benzylic alcohol was also converted to the corresponding ketone in excellent yield (Entry 5), although an excess pyridine (1 mmol) was needed for sufficient reaction without loss of a catalytic activity. Non-activated primary and secondary aliphatic alcohols were also transformed into the corresponding carbonyl compounds using Pd(II)-hydrotalcite, although reactions were relatively slow (Entries 6-8). The reaction rate of secondary alcohols was lower than that of primary ones.

Table 1. Pd(II)-Hydrotalcite-Catalyzed Oxidation of Alcohols by Molecular Oxygen[a]

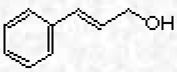
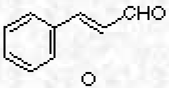
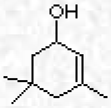
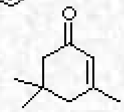
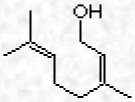
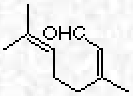
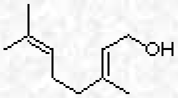
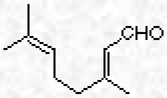
Entry	Substrate	Product	Reaction time (h)	Conversion (%)	Isolated Yield(%)
1			2	100	quant.[b]
2			2	98	92
3			2	97	90
4			2	84	69
5[d]			3	98	95
6			6	97	86
7[d]			11	100	93
8[d]			11	100	92

[a] Pd-hydrotalcite (300 mg, ca. 5 mol%), alcohol (1.0 mmol), pyridine (0.2 mmol), toluene (10 mL), 80 °C, O_2. [b] GLC yield. [c] The reaction was performed in the absence of pyridine. [d] Pyridine (1 mmol) was used.

Oxidation of Unsaturated Alcohols.

The oxidation of alkenic alcohols using both Pd(II)-hydrotalcite system and $Pd(OAc)_2$ / pyridine / MS3A system (homogeneous catalytic system; abbreviated as MS-system) [7b] was performed for comparison, and the results were summarized in Table 2. In the oxidation of alkenic alcohols, a quite excess of pyridine (25 times as much as a standard condition) was necessary to complete the reaction. The excess of pyridine may prevent the complexation of Pd(II)-intermediates with an alkenic moiety which might accelerate the reduction of Pd(II) [15]. When the oxidation of cinnamyl alcohol using both catalytic systems was compared, Pd(II)-hydrotalcite system showed a slightly higher activity than MS-system to give cinnamaldehyde in 95% isolated yield (Entry 1). In the oxidation of a secondary allylic alcohol, a similar trend was observed (Entry 2). Alkenic alcohols such as 10-undecen-1-ol could also be smoothly oxidized to give the corresponding aldehyde in good yield without affecting the alkenic moieties (Entry 3). Next, the oxidation of nerol [(*Z*)-isomer] and geraniol [(*E*)-isomer] was carried out. Using MS-system, the yields of aldehydes were low (39 and 56%, respectively) and *E*/*Z* ratios of the products were seriously disturbed (*E*/*Z* ratios were 31/69 and 63/37, respectively) [16]. On the other hand, Pd(II)-hydrotalcite-catalyzed reaction smoothly proceeded to give the corresponding aldehydes in 89% and 91% yields without any geometrical isomerization (*E*/*Z* ratios were 6/94 and 96/4) (Entries 4 and 6). Further, under these conditions reaction rates dramatically increased using Pd(II)-hydrotalcite. It is well known that a Pd(II) species is generally not the effective catalysts for oxidation of allylic alcohols because of its strong complexation with unsaturated carbon-carbon bonds [9a]. Recently, such drawbacks in palladium chemistry have been overcome and some good examples have been reported on palladium-catalyzed oxidation of allylic alcohols into the corresponding aldehydes or ketones [5,9e,f]. Our results also provide a good method for the selective aerobic oxidation of allylic alcohols [17]. Although the reason for preservation of the *E*/*Z* geometry in products in the case of Pd(II)-hydrotalcite system was not yet clear, the complexation of the palladium species with the alkenic part may be inhibited because of the steric bulkiness of hydrotalcite surface.

Table 2. Pd(II)-Hydrotalcite or Pd(OAc)$_2$ / Pyridine / MS3A System-Catalyzed Oxidation of Alkenic Alcohols by Molecular Oxygen[a]

Entry	Substrate	Product	Pd(II)-hydrotalcite system[b]		Pd(OAc)$_2$ / pyridine / MS3A system[c]	
			Time (h)	Isolated yield (%)[d]	Time (h)	Isolated yield (%)[d]
1			3	95 (100)	4	91 (96)
2[e]			3	96 (100)	4	87 (100)
3			8	93 (100)	17	91 (95)
4[f]	 *E*/*Z* = 2/98		4.5	89 (100) *E*/*Z* = 6/94	15	39 (71) *E*/*Z* = 31/69
5[f g]	 *E*/*Z* = 98/2		12	45 (58) *E*/*Z* = 95/5		
6[f]			4.5	91 (98) *E*/*Z* = 96/4	15	56 (76) *E*/*Z* = 63/37

[a] Reaction conditions: alcohol (1.0 mmol), pyridine (5.0 mmol), toluene (10 mL), O$_2$, 80 °C. [b] Pd(II)-hydrotalcite (300 mg, ca. 5 mol% Pd). [c] Pd(OAc)$_2$ (0.05 mmol), MS3A (500 mg). [d] The value in parentheses is the conversion of the alcohol (%). [e] GLC yield. [f] *E*/*Z* ratio was determined by ^{1}H NMR. [g] Pyridine (0.2 mmol) was used.

Recycle of the Catalyst.

Pd(II)-hydrotalcite can be easily separated from the reaction mixture by simple filtration after the reaction. The recovered Pd(II)-hydrotalcite could be reused for the next oxidation (Table 3), although a slight decrease of the catalytic activity was observed in the third use of Pd(II)-hydrotalcite for the oxidation of benzyl alcohol (Table 3, Entry 1; first: 98%, second: 89%, third: 77%). In order to prevent this deactivation of the catalyst, another Pd(II)-hydrotalcite [Pd(II)-hydrotalcite*, Pd: 0.092 mmol g^{-1} (estimated by ICP atomic emission analysis): ca. a half amount of Pd content compared with the so far described Pd(II)-hydrotalcite] was prepared by a similar method. It was eventually disclosed that Pd(II)-hydrotalcite* could be reused without an appreciable loss of the catalytic activity in the same reaction (Entry 2; first: 96%, second: 97%, third: 90%). With Pd(II)-hydrotalcite* the oxidation of 4-methoxybenzyl alcohol giving 4-methoxybenzaldehyde proceeded well even at fourth time using (Entry 3; first: 84%, second: 88%, third: 84%, fourth: 85%).

Possible reasons of the deactivation of the catalysts (especially in the case Pd(II)-hydrotalcite) might be due to 1) leaching of Pd(II) salt and 2) reduction of an active Pd(II) species to Pd(0). In order to clarify whether Pd(II) salt leaches or not under the reaction conditions, we carried out the following experiment. That is, the oxidation of benzyl alcohol using Pd(II)-hydrotalcite was allowed to proceed for 30 min, and the catalyst was filtered at 80°C. Then, the filtrate containing the product benzaldehyde and the unreacted benzyl alcohol was stirred under O_2 at 80°C. As a result, it was revealed that the leaching of a small amount of Pd(II) salt from Pd(II)-hydrotalcite occurred [a further conversion of benzyl alcohol to benzaldehyde (ca. 9%) was observed after 21 h]. In contrast, using Pd(II)-hydrotalcite* in the same experiment, such further oxidation did not proceed even after 24 h. These results showed that the leaching of Pd can be diminished by decreasing the amount of Pd complex supported.

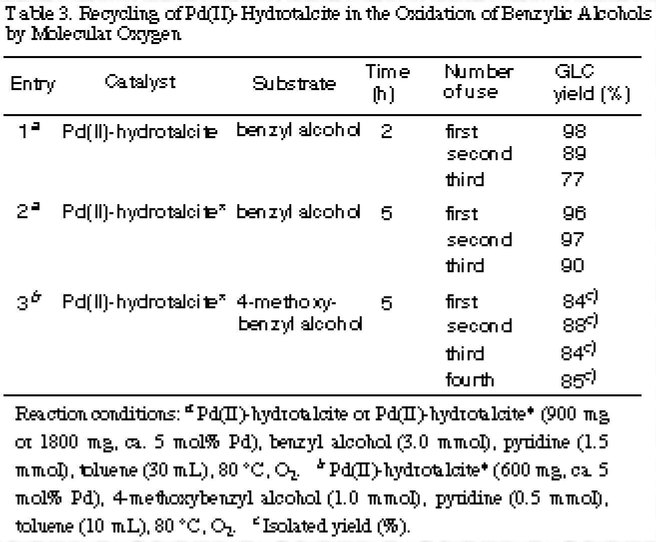


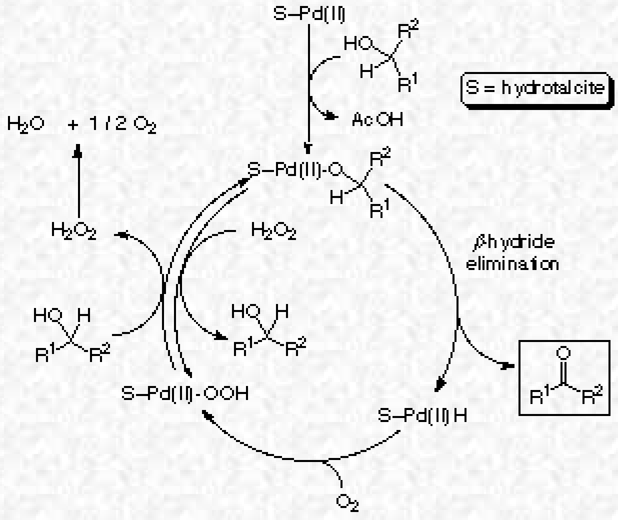
Table 3. Recycling of Pd(II)-Hydrotalcite in the Oxidation of Benzylic Alcohols by Molecular Oxygen

Entry	Catalyst	Substrate	Time (h)	Number of use	GLC yield (%)
1[a]	Pd(II)-hydrotalcite	benzyl alcohol	2	first	98
				second	89
				third	77
2[a]	Pd(II)-hydrotalcite*	benzyl alcohol	5	first	96
				second	97
				third	90
3[b]	Pd(II)-hydrotalcite*	4-methoxy-benzyl alcohol	5	first	84[c]
				second	88[c]
				third	84[c]
				fourth	85[c]

Reaction conditions: [a] Pd(II)-hydrotalcite or Pd(II)-hydrotalcite* (900 mg or 1800 mg, ca. 5 mol% Pd), benzyl alcohol (3.0 mmol), pyridine (1.5 mmol), toluene (30 mL), 80 °C, O_2. [b] Pd(II)-hydrotalcite* (600 mg, ca. 5 mol% Pd), 4-methoxybenzyl alcohol (1.0 mmol), pyridine (0.5 mmol), toluene (10 mL), 80 °C, O_2. [c] Isolated yield (%).

Reaction Scheme.

We propose a plausible reaction pathway illustrated in Scheme 1 for the oxidation of alcohols in this system, the pathway being intrinsically the same as proposed in homogeneous system [7b].



Scheme 1. Plausible Reaction Pathway

Conclusion

Pd(II)-hydrotalcite was newly prepared by simple operation from commercially available hydrotalcite, $Pd(OAc)_2$ and pyridine. This novel clay compound efficiently catalyzed the aerobic oxidation of various kinds of alcohols including unsaturated ones. This catalyst could be reused for several times keeping its catalytic activity.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were measured on JEOL EX-400, JNM-AL300, and JEOL GSX-270 spectrometers for solutions in $CDCl_3$ with Me_4Si as an internal standard. GLC analyses were carried out with a Shimadzu GC-14A instrument (2 m × 3 mm glass column packed with 5% OV®-17 on Chromosorb® W, 5.0 mm film thickness and Shimadzu fused silica capillary column (HiCap CBP10-S25-050) using helium as a carrier gas. GLC yields were determined using bibenzyl, cyclododecanone or pentamethylbenzene as internal standards. Analytical thin layer chromatographies (TLC) were performed with Merck silica gel 60 F-254 plates. Column chromatographies were performed with Merck silica gel 60. XRD data were obtained on a Shimadzu XD-D1 diffractometer using Cu Ka radiation and a carbon monochrometer. IR spectra were recorded with a Nicolet Impact 400 FT-IR spectrometer. UV spectra were analyzed with a Shimadzu MSP 200 spectrophotometer equipped with diffuse-reflectance unit. CP-MAS ^{13}C NMR spectra were measured on a JEOL GSX-270 spectrometer with pentamethylbenzene as an external standard. TEM analysis was performed by a Hitachi H 800 transmission electron microscope. TG/MS analysis was done with a Shimadzu QP 1000 mass spectrometer equipped with a Shimadzu TG-50 thermogravimeter. TG-DTA data were obtained with a Shimadzu TG-50A thermal analyzer. ICP atomic emission analysis for leaching of Pd was performed with a Shimadzu ICPS-1000 sequential plasma spectrometer.

Materials. $Pd(OAc)_2$ was purchased from Wako Pure Chemical Ind., Ltd., and used without further purification. Hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, brand name KYOWAAD®500) was kindly supplied by Kyowa Chemical Ind., Ltd. Pyridine was purchased and used without further purification. Toluene was distilled before use. MS3A powder was commercially available from Nacalai Tesque Chemical Co., Inc., which was activated by calcination (by a gas burner) just before use

General Procedure for Preparation and Characterization of Pd(II)-Hydrotalcite. To a mixture of $Pd(OAc)_2$ (375 mg, 1.67 mmol) and toluene (100 mL) in a 200 mL two-necked flask was added pyridine (331 mg, 4.18 mmol) at 80°C. The brown suspension turned to a yellow-white suspension when pyridine was added. Hydrotalcite (KYOWAAD®500, 10.0 g) was added and the mixture was stirred vigorously for 1 h at 80°C. Then, the resulting slurry was cooled to 0°C, followed by filtration and washing with diethyl ether (2 × 20 mL). The resulting solid was dried under vacuum at room temperature to give ca. 10 g of a light-yellow powder of Pd(II)-hydrotalcite. The Pd content in the Pd(II)-hydrotalcite was 0.16 mmol g^{-1} estimated by ICP atomic emission analysis. Elemental analysis; Pd(II)-hydrotalcite; N, 0.35% [Calcd. N, 0.45% calculated from the result of ICP emission analysis, assuming that Pd atoms exist in the $Pd(OAc)_2 \cdot (Py)_2$ form in Pd(II)-hydrotalcite]. The values of atomic spacing d003 were estimated by XRD analysis as follows: commercially available hydrotalcite, 7.81Å; Pd(II)-hydrotalcite, 7.75Å. Pd(II)-hydrotalcite* was prepared by a similar method as described above using a half scale of $Pd(OAc)_2$ (188 mg), pyridine (165 mg), and toluene (50 mL) with 10 g of hydrotalcite. The Pd content in the

Pd(II)-hydrotalcite* was 0.092 mmol g^{-1} estimated by ICP atomic emission analysis.

General Procedure for Pd(II)-Hydrotalcite or Pd(II)-Hydrotalcite*-Catalyzed Oxidation of Alcohols Using Molecular Oxygen. A typical experimental procedure is as follows: to a suspension of the Pd(II)-hydrotalcite (300 mg, ca. 5 mol% as Pd) or Pd(II)-hydrotalcite* (600 mg, ca. 5 mol% as Pd) in toluene (6 mL) in a 20 mL two-necked flask was added pyridine (0.2-5 mmol) and the mixture was stirred. Then, oxygen gas was introduced into the flask from an O_2-balloon under atmospheric pressure, and the mixture was heated to 80°C for ca. 10 min. Next, an alcohol (1 mmol) in toluene (4 mL) was added and the mixture was stirred vigorously for 2 h (or appropriate time) at 80°C under oxygen. After the reaction, the catalyst was separated by filtration through a glass filter. Removal of the solvent from the filtrate under the reduced pressure left an oily residue which was subjected to column chromatography (Merck silica gel 60; eluents, hexane-diethyl ether) to give a product. Products obtained were determined by ^{1}H and ^{13}C NMR and GC/MS.

General Procedure for $Pd(OAc)_2$ / Pyridine / MS3A System-Catalyzed Oxidation [7b] of Unsaturated Alcohols Using Molecular Oxygen. An improved procedure for the oxidation of unsaturated alcohols using homogeneous catalyst is as follows: to a suspension of the $Pd(OAc)_2$ (11.2 mg 0.05 mmol) in toluene (4 mL) in a 20 mL two-necked flask were added pyridine (5 mmol) and MS3A (500 mg), and the mixture was stirred at room temperature. Then, oxygen gas was introduced into the flask from an O_2-balloon under atmospheric pressure. Next, an alcohol (1 mmol) in toluene (6 mL) was added at room temperature and the mixture was heated to 80°C and stirred vigorously for appropriate time under oxygen.

General Procedure for Recycling of the Catalyst. First run of the oxidation of benzyl alcohol catalyzed by Pd(II)-hydrotalcite or Pd(II)-hydrotalcite* was performed using the same procedure described above. Recovered Pd(II)-hydrotalcite or Pd(II)-hydrotalcite* was washed with diethyl ether (2 × 20 mL) and dried under vacuum at room temperature before use for the next run. The method of the test for Pd-leaching was as follows; the usual oxidation of benzyl alcohol was allowed to proceed for 30 min, and the catalyst was filtered at 80°C. Then, the filtrate containing the product benzaldehyde and the unreacted benzyl alcohol was stirred under O_2 at 80°C. The reaction was monitored with GLC using cyclododecane as an internal standard.

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(See ref. 5c).

14 The presence of an excess pyridine (to palladium) is essential for maintaining the oxidation state of Pd(II). The absence of additional pyridine might cause the formation of Pd(0) species, resulting in a low catalytic activity. Actually, the color of the powder of the recovered catalyst changed from yellow-white to gray after the reaction without a further addition of pyridine, while such color change was not observed in the reaction with additional pyridine.

15 We suppose that the present reaction proceeds in a similar pathway to the homogeneous catalytic system as previously described (See, ref. 7b). Thus, pyridines coordinate to Pd(II) as ligands and stabilize the Pd(II)-hydride species to avoid the reductive elimination of HX from HPdX species to give Pd(0).

16 In our previous report (ref. 7b), we failed the oxidation of geraniol in $Pd(OAc)_2$ / pyridine / MS3A system. However, this limitation could be overcome by slightly improving the procedure. See experimental section.

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