Pd(II)-Hydrotalcite-Catalyzed Oxidation of Alcohols to Aldehydes and Ketones Using Atmospheric Pressure of Air

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A heterogenized Pd catalyst, Pd(II)—hydrotalcite (palladium(II) acetate—pyridine complex supported by hydrotalcite) catalyzes the aerobic oxidation in toluene of a variety of primary and secondary alcohols into the corresponding aldehydes and ketones in high yields using *atmospheric pressure of air* as a sole oxidant under mild conditions. This catalyst is also effective for the oxidation of allylic alcohols, especially such as geraniol and nerol, without any isomerization of an alkenic part. The catalyst can be easily prepared from all commercially available reagents and reused several times.

Introduction

Oxidation of alcohols to the corresponding aldehydes or ketones is one of the most fundamental reactions in organic chemistry.¹ Many effective reaction systems have been developed using a stoichiometric amount of chromium salts² or other oxidants such as oxalyl chloride³ and hypervalent iodines.⁴ Although these traditional procedures are quite useful in laboratory-scale reactions, the waste of heavy metals or stoichiometric reagents and the generation of undesirable coproducts damage the environment seriously in bulk-scale reaction. From the standpoint of the so-called green and sustainable chemistry, another approach to construct the cleaner catalytic system for this reaction has been demanded. Recently, metal-catalyzed oxidation of alcohols using clean and cheap oxidants such as H₂O₂,⁵ O₂, and/or air has been investigated. Especially, air is the most suitable oxidant because it is safe, clean, and available free. Metalcatalyzed aerobic oxidation of alcohols is regarded as the most attractive and ideal technology considering its atomefficiency, and many procedures using metal catalysts such as Ru,⁶ Pd,⁷ Co,⁸ Cu,⁹ Pt,¹⁰ Rh,¹¹ V,¹² Os,¹³ Ce,¹⁴ and Ni¹⁵ have so far been reported. However, the utilities of atmospheric pressure of air are still limited in most of these aerobic oxidation systems, where pure oxygen or a high pressure of air under severe reaction conditions was generally required in order to maintain the activity of the metal catalysts, and even in the rare example using

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atmospheric pressure of air a relatively narrow range of substrates such as benzylic alcohols could be oxidized.^{16,17} For example, Sheldon et al. reported a quite sophisticated catalytic system for oxidation of alcohols in water using palladium salt as a catalyst and air as a sole oxidant, where the oxidation was performed at 100 °C under 30 bar pressure of air.^{7j} Recently, we have reported that the combination of Pd(OAc)₂/pyridine/MS3A could catalyze the aerobic oxidation of alcohols using pure oxygen.¹⁸ This novel homogeneous oxidation system was also expanded to palladium-reusable system using а clay

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as a support.¹⁹ Thus, palladium(II) acetate-pyridine complex was found to be easily supported by hydrotalcite (Mg₆Al₂(OH)₁₆CO₃•4H₂O, basic clay mineral)²⁰ to give a heterogeneous palladium catalyst (abbreviated as Pd(II)hydrotalcite).^{19a,b} For the purpose of constructing "greener" oxidation system, we investigated the Pd(II)-hydrotalcite-catalyzed oxidation of alcohols using atmospheric pressure of air instead of pure molecular oxygen. The successful result of this catalytic reaction is described in this paper.

Results and Discussion

Optimization of Reaction Conditions. First, the oxidation of benzyl alcohol using previously reported homogeneous and heterogeneous Pd(II)-catalytic sys $tems^{1\overline{8},19a,b}$ was performed under atmospheric pressure of air in balloon (Table 1). In Pd(OAc)₂/pyridine or Pd-(OAc)₂/pyridine/MS3A system (homogeneous system), benzaldehyde was obtained in good yield within 3 h (Table 1, entries 1 and 2), and Pd(II)-hydrotalcite system gave the best result (98% yield, entry 3). Furthermore, the recovered catalyst could be used for further reaction (90% yield).

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Table 1. Pd-Catalyzed Oxidation of Benzyl Alcohol under 1 Atm Air^a

	ОН	5 mol% Pd-ca 20 mol% pyrie	at. dine	~СНО
	(1 mmol)	toluene (10 m 65 °C, 3 h, ai	nL) r (1 atm)	
entry	Pd-catalyst		conv. (%) ^b	GLC yield (%)
1	Pd(OAc) ₂		80	80
2 ^{<i>c</i>}	Pd(OAc) ₂ / MS	3A	81	81
3	Pd(II)-hydrotal	cite first use	98	98
		second	use 90	90

^a Reaction conditions: Pd-catalyst (0.05 mmol), benzyl alcohol (1.0 mmol), pyridine (0.2 mmol), toluene (10 mL), air (balloon, 1 atm) at 65 °C for 3 h. b Conversion of benzyl alcohol. c MS3A (500 mg) was used.

Table 2. Effect of Reaction Temperature for Pd(II)-Hydrotalcite-Catalyzed Oxidation of Alcohols under 1 Atm Air^a

	- ^	5 mol% Pd(20 mol% py	II)-hydrot ridine	talcite	0 II		
	R´ `OH — (1 mmol)	toluene (10 mL) air (1 atm)		—→ R´	́н		
entry	substrate	temp. (°C)	time (h)	conv. (%) ^b	GLC yield (%)		
1 ^{<i>c</i>}	benzyl alcohol	80	2	100	quant.		
2 ^{<i>c</i>}	benzyl alcohol	70	3	100	quant.		
3	benzyl alcohol	65	3	98	98		
4 ^{<i>c</i>}	dodecan-1-ol	80	13	72	70 ^d		
5	dodecan-1-ol	65	10	91	91 ^d		

^a Reaction conditions: Pd(II)-hydrotalcite (0.05 mmol), alcohol (1.0 mmol), pyridine (0.2 mmol), toluene (10 mL), air (balloon, 1 atm). ^b Conversion of alcohol. ^c The color of Pd(II)-hydrotalcite turned black. ^d Isolated yield.

Table 2 shows the result of aerobic oxidation of benzyl alcohol and dodecan-1-ol using Pd(II)-hydrotalcite as a catalyst. At 80 °C or 70 °C, benzyl alcohol was converted into benzaldehyde in quantitative yield. In these reactions, however, the color of the catalyst turned from white-yellow to black, showing the formation of an inactive Pd-black by the reduction of Pd(II) species. On the other hand, benzaldehyde was obtained in 98% yield without any formation of such Pd-black at 65 °C. In the oxidation of dodecan-1-ol at 80 °C, Pd-black was formed during the reaction resulting in the slow reaction (70% yield of dodecanal, after 13 h), while dodecanal was obtained in 91% yield at 65 °C for 10 h.

Next, the effect of the amount of pyridine on the oxidation of benzyl alcohol was investigated. As shown in Figure 1, when pyridine was not added, oxidation did not proceed efficiently; at least 4 mol equiv of pyridine to Pd(II) was needed to maintain the catalytic activity. Concentration of the substrate was also an important factor. When the oxidation of benzyl alcohol was performed using toluene (0.2 M), the color of Pd(II)hydrotalcite turned black and the yield of benzaldehyde decreased (77%). Therefore, we decided the optimum reaction condition to be the use of alcohol, Pd(II)hydrotalcite (5 mol %), pyridine (20 mol %) in toluene (0.1 M) under 1 atm air (in balloon) at 65 °C.

Oxidation of Benzylic and Aliphatic Alcohols. We performed the oxidation of various benzylic and aliphatic alcohols under the above-described optimum condition, the results of which are listed in Table 3. Primary benzylic alcohols were readily oxidized to the correspond-

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Figure 1. Time profile of the aerobic oxidation of benzyl alcohol: effect of the amount of pyridine to product yield.

ing aldehydes in 76-98% yields (Table 3, entries 1, 2, 4-9). It should be noted that this catalytic system showed the compatibility with either electron-donating or electronwithdrawing substituents in the benzene ring although the oxidation of the compound having a substituent at ortho-position was slightly slow. The amount of Pd(II)hydrotalcite could be reduced to 1 mol % to the substrate (30 h, entry 5). A slightly larger-scale oxidation of p-methoxybenzyl alcohol (1.385 g, 10.0 mmol) was found to give *p*-methoxybenzaldehyde in high isolated yield (1.244 g, 9.1 mmol, entry 6). When the oxidation of 2-phenylethanol was attempted for 5 h under the above optimum condition, acetophenone was obtained in 75% yield (entry 10), but its yield became quantitative using more pyridine (entry 11). Other secondary benzylic alcohols were also easily converted to the corresponding ketones in excellent yields. The oxidation of α -ketol such as benzoin proceeded to give the corresponding diketone in 98% yield, although longer reaction time (32 h) and more pyridine were required (entry 14). The saturated aliphatic primary and secondary alcohols could be oxidized to the corresponding aldehydes and ketones selectively in high yields (entries 15, 16, 18, 19, and 21). The oxidation of aliphatic alcohols was slower than that of benzylic ones. The undesired byproducts such as the corresponding carboxylic acids, and their esters were hardly produced in the oxidation of these alcohols. For comparison, the representative data using oxygen as an oxidant are also shown in Table 3 (entries 3, 12, 17, and 20). The results of entries 2 and 16 showed that the oxidation in an open flask equipped with CaCl₂ drying tube (in place of air balloon) also proceeded smoothly to give the corresponding products in similar yields.

Oxidation of Alkenic Alcohols. The oxidation of alkenic alcohols using Pd(II)-hydrotalcite under air was carried out, the typical results of which are shown in Table 4. There are still few reports about effective oxidation of alkenic alcohols by palladium catalysts because of their strong complexation with unsaturated carbon-carbon double bonds. It has been revealed that Pd(II)-hydrotalcite was an effective catalyst for the aerobic oxidation of variety of alkenic alcohols using molecular oxygen in our previous reports.^{19a,b} Reactions also proceeded smoothly under atmospheric air, and several alkenic alcohols were converted into the corresponding aldehydes and ketones in high to excellent yields. The addition of a quite excess of pyridine was essential for the sufficient conversion of alkenic alcohols.

The excess pyridine may prevent from the formation of Pd(II)-alkene complex which might accelerate the reduction of Pd(II). Citronellol and 10-undecen-1-ol were converted to the corresponding aldehydes in good yields (Table 4, entries 1 and 2). A variety of allylic alcohols were also efficiently oxidized by Pd(II)-hydrotalcite (Table 4, entries 3, 5-8, 10, 11). The selective oxidation of geraniol [(E)-isomer] and nerol [(Z)-isomer] proceeded smoothly to give the corresponding aldehydes in 90% and 85% yields without any change of E/Z ratios (Table 4, entries 6-8). Similarly, trans-4,8-dimethyl-3,7-nonadien-2-ol and farnesol were oxidized to the corresponding ketone and aldehyde, keeping their E/Z ratios unchanged (Table 4, entries 10 and 11). We have already reported that the geometrical isomerization occurred to change the E/Z ratios of products in the oxidation of these substrates using Pd(OAc)₂/pyridine/MS3A system.^{19b} We suppose that the interaction of Pd(II)-intermediate species such as Pd(II)-H with allylic moieties in both substrates and products causes such isomerization in Pd(OAc)₂/pyridine/ MS3A system. Although details are not vet known, such interaction may be prevented by the steric bulkiness of hydrotalcite surface to result in no isomerization.^{19b} For comparison, the representative data using oxygen as an oxidant are also shown in Table 4 (entries 4, 9, and 12).

Oxidation of Diols. We carried out the oxidation of decane-1,10-diol under the above optimum condition, but the reaction could not proceed completely (Table 5, entry 1). Even the addition of an excess pyridine was found to be ineffective (entry 2). However, its oxidation proceeded smoothly under 3 atm of air at 80 °C to afford decanedial **2** as the major product with a small amount of hydroxy aldehyde 1 (entry 3). In the case of cyclohexane-1,4-diol, the reaction could not proceed completely and a ca. 4:1 mixture of mono- and diketones was obtained even under 3 atm of air (entry 4), while vic-diol such as 1,2diphenylethane-1,2-diol was converted to the corresponding diketone in 74% yield (entry 5). Oxidative lactonization took place to give the corresponding lactone in the oxidation of α , ω -primary diol in 76% isolated yield under 3 atm air (entry 6).²¹ In the case of this substrate, the oxidation under 1 atm oxygen gave a slightly better result than that of under 3 atm air (entry 7).

Oxidation of Benzyl Alcohol under 3 atm of Air. From the viewpoint of economical and environmental concerns, we attempted to reduce the amount of solvent. As described above, higher concentration of alcohol decreased the reaction rate when the oxidation was performed under 1 atm of air. However, it was disclosed that the oxidation under 3 atm of air smoothly proceeded even at higher concentration (Table 6, entries 1 and 2). Furthermore, even in the case of reactions using 1 mol % catalyst, benzaldehyde was obtained in high yield within 5 h (entries 3 and 4).

Limitations. Pd(II)—hydrotalcite could act as an effective catalyst for the oxidation of a wide variety of alcohols, but some limitations in substrates exist (Figure 2). The oxidation of **5** and **6** could not proceed. The oxidation of **7** and **8** was very slow, and some unidentified products were produced. In the cases of **9** and **10**, which had an alkynic part, undesirable polymerization occurred to give a complex mixture. When the oxidation of alcohola.

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Table 3. Pd(II)-Hydrotalcite-Catalyzed Oxidation of Alcohols under 1 Atm Air^a

entry	substrate	product	pyridine (mmol)	time (h)	conv. (%) ^b	isolated yield (%)
1	СОН	СНО	0.2	3	98	98 ^c
2 ^d			0.2	3	97	97 ^c
3″			0.2	2	100	quant. ^c
4	ОН	СНО	0.2	3	95	94
5′			0.2	30	97	96
6 ^{r, g}	MeO	MeO	2.0	30	94	91
7	оОн	СНО	0.2	22	79	76
8	<i>m</i> - CI- <u>t</u>		0.2	11	95	90
9	p-		0.2	11	100	95
10	он	O II	02	5	80	75 [°]
11			1.0	10	100	quant. ^c
12 ^{<i>e</i>}			1.0	3	100	quant. ^c
	ОН	~ о				4
40		, Ì,		10	4.0.0	00
13			1.0	10	~100	98
	0	0				
14			1.0	32	100	98
						••
	OH	0				
15	$\sqrt{1}$		0.2	10	91	91
16 ^d	M ₁₀ OH	M10	0.2	10	92	90
17°			0.2	6	97	86
18	CH OH	Асно	0.2	12	93	88
	V/16	16			••	•••
19		()	0.2	20	97	97
20 ^e	M	M	1.0	11	100	93
	· /9	, 'a				
	\sim	AT				
21			0.2	36	97	93
	HOLI					

^{*a*} Reaction conditions: Pd(II)–hydrotalcite (0.05 mmol), alcohol (1.0 mmol), pyridine, toluene (10 mL), air (balloon, 1 atm) at 65 °C. ^{*b*} Conversion of alcohol. ^{*c*} GLC yield. ^{*d*} Open air system using CaCl₂ drying tube. ^{*e*} Oxygen (balloon, 1 atm) at 80 °C. ^{*f*} Pd(II)–hydrotalcite (0.01 mmol; 1 mol % Pd) was used. ^{*g*} 10 Fold scale reaction.

hols, which had a nitrogen atom such as **11** and **12**, was performed, no reaction was observed even using excess pyridine probably due to the complexation of palladium with the nitrogen atom. 3-Thiophenemethanol **13** was converted to the corresponding aldehyde only in low yield even using excess pyridine (13%, after 14 h).

Recycling of the Catalyst. Pd(II)-hydrotalcite can be recovered easily from the reaction media by simple filtration after the reaction and could be reused for the next run (Table 7). In the air oxidation of benzyl alcohol using Pd(II)-hydrotalcite, benzaldehyde was obtained in the following yield; first: 98%, second: 90%, third: 72% (entry 1). In the third run, the yield of benzaldehyde slightly decreased, mainly because of leaching of Pd(II) species.²² It has been revealed that leaching of palladium could be avoided by using a slightly modified catalyst, abbreviated as Pd(II)-hydrotalcite(m) in which Pd content was ca. a half amount compared with the standard Pd(II)-hydrotalcite (see Experimental Section). As expected, the loss of catalytic activity was prevented in some extent (entry 2; first: 98%, second: 94%, third: 82%).

Conclusions

Pd(II)-hydrotalcite which can be prepared by simple operation from commercially available hydrotalcite, Pd-(OAc)₂, and pyridine, efficiently catalyzes the aerobic oxidation of a variety of primary and secondary alcohols to the corresponding aldehydes and ketones, respectively, using *atmospheric pressure of air* as a sole oxidant in toluene at 65 °C. The results are intrinsically quite similar to those obtained using molecular oxygen, but the air oxidation proceeds at lower temperature. This catalyst can be easily recovered and reused for several times. These features match to today's demands for construction of clean and environmentally friendly catalytic reactions.

Experimental Section

General Methods. ¹H NMR spectra were obtained in CDCl₃ at 300 or 400 MHz with Me₄Si as an internal standard. ¹³C NMR spectra were obtained at 75.5 or 100 MHz. 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 μ m film thickness) and Shimadzu fused silica capillary column (HiCap CBP10–S25–050) using helium as a carrier gas. GLC yields were determined using cyclododecane as an internal standard. Analytical thin layer chromatographies (TLC) were performed with Merck silica gel 60 F-254 plates. Column chromatographies were performed with Merck silica gel 60.

Materials. $Pd(OAc)_2$ was purchased from Wako Pure Chemical Ind., Ltd., and used without further purification. Hydrotalcite (Mg₆Al₂(OH)₁₆CO₃·4H₂O, brand name KYOWAAD

⁽²²⁾ By ICP atomic emission analysis, the amount of leached palladium in oxidation of benzyl alcohol under O_2 was estimated; in the case of Pd(II)-hydrotalcite, av. 14%; Pd(II)-hydrotalcite(m), av. 0.8%. See ref 19b.

Table 4. Pd(II)-Hydrotalcite-Catalyzed Oxidation of Alkenic Alcohols under 1 Atm Air^a

entry	substrate	product	time (h)	conv. (%) ^b	isolated yield (%)
1	Долон л	СНО	15	88	82
2	() ₈ он	CHO 8	18	90	87
3	ОН	СНО	12	100	96
4 ^{<i>c</i>}			3	100	95
5	ОН	СНО	15	~100	quant.
6 ^{<i>d</i>}		↓ ↓ сно	12	~100	90
7 ^{d, e}	E/Z=98/2	<i>E / Z</i> = 98 / 2	12	~100	90
8 ^d			12	97	85
9 ^{c, d, 1}	f E/Z=2/98 OH	<i>E Z</i> = 2 / 98 CHO	4.5	100	89
10 ^d	Б/7-9/1 ОН	E/7-9/1	15	93	85
11 ^d 12 ^{c, d}	<i>F</i> / <i>Z</i> =9/1	<i>Е/Z=9/1</i> <i>Е/Z=9/1</i>	12 4.5	97 100	90 91
-					

^{*a*} Reaction conditions: Pd(II)-hydrotalcite (0.05 mmol), alcohol (1.0 mmol), pyridine (5.0 mmol), toluene (10 mL), air (balloon, 1 atm) at 65 °C. ^{*b*} Conversion of alcohol. ^{*c*} Oxygen (balloon, 1 atm) at 80 °C. ^{*d*} *E*/*Z* ratio was determined by ¹H NMR. ^{*e*} Open air system using CaCl₂ drying tube. ^{*f*} *E*/*Z* ratio of neral was 4/96.

 Table 5.
 Pd(II)-Hydrotalcite-Catalyzed Oxidation of Diols under 3 Atm Air^a

entry	substrate	product	pyridine (mmol)	time (h)	conv. (%) ^b	isolated yield (%)
1°	~~~~~		0.2	17	89	79 (1/2 =63/37)
2 ^{<i>c</i>}	но Мајон	HO Monte + Marte	1.0	15	82	63 (1/2= 57/43)
3	o	1 2	1.0	12	100	78 (1/2 =7/93)
4 H	Ю-ОН		2.0	6	57	51 (3/4 =80/20)
5	OH OH		2.0	15	100	74
6	ОН	\sim	0.2	3	~100	76
7 ^d	∽ ́ ́ ́ ́ ́ ́ ́ ́ ́ ́ ́ ́ ́ ́ ́ ́ ́ ́ ́	\bigvee	0.2	2.5	100	88

^{*a*} Reaction conditions: Pd(II)–hydrotalcite (0.05 mmol), alcohol (1.0 mmol), pyridine, toluene (10 mL), air (3 atm) at 80 °C. ^{*b*} Conversion of alcohol. ^{*c*} Air (balloon, 1 atm) at 65 °C. ^{*d*} Oxygen (balloon, 1 atm) at 80 °C.

 Table 6.
 Pd(II)-Hydrotalcite-Catalyzed Oxidation of Benzyl Alcohol under 3 Atm Air^a

entry	catalyst (mmol)	toluene (mL)	time (h)	conv (%) ^b	GLC yield (%)
1	0.05	10	1	97	95
2	0.05	5	1	100	96
3	0.01	3	5	93	91
4	0.01	2	5	97	95

^{*a*} Reaction conditions: Pd(II)–hydrotalcite, benzyl alcohol (1.0 mmol), pyridine (0.20 mmol), toluene, air (3 atm) at 80 °C. ^{*b*}Conversion of benzyl alcohol.

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. Air was not dried. All of the alcohols except for one described below were commercial products and purified by known methods just before use. Pd(II)-hydrotalcite and Pd(II)-hydrotalcite(m) were prepared by using the reported procedure.^{19b} The Pd content in the Pd(II)-hydrotalcite and Pd(II)-hydrotalcite(m) was 0.16 mmol g⁻¹ and 0.092 mmol g⁻¹, respectively, as estimated by ICP atomic emission analysis.

trans-4,8-Dimethyl-3,7-nonadien-2-ol (Table 4, entry **10**). The compound was prepared by the reaction of *trans*-3,7-dimethyl-2,6-octadien-1-one (geranial) with MeLi.²³ A colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 1.23 (d, J = 6.3 Hz, 3H), 1.36 (br s, 1H), 1.60 (s, 3H), 1.68–1.70 (m, 6H), 1.97–2.12 (m, 4H), 4.58 (dq, J = 8.6 Hz, 6.3 Hz, 1H), 5.07–5.11 (m, 1H), 5.20–5.23 (m, 1H); ¹³C NMR (75.5 MHz, CDCl₃) δ 16.4, 17.7, 23.6, 25.7, 26.4, 39.4, 64.8, 123.9, 129.1, 131.7, 137.6.

⁽²³⁾ Adam, W.; Mitchell, C. M.; Paredes, R.; Smerz, A. K.; Veloza, L. A. *Liebigs Ann./Recueil* **1997**, 1365.



Figure 2. Limitations.

Table 7. Recycling of Pd(II)-Hydrotalcite^a

entry	catalyst	pyridine (mmol)	time (h)	time of use	conv (%) ^b	GLC yield (%)
1	Pd(II)-hydrotalcite	0.2	3	first	98	98
				second	90	90
				third	73	72
2	Pd(II)-hydrotalcite(m)	0.5	11	first	99	98
	č			second	98	94
				third	85	82

^{*a*} Reaction conditions: Pd(II)–hydrotalcite (0.05 mmol), benzyl alcohol (1.0 mmol), pyridine, toluene (10 mL), air (balloon, 1 atm) at 65 °C. ^{*b*} Conversion of benzyl alcohol.

General Procedure for Pd(II)-Hydrotalcite-Catalyzed Oxidation of Alcohols Using Air (1 atm). A typical experimental procedure is as follows: to a suspension of Pd(II)hydrotalcite (300 mg, 0.05 mmol as Pd) and toluene (6 mL) in a 30 mL two-necked flask was added pyridine (0.2-5.0 mmol), and the mixture was stirred at room temperature. Then, unpurified air was introduced into the flask from a balloon under atmospheric pressure and the mixture was heated to 65 °C for ca. 10 min (caution: it is possible that one is working within explosion limit of toluene/oxygen mixtures in the gas phase at temperature lower than ca. 40 °C). Next, an alcohol (1.0 mmol) in toluene (4 mL) was added, and the mixture was stirred vigorously with a magnetic stirrer for 3 h (or some appropriate time) at 65 °C under air in balloon. 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, hexanediethyl ether) to give a product. Products obtained were

determined by $^1\!\mathrm{H}$ and $^{13}\mathrm{C}$ NMR and GC/MS. GLC yields were determined using cyclododecane as an internal standard.

trans-4,8-Dimethyl-3,7-nonadien-2-one (Table 4, entry **10).** A colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 1.61 (s, 3H), 1.69 (s, 3H), 2.13–2.18 (m, 10H), 5.06–5.08 (m, 1H), 6.07 (s, 1H); ¹³C NMR (75.5 MHz, CDCl₃) δ 17.7, 19.3, 25.7, 26.2, 31.7, 41.2, 123.1, 123.6, 132.5, 158.2, 198.7.

10-Hydroxydecanal (1). A white solid; ¹H NMR (300 MHz, CDCl₃) δ 1.26–1.43 (m, 11H), 1.52–1.67 (m, 4H), 2.42 (td, J = 7.3 Hz, 1.6 Hz, 2H), 3.62–3.66 (m, 2H), 9.76 (t, J = 1.6 Hz, 1H); ¹³C NMR (75.5 MHz, CDCl₃) δ 22.1, 25.7, 29.2, 29.3, 29.3, 29.4, 32.8, 43.9, 63.1, 203.0.

1,10-Decanedial (2). A colorless oil; ¹H NMR (300 MHz, CDCl₃) δ 1.26–1.43 (m, 8H), 1.60–1.65 (m, 4H), 2.43 (td, J = 7.3 Hz, 1.7 Hz, 4H), 9.76 (t, J = 1.7 Hz, 2H); ¹³C NMR (75.5 MHz, CDCl₃) δ 22.0, 29.1, 29.1, 43.9, 202.9.

General Procedure for Pd(OAc)₂/**Pyridine**/**MS3A System-Catalyzed Oxidation of Alcohols Using Air (1 atm).** A typical experimental procedure for the oxidation of unsaturated alcohols using the title system is as follows: to a suspension of 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, unpurified air was introduced into the flask from a balloon under atmospheric pressure. Next, an alcohol (1 mmol) in toluene (6 mL) was added at room temperature, and the mixture was heated to 65 °C and stirred vigorously for 3 h (or some appropriate time) under air in balloon. After the reaction, the mixture was treated as described above to obtain a product.

General Procedure for $\dot{Pd}(II)$ -Hydrotalcite-Catalyzed Oxidation of Alcohols Using Air (3 atm). A typical experimental procedure is as follows: a mixture of Pd(II)-hydrotalcite (60–300 mg, 0.01–0.05 mmol as Pd), pyridine (0.04– 0.20 mmol), alcohol (1 mmol) and toluene (2–10 mL) in a highpolymer autoclave with a glass container was stirred vigorously with a magnetic stirrer under unpurified air pressure (initial pressure of 3 atm) at 80 °C for 3 h (or some appropriate time). After the reaction, the mixture was treated as described above to obtain a product.

General Procedure for Reuse of the Catalyst. First run of the oxidation of benzylic alcohols catalyzed by Pd(II)-hydrotalcite or Pd(II)-hydrotalcite(m) was performed by the above-described procedure. Recovered Pd(II)-hydrotalcite or Pd(II)-hydrotalcite(m) was washed with hexane (20 mL \times 2) and dried under vacuum at room temperature before use for the next run.

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