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Pd(II)-Hydrotalcite-Catalyzed Selective Oxidation of Alcohols Using Molecular Oxygen

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A 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 cases. The catalyst also has advantages such as ease of handling, easy preparation, and reusability for several times.

The increasing environmental and economical concerns have led chemists to develop the clean and high-performance catalytic reactions. Especially, much attention has been paid to 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 a target of interest to 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 tetraoxoruthenate(VII)][3,4] and TiO_2-supported palladium cluster.[5b,5c] Ruthenium-doped hydrotalcites (layered basic clay minerals) were also reported as efficient heterogeneous catalysts for the oxidation of alcohols under O_2.[6] Quite recently, monomeric ruthenium supported by hydroxyapatite (RuHAP) was also synthesized for the same purpose.[7]

Recently, we reported the oxidation of alcohols using a homogeneous palladium catalyst under atmospheric pressure of oxygen,[8] 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.[9] In this paper we describe the full scope of this aerobic oxidation using Pd(II)-hydrotalcite as catalyst.[10]

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 $[Pd(OAc)_2(py)_2]$ complex[11] 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}, as estimated by inductively coupled plasma (ICP) atomic emission spectrometry analysis. Hydrotalcite has a layered structure consisting of positively charged brucite-like layers and negatively charged counter ions and water molecules located in the interlayers.[12] 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 plate-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 plate-like crystals of the hydrotalcite. However, because of severe dehydration of hydrotalcite by irradiation of the 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 wt% of N atom was contained in Pd(II)-hydrotalcite, which was quite close to a theoretical percentage of nitrogen (0.45 wt% calculated from the result of ICP atomic emission analysis, assuming that Pd atoms exist in the $[Pd(OAc)_2(py)_2]$ 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. The MS peak of pyridine (m/z = 79) desorbed from Pd(II)-hydrotalcite was observed at around 160 °C.[13] 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.

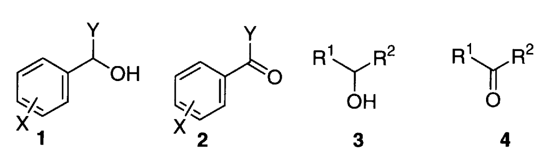
Finally, we tried to identify the palladium-pyridine complex itself which might be supported on Pd(II)-hydrotalcite. For this purpose, several physical analyses such as cross polarization-magic angle spinning (CP-MAS) ^{13}C NMR, absorption and diffuse reflectance of IR, UV, and thermogravimetry-differential thermal analysis (TG-DTA) were employed, but unfortunately, no exact and clear information was obtained. In order to know whether the palladium complex in Pd(II)-hydrotalcite contains acetate or not, Pd(II)-hydrotalcite was washed with an excess amount of pyridine repeatedly to compel the palladium complex to leach from Pd(II)-hydrotalcite; then the resulting filtrate was concentrated. As a result, the yellowish solids, which mainly consisted of $[Pd(OAc)_2(py)_2]$ complex,[14] were obtained.

Thus, we concluded that the palladium-pyridine complex was immobilized on the external surface of brucite layers of Pd(II)-hydrotalcite.[15]

Pd(II)-Hydrotalcite-Catalyzed Oxidation of Alcohols. The oxidation of alcohols was performed as follows: Pd(II)-hydrotalcite (300 mg, Pd: 0.05 mmol), 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.[16] The results of the oxidation of primary and secondary alcohols are shown in Chart 1 and Table 1. In the oxidation of primary benzylic alcohols (**1a**–**h**), substrates were smoothly consumed to afford the corresponding aldehydes (**2a**–**h**) in high yields (Table 1, Entries 1, 4–10), irrespective of the presence of either electron-donating substituents (**1b**–**e**) or electron-withdrawing substituents (**1f**–**h**). However, 3-nitrobenzyl alcohol (**1i**) yielded the corresponding aldehyde (**2i**) in a slightly lower yield (69%) in spite of the high conversion of **1i**. Secondary benzylic alcohols (**1j** and **k**) were also converted to the corresponding ketones (**2j** and **k**) in excellent yields for 3 h (Entries 12 and 13), although some excess pyridine (1 mmol) was needed for sufficient reaction without loss of a catalytic activity.

Non-activated primary and secondary aliphatic alcohols (**3a**–**d**) were also transformed into the corresponding carbonyl compounds (**4a**–**d**) using Pd(II)-hydrotalcite, although reactions were relatively slow (Entries 14–17). The reaction rate of secondary alcohols was lower than that of primary ones (Entries 16 and 17).

Oxidative Lactonization of Diols. In the oxidation of α,ω-primary diols, oxidative lactonization occurred to give the corresponding lactones (Chart 2, Table 2, Entries 1–4).[17] Unfortunately, little chemoselectivity was observed in the reaction of an unsymmetrical diol in our system (Table 2, Entry 4).[18]



1a X: H Y: H
1b X: 4-Me Y: H
1c X: 4-MeO Y: H
1d X: 3-MeO Y: H
1e X: 2-MeO Y: H
1f X: 4-Cl Y: H
1g X: 3-Cl Y: H
1h X: 2-Cl Y: H
1i X: 3-NO_2 Y: H
1j X: H Y: Me
1k X: H Y: Et

3a R^1: $CH_3(CH_2)_{10}$ R^2: H
3b R^1: $CH_3(CH_2)_{16}$ R^2: H
3c R^1: $CH_3(CH_2)_9$ R^2: Me
3d R^1, R^2: 4-*tert*-butylcyclohexyl

Chart 1.

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

Entry	Substrate	Product	Time h	Conv. %	Isolated yield/%
1	**1a**	**2a**	2	100	quant.[b]
2[c]	**1a**	**2a**	12	98	91[b]
3[d]	**1a**	**2a**	12	94	87[b]
4	**1b**	**2b**	2	98	94
5	**1c**	**2c**	2	98	92
6	**1d**	**2d**	5	100	97
7	**1e**	**2e**	8	96	95
8	**1f**	**2f**	2	97	90
9	**1g**	**2g**	2	97	93[b]
10	**1h**	**2h**	2	87	84[b]
11	**1i**	**2i**	2	84	69
12[e]	**1j**	**2j**	3	100	quant.[b]
13[e]	**1k**	**2k**	3	98	95
14	**3a**	**4a**	6	97	86
15	**3b**	**4b**	6	97	85
16[e]	**3c**	**4c**	11	100	93
17[e]	**3d**	**4d**	11	100	92

a) Reaction conditions; Pd(II)-hydrotalcite (300 mg, 0.05 mmol Pd), alcohol (1.0 mmol), pyridine (0.2 mmol), toluene (10 mL), 80 °C, O_2. b) GLC yield. c) 1 mol% Pd(II)-hydrotalcite, for 12 h. d) 10 fold scale reaction using 1 mol% Pd(II)-hydrotalcite for 12 h. e) Pyridine (1.0 mmol) was used.

Oxidation of Unsaturated Alcohols. The oxidation of alkenic alcohols using either Pd(II)-hydrotalcite system or $Pd(OAc)_2$/pyridine/MS3A system (homogeneous catalytic system; abbreviated as MS-system)[8b] was performed for comparison; the results are summarized in Table 3. 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 (footnotes of Table 3). Such an excess of pyridine may prevent the complexation of Pd(II)-intermediates with an alkenic moiety which might accelerate the reduction of Pd(II).[19] When the oxidation of cinnamyl alcohol using both catalytic systems was compared, Pd(II)-hydrotalcite system showed a slightly higher

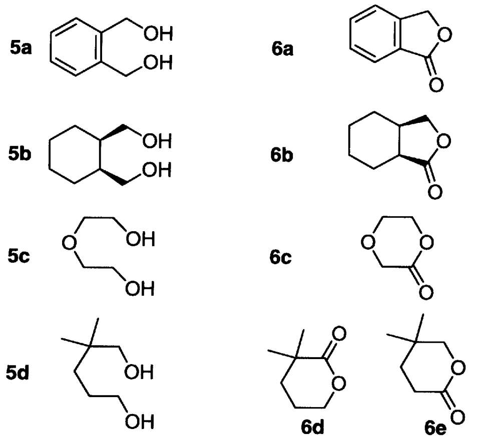


Chart 2.

Table 2. Pd(II)-Hydrotalcite-Catalyzed Oxidation of Diols Using Molecular Oxygen[a)]

Entry	Substrate	Product	Time/h	Isolated yield/%[b)]
1	**5a**	**6a**	2.5	56
2	**5b**	**6b**	2.5	88
3	**5c**	**6c**	2	24[c)]
4	**5d**	**6d** + **6e**	5	58 (**6d**/**6e** = 44/56)[d)]

a) Reaction conditions; Pd(II)-hydrotalcite (300 mg, 0.05 mmol Pd), alcohol (1.0 mmol), pyridine (0.2 mmol), toluene (10 mL), 80 °C , O_2. b) Substrates were completely consumed. c) GLC yield. d) Determined by ^{1}H NMR.

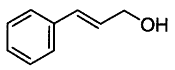
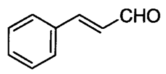
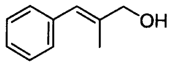
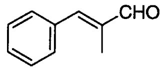
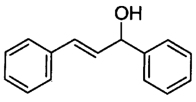
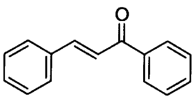
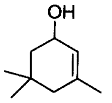
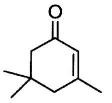
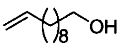
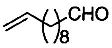
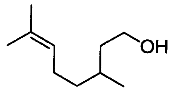
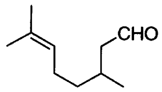
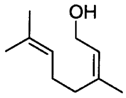
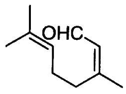
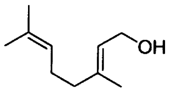
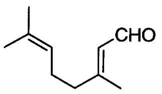
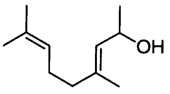
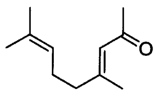
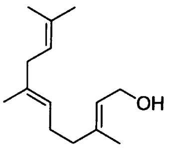
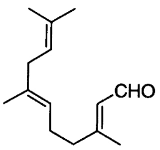
activity than MS-system to give cinnamaldehyde in 95% isolated yield (Entry 1). In the oxidation of other allylic alcohols, a similar trend was observed (Entries 2–4). Alkenic alcohols such as 10-undecen-1-ol and citronerol could also be smoothly oxidized to give the corresponding aldehydes in good yields without affecting the alkenic moieties (Entries 5 and 6). 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 changed (*E*/*Z* ratios were 31/69 and 63/37, respectively).[20] 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 7 and 9). Further, in these oxidations reaction rates dramatically increased using Pd(II)-hydrotalcite. In the cases of *trans*-4,8-dimethyl-3,7-nonadien-2-ol and farnesol (Entries 10 and 11), the difference between Pd(II)-hydrotalcite and MS-system is smaller than that in the former two substrates, but *E*/*Z* ratios were also much changed by using the MS-system (8/2). It is well known that Pd(II) species are generally not such effective catalysts for oxidation of allylic alcohols because of their strong complexation with unsaturated carbon–carbon bonds.[10a] 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 and ketones. Our results also provide a good method for the selective aerobic oxidation of allylic alcohols. In order to explain this superiority of heterogeneous catalyst compared with homogeneous one in the oxidation of allylic alcohols, we tried several experiments. Geranial was kept under the reaction conditions of either Pd(II)-hydrotalcite system or MS-system (Eq. 1, Table 4). In both systems, the *E*/*Z* ratio of geranial did not change much (Entries 2 and 3). The result indicates that the geometrical isomerization might be due to the interaction between an intermediate Pd(II) species such as Pd(II)H, which was generated during the reaction of substrates, and allylic moieties which exist in both substrates and products in the reaction media. In the MS-system, such isomerization could not be prevented even by using excess pyridine (Table 3, Entries 7 and 9). Although the reason for preservation of the *E*/*Z* geometry in products in the case of Pd(II)-hydrotalcite system is not yet clear, the complexation of the palladium species with an alkenic part may be inhibited because of the steric bulkiness of hydrotalcite surface.

The oxidation of alkynic alcohols (Chart 3) was next attempted. An alkynic alcohol **7a** which has an internal carbon–carbon triple bond was converted to the corresponding aldehyde **8a** in low yield (23%, after 24 h), while alcohols which have a terminal alkynic moiety such as **7b** and **7c** did not give the corresponding ketones because of non-controlled polymerization.

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 5), 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 5, Entry 1; first: 98%, second: 89%, third: 77%). In order to prevent this deactivation of catalyst, another modified Pd(II)-hydrotalcite [abbreviated as Pd(II)-hydrotalcite(m), 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(m) 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(m) the oxidation of 4-methoxybenzyl alcohol giving 4-methoxybenzaldehyde proceeded well even when used for the fourth time (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 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.

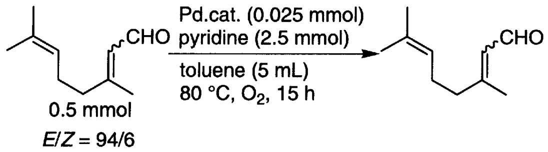
Table 3. Pd(II)-Hydrotalcite or $Pd(OAc)_2$/Pyridine/MS3A System-Catalyzed Oxidation of Alkenic Alcohols Using Molecular Oxygen[a]

Entry	Substrate	Product	Pd(II)-hydrotalcite system[b] Time h	Pd(II)-hydrotalcite system[b] Isolated yield %[d]	$Pd(OAc)_2$/pyridine/MS3A system[c] Time h	$Pd(OAc)_2$/pyridine/MS3A system[c] Isolated yield %[d]
1			3	95 (100)	4	91 (96)
2			5	97 (100)	12	93 (100)
3			3	97 (100)	4	83 (90)
4[e]			3	96 (100)	4	87 (100)
5			8	93 (100)	17	91 (95)
6			4.5	94 (98)	6	81 (86)
7[f]	 E/Z = 2/98		4.5	89 (100) $E/Z = 6/94$	15	39 (71) $E/Z = 31/69$
8[f],[g]	 E/Z = 98/2		12	45 (58) $E/Z = 95/5$		
9[f]			4.5	91 (98) $E/Z = 96/4$	15	56 (76) $E/Z = 63/37$
10[f]	 E/Z = 9/1		4.5	90 (98) $E/Z = 9/1$	15	72 (91) $E/Z = 8/2$
11[f]	 E/Z = 9/1		4.5	91 (100) $E/Z = 9/1$	15	61 (80) $E/Z = 8/2$

a) Reaction conditions; alcohol (1.0 mmol), pyridine (5.0 mmol), toluene (10 mL), O_2, 80 °C. b) Pd(II)-hydrotalcite (300 mg, 0.05 mmol 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.

9%) was observed after 21 h]. In contrast, using Pd(II)-hydrotalcite(m) in the same experiment, such further oxidation did not proceed even after 24 h. To determine the exact amount of palladium salt in the filtrate which leached from Pd(II)-hydrotalcite and Pd(II)-hydrotalcite(m), we performed ICP atomic emission analysis for the filtrate after the reaction. As a result, 14% of Pd leached from Pd(II)-hydrotalcite was detected, while in the case of Pd(II)-hydrotalcite(m) only 0.8% leaching was observed. These results showed that the leaching of Pd can be much diminished by decreasing the amount of Pd complex supported on hydrotalcite.

Shape Selective Oxidation of Cyclic Alcohols. Next, we carried out the oxidation of a variety of cyclic alcohols having the different sizes and substituents using Pd(II)-hydrotalcite(m).[21] Sterically less hindered substrates were converted to the corresponding ketones much faster than the hindered ones. For example, cyclohexanol was converted to cyclohexanone in 79% yield for 15 h (Table 6, Entry 1), while larger-sized cyclic alcohols were oxidized to the corresponding ketones only in 32–77% yields in the same reaction time (Entries 2–7). On the other hand, all alcohols shown in Table 6 were converted into the corresponding ketones completely within 2 h in MS-system. The reason of the differences of the reaction rate according to the shape of alcohols using Pd(II)-hydrotalcite(m) may



(1)

Table 4. Attempts for Isomerization of *E*/*Z* Ratio of Geranial

Entry	Pd cat.	*E*/*Z* ratio[a)]
1	none	90/10
2	$Pd(OAc)_2$/MS3A	92/8
3	Pd(II)-hydrotalcite	94/6

a) *E*/*Z* ratio was determined by ^1H NMR.

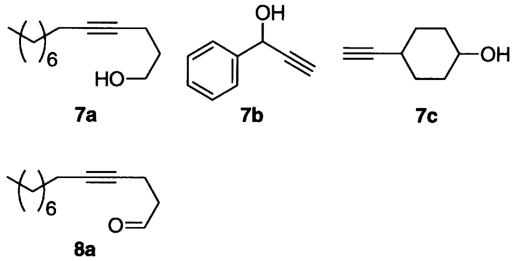


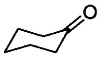
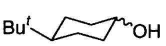
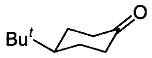
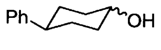
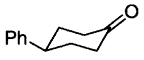
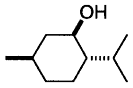
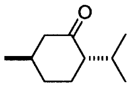
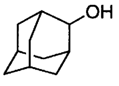
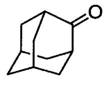
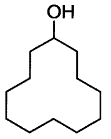
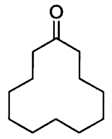
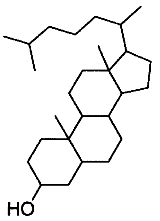
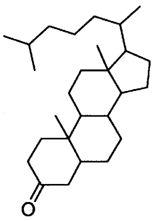
Chart 3.

Table 5. Recycling of Pd(II)-Hydrotalcite and Pd(II)-Hydrotalcite(m) in the Oxidation of Benzylic Alcohols Using Molecular Oxygen[a)]

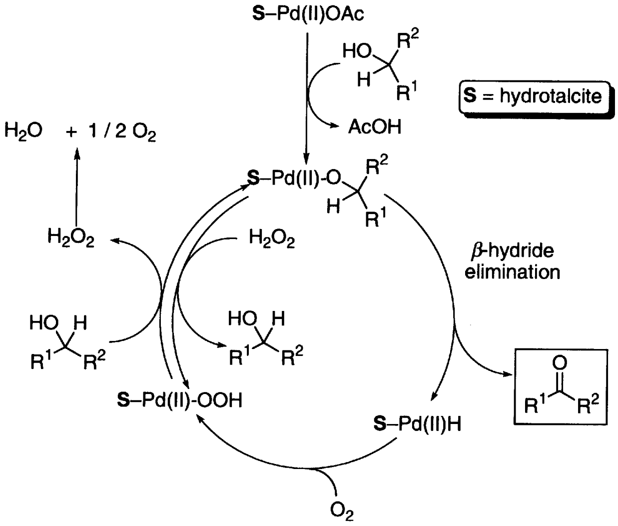
Entry	Catalyst	Substrate	Time h	Number of use	GLC yield/%
1[a)]	Pd(II)-hydrotalcite	benzyl alcohol	2	first	98
				second	89
				third	77
2[a)]	Pd(II)-hydrotalcite(m)	benzyl alcohol	5	first	96
				second	97
				third	90
3[b)]	Pd(II)-hydrotalcite(m)	4-methoxy-benzyl alcohol	5	first	84[c)]
				second	88[c)]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

a) Reaction conditions; Pd(II)-hydrotalcite or Pd(II)-hydrotalcite(m) (900 mg or 1800 mg, 0.15 mmol Pd), benzyl alcohol (3.0 mmol), pyridine (1.5 mmol), toluene (30 mL), 80 °C, O_2. b) Reaction conditions; Pd(II)-hydrotalcite(m) (600 mg, 0.05 mmol Pd), 4-methoxybenzyl alcohol (1.0 mmol), pyridine (0.5 mmol), toluene (10 mL), 80 °C, O_2. c) Isolated yield (%).

Table 6. Pd(II)-Hydrotalcite(m)-Catalyzed Oxidation of Cyclic Alcohols Using Molecular Oxygen[a)]

Entry	Substrate	Product	Isolated yield %[b)]	
1			79[c)]	(80)
2			43	(45)
3			39	(49)
4			32	(43)
5			58	(64)
6			77	(79)
7			35	(36)

a) Reaction conditions; Pd(II)-hydrotalcite(m) (600 mg, 0.05 mmol Pd), alcohol (1.0 mmol), pyridine (1.0 mmol), toluene (10 mL), 80 °C, O_2. b) Based on the starting substrate. The value in parentheses is the conversion of alcohol (%). c) GLC yield.



Scheme 1. Plausible reaction pathway.

be the steric bulkiness of Pd(II)-species immobilized on the external surface of hydrotalcite.

Reaction Scheme. We propose a plausible reaction pathway as illustrated in Scheme 1 for the oxidation of alcohols in this system, the pathway being intrinsically the same as that proposed in the homogeneous system, in which the formation of H_2O_2 was detected by KI-starch test.[8b] In the case of Pd(II)-hydrotalcite system, the result of KI-starch test was negative, suggesting that the decomposition of H_2O_2 may occur. Furthermore, the study of an oxygen uptake in the oxidation of benzyl alcohol supported this reaction pathway. In the oxidation of benzyl alcohol using catalytic amounts of $Pd(OAc)_2$ and pyridine, ca. 1 : 1 ratio of the amount of oxygen uptake to the

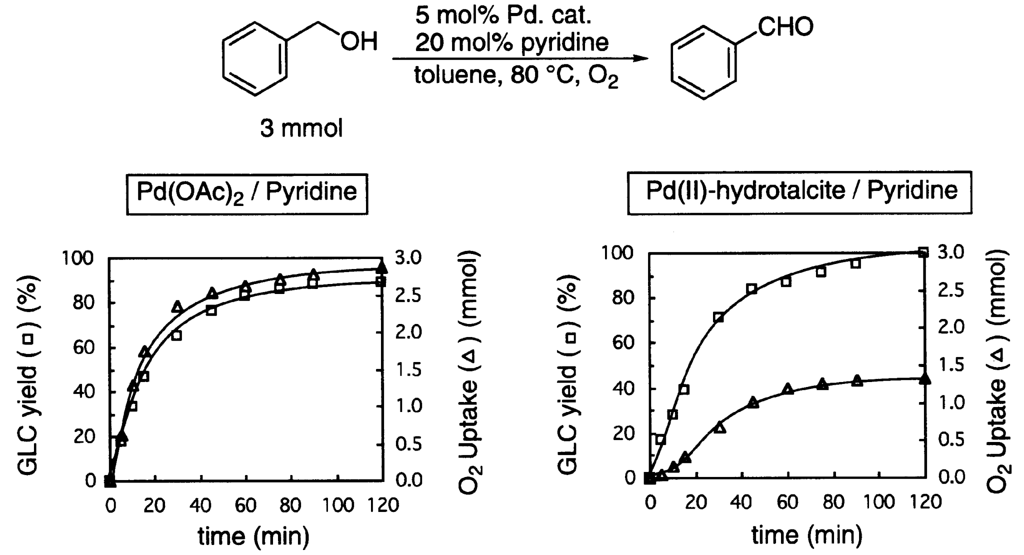


Fig. 1. Measurement of O_2 uptake using gas burette.

yield of benzaldehyde was observed, whereas ca. 1:2 ratio was observed when the reaction was carried out in the presence of Pd(II)-hydrotalcite (Fig. 1). In MS-system, a 2:3 ratio was observed.[8b] These results indicated that a generated H_2O_2 could be decomposed by MS3A as well as hydrotalcite and that hydrotalcite works more effectively than MS3A for the decomposition.

Conclusion. Pd(II)-hydrotalcite was newly prepared by a 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. Modified Pd(II)-hydrotalcite [Pd(II)-hydrotalcite(m)] could be reused several times while keeping its catalytic activity.

Experimental

General. ^{1}H and ^{13}C NMR spectra were measured on JEOL EX-400, JNM-AL300, and JEOL GSX270 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 x 3 mm glass column packed with 5% OV®-17 on Chromosorb® W, 5.0 μm film thickness) and Shimadzu fused silica capillary column (HiCap CBP10-S25-050) using helium as a carrier gas. GLC yields were determined using bibenzyl, cyclododecane or pentamethylbenzene 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. XRD data were obtained on a Shimadzu XD-D1 diffractometer using Cu $K\alpha$ 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 a diffuse-reflectance unit. CP-MAS ^{13}C NMR spectra were measured on a JEOL GSX270 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. Hydrotalcites ($Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$, brand name KYOWAAD® 500 and ALCAMAC<L>®) were 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. All of alcohols except for three that are described below were commercially available and were purified by known methods just before use. Geranial was obtained by Swern oxidation of geraniol. $[Pd(OAc)_2(py)_2]$ complex was prepared by the reported method.[11]

2,2-Dimethyl-1,5-pentanediol (Table 2, Entry 4, 5d). The compound was prepared by the hydroboration-oxidation of 2,2-dimethyl-4-pentenal. Colorless oil; ^{1}H NMR (270 MHz) δ 0.89 (s, 6H), 1.25–1.35 (m, 2H), 1.48–1.60 (m, 2H), 1.87 (br s, 2H), 3.33 (s, 2H), 3.64 (t, J = 6.3 Hz, 2H); ^{13}C NMR (100 MHz) δ 24,0, 27.0, 34.3, 34.8, 63.6, 71.3.

***trans*-4,8-Dimethyl-3,7-nonadien-2-ol (Table 3, Entry 10).** The compound was prepared by the reaction of *trans*-3,7-dimethyl-2,6-octadien-1-one (geranial) with MeLi.[22] Colorless oil; ^{1}H NMR (400 MHz) 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, 6.3 Hz, 1H), 5.07–5.11 (m, 1H), 5.20–5.23 (m, 1H); ^{13}C NMR (75.5 MHz) δ 16.4, 17.7, 23.6, 25.7, 26.4, 39.4, 64.8, 123.9, 129.1, 131.7, 137.6.

4-Tridecyn-1-ol (Chart 3, 7a). The compound was prepared by the reported procedure.[23] Colorless oil; ^{1}H NMR (400 MHz) δ 0.88 (t, J = 6.8 Hz, 3H), 1.27–1.39 (m, 10H), 1.44–1.51 (m, 2H), 1.74 (tt, J = 6.4, 6.4 Hz, 2H), 1.86 (br s, 1H), 2.13 (dt, J = 6.8, 2.4 Hz, 1H), 2.14 (dt, J = 6.8, 2.4 Hz, 1H), 2.28 (dt, J = 6.8, 2.4 Hz, 1H), 2.29 (dt, J = 6.8, 2.4 Hz, 1H), 3.76 (t, J = 6.2 Hz, 2H); ^{13}C NMR (75.5 MHz) δ 14.1, 15.5, 18.7, 22.7, 28.9, 29.1, 29.2, 29.2, 31.7, 31.9, 62.0, 79.3, 81.1.

General Procedure for Preparation and Characterization of Pd(II)-Hydrotalcite and Pd(II)-Hydrotalcite(m). 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)[24] 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 (20 mL × 2). 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} as estimated by ICP atomic emission analysis. Elemental analysis, Pd(II)-hydrotalcite: N, 0.35% [Calcd N, 0.45 wt% calculated from the result of ICP atomic emission analysis, assuming that Pd atoms exist in the $[Pd(OAc)_2(py)_2]$ form in Pd(II)-hydrotalcite]. The values of spacing d_{003} were estimated by XRD analysis as follows: commercially available hydrotalcite (KYOWAAD® 500), 7.81 Å, and Pd(II)-hydrotalcite, 7.75 Å. Pd(II)-hydrotalcite(m) was prepared by a similar method to that 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(m) was 0.092 mmol g^{-1} estimated by ICP atomic emission analysis.

The residue which was obtained by washing Pd(II)-hydrotalcite with pyridine was analyzed by ^1H and ^{13}C NMR. Major peaks of ^1H and ^{13}C NMR spectra were the same as those of the $[Pd(OAc)_2(py)_2]$ complex.

General Procedure for Pd(II)-Hydrotalcite or Pd(II)-Hydrotalcite(m)-Catalyzed Oxidation of Alcohols Using Molecular Oxygen.[9] A typical experimental procedure is as follows: to a suspension of the Pd(II)-hydrotalcite (300 mg, 0.05 mmol as Pd) or Pd(II)-hydrotalcite(m) (600 mg, 0.05 mmol 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 some 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 ^1H and ^{13}C NMR and GC/MS.

General Procedure for $Pd(OAc)_2$/Pyridine/MS3A System-Catalyzed Oxidation of Unsaturated Alcohols Using Molecular Oxygen.[8b] 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 an appropriate time under oxygen. After the reaction, the mixture was filtered through a pad of Florisil. 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.

***trans*-4,8-Dimethyl-3,7-nonadien-2-one (Table 3, Entry 10).** Colorless oil; ^1H NMR (400 MHz) 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); ^{13}C NMR (75.5 MHz) δ 17.7, 19.3, 25.7, 26.2, 31.7, 41.2, 123.1, 123.6, 132.5, 158.2, 198.7.

4-Tridecyn-1-al (Chart 1, 8a). Colorless oil; IR (neat) 2955, 2927, 2855, 2724, 2353, 2232, 1731, 1464, 1455, 1435, 1411, 1386, 1358, 1332, 1116, 1058, 895, 848, 722 cm^{-1}. ^1H NMR (300 MHz) δ 0.88 (t, J = 6.8 Hz, 3H), 1.27–1.36 (m, 10H), 1.41–1.51 (m, 2H), 2.11 (dt, J = 7.1, 2.3 Hz, 1H), 2.13 (dt, J = 6.9, 2.4 Hz, 1H), 2.46–2.51 (m, 2H), 2.59–2.65 (m, 2H), 9.79 (t, J = 1.4 Hz, 1H); ^{13}C NMR (75.5 MHz) δ 12.2, 14.1, 18.7, 22.7, 28.9, 28.9, 29.1, 29.2, 31.9, 43.0, 77.7, 81.7, 201.1. Found: C, 80.47; H, 11.37%. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41%.

General Procedure for Recycling of the Catalyst. First run of the oxidation of benzylic alcohols catalyzed by Pd(II)-hydrotalcite or Pd(II)-hydrotalcite(m) was performed using the procedure described above. Recovered Pd(II)-hydrotalcite or Pd(II)-hydrotalcite(m) was washed with diethyl ether (20 mL × 2) 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 removed by filtration at 80 °C. Then the filtrate containing the product benzaldehyde and unreacted benzyl alcohol was stirred under O_2 at 80 °C. The reaction was monitored with GLC using cyclododecane as an internal standard. By ICP atomic emission analysis, the amount of leached palladium in oxidation of benzyl alcohol under the conditions shown in Table 5 was estimated; in the case of Pd(II)-hydrotalcite, av 14%; Pd(II)-hydrotalcite(m), av 0.8%.

The authors are grateful to Kyowa Chemical Ind., Ltd. for the gift of hydrotalcites ($Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$, brand name KYOWAAD® 500 and ALCAMAC<L>®) for this study. We also thank Dr. Tatsuya Takeguchi (Kyoto Univ.) for his help in CP-MAS ^{13}C-NMR analysis and Dr. Shinji Iwamoto (Kyoto Univ.) for his help in ICP atomic emission analysis. T. N. gratefully acknowledges a Fellowship of the Japan Society for the Promotion of Science for Young Scientists.

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15 Although it is not clear what kinds of interactions let a palladium–pyridine complex be immobilized on hydrotalcite, there is a possibility of ionic bonding between an acetoxy carbonyl moiety of the palladium–pyridine complex and hydroxyl groups on the surface of the hydrotalcite. Short comment about this kind of interaction was stated (See Ref. 5c).

16 The presence of 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.

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20 In our previous report, we failed the oxidation of geraniol in MS-system. However, this limitation could be overcome by slightly improving the procedure. See experimental section.

21 The difference of the reaction rates by the size of alcohols was little when the oxidation of these cyclic alcohols was carried out using Pd(II)-hydrotalcite as a catalyst.

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