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Palladium(II)-supported hydrotalcite as a catalyst for selective oxidation of alcohols using molecular oxygen

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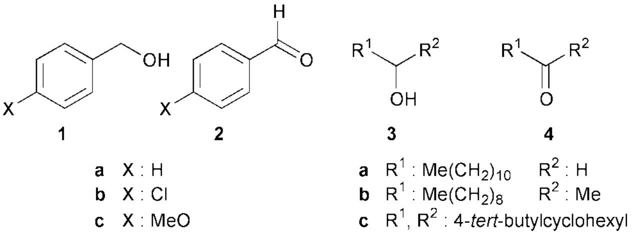
Palladium(II)-supported hydrotalcite acts as a reusable catalyst for the oxidation of alcohols to aldehydes and ketones in the presence of pyridine under atmospheric pressure of oxygen.

Heterogeneous catalysts are currently receiving considerable attention from the standpoint of environmental and economical concerns because of their unique properties such as easy handling, simple separation and reusability.[1] Hydrotalcite [$Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$] is a naturally produced basic clay mineral which has a layered structure consisting of positively charged brucite-like layers and negatively charged counter ions located in the interlayers.[2] It has been used as a solid base catalyst in several reactions[3] and also some modified hydrotalcites have been prepared and used for aerobic oxidation of alcohols.[4] The utility of hydrotalcite as a support for transition metals has also been investigated[5] and further elaboration of its use in organic synthesis is awaited.

Recently we have reported the palladium-catalysed oxidation of alcohols to aldehydes and ketones using a catalytic amount of $Pd(OAc)_2$, pyridine and 3 Å molecular seives (MS3A) under atmospheric pressure of oxygen.[6] In order to construct a high-performance catalytic system, we have attempted heterogenization of this system to produce a reusable and efficient solid catalyst. Among several clay supports examined, we found that hydrotalcite was an effective support for Pd(II) in the oxidation of alcohols. We report here, the synthesis of a new heterogeneous catalyst, a palladium(II) salt supported hydrotalcite [Pd(II)-hydrotalcite] from commercially available reagents, and its application as a catalyst for aerobic oxidation of alcohols under oxygen.[7]

Pd(II)-hydrotalcite† (1.56 mmol g^{-1} Pd) was prepared by mixing $Pd(OAc)_2$, pyridine and hydrotalcite in toluene at 80 °C for 1 h, followed by filtration, washing and drying under reduced pressure at room temperature.[8] A residue was scarcely observed in the filtrate after removing solvents under reduced pressure, showing that virtually all of the $Pd(OAc)_2$ initially employed was adsorbed on hydrotalcite. The basal spacing (d_{003}) of the commercially available hydrotalcite was 7.8 Å as estimated by a sharp peak obtained from X-ray diffraction (XRD) analysis, while that of the prepared Pd(II)-hydrotalcite was essentially the same with no differences of peak pattern between hydrotalcite and Pd(II)-hydrotalcite being observed. This result suggests that the palladium salt is immobilised on the surface of hydrotalcite.[9]

Initially the catalytic oxidation of benzyl alcohol **1a** using Pd(II)-hydrotalcite‡ was performed (Scheme 1), and typical results are listed in Table 1. The oxidation of benzyl alcohol **1a** (1 mmol) in toluene at 80 °C for 2 h in the presence of 5 mol% Pd(II)-hydrotalcite (0.05 mmol Pd) under O_2 afforded benzaldehyde **2a** in 62% yield (Table 1, entry 1). By further addition of pyridine (0.2 mmol) in the reaction media, efficient oxidation proceeded to give a quantitative yield of **2a** (entry 2). The amount of the catalyst could be reduced to 1 mol%, although a longer reaction time was required to achieve the complete conversion of **1a** (entries 3 and 4). Other benzylic alcohols (**1b** and **1c**) were also smoothly oxidized to the corresponding aldehydes in high yields (entries 5 and 6). Non-activated primary and secondary aliphatic alcohols **3a–c** were easily transferred to the corresponding aldehydes and ketones in high yields (entries 7–9). In the latter case, however, the reaction was slower and an excess of pyridine (1.0 mmol) was required (entries 8 and 9). The reactions of alkenic alcohols using Pd(II)-hydrotalcite or $Pd(OAc)_2$/pyridine/MS3A (homogeneous catalytic system; abbreviated as MS-system)[6] were then carried out and compared, the results of which are summarized in Table 2. In the oxidation of geraniol **5** and nerol **7**, the presence of an excess of pyridine was required (entries 1–3). When the reaction of **5** was carried out using the MS-system, the yield of the corresponding aldehyde **6** was low (56%) even after long



Scheme 1

Table 1 Pd(II)-hydrotalcite-catalysed oxidation of alcohols by molecular oxygen[a]

Entry	Substrate	Catalyst	Pyridine/ mmol	Reaction time/h	Product	Conversion (%)	Isolated yield (%)[b]
1	**1a**	0.30 g, 5 mol%	—	2	**2a**	74	62[c]
2	**1a**	0.30 g, 5 mol%	0.2	2	**2a**	100	quant.[c]
3	**1a**	0.06 g, 1 mol%	0.2	12	**2a**	98	91[c]
4[d]	**1a**	0.60 g, 1 mol%	2.0	12	**2a**	94	87[c]
5	**1b**	0.30 g, 5 mol%	0.2	2	**2b**	97	90
6	**1c**	0.30 g, 5 mol%	0.2	2	**2c**	98	92
7	**3a**	0.30 g, 5 mol%	0.2	6	**4a**	97	86
8	**3b**	0.30 g, 5 mol%	1.0	11	**4b**	100	93
9	**3c**	0.30 g, 5 mol%	1.0	11	**4c**	100	92

[a] *Reaction conditions*: Pd(II)-hydrotalcite (1.56 mmol g^{-1} Pd), alcohol (1.0 mmol), pyridine, toluene (10 mL), 80 °C, O_2. [b] Based on alcohol employed. [c] GLC yield. [d] 10-Fold scale reaction.

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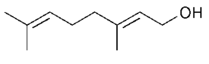
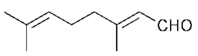
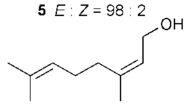
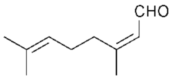
Table 2 Catalytic oxidation of geraniol and nerol using Pd(II)-hydrotalcite and Pd(OAc)$_2$/pyridine/MS3A[a]

Entry	Substrate	Product	Pd(II)-hydrotalcite[b]		Pd(OAc)$_2$/pyridine/MS3A[c]	
			Time/h	Isolated yield (%)[d]	Time/h	Isolated yield (%)[d]
1[e]	 **5** E : Z = 98 : 2	 **6**	12	45 (58) E : Z = 95 : 5		
2			4.5	91 (98) E : Z = 96 : 4	15	56 (76) E : Z = 63 : 37
3	 **7** E : Z = 2 : 98	 **8**	4.5	89 (100) E : Z = 6 : 94	15	39 (71) E : Z = 31 : 69

[a] *Reaction conditions*: alcohol (1.0 mmol), pyridine (5.0 mmol), O$_2$, 80 °C. [b] Pd(II)-hydrotalcite (1.56 mmol g^{-1} Pd; 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 alcohol (%). E:Z ratio determined by ^{1}H NMR. [e] Pyridine (0.2 mmol) used.

reaction times and the E:Z ratio was seriously disturbed (E:Z = 63:37), while the Pd(II)-hydrotalcite catalysed reaction smoothly proceeded to give **6** in 91% isolated yield without geometrical isomerization (E:Z = 96:4, entry 2). Similarly, aldehyde **8** was obtained highly selectively from **7** in high yield using Pd(II)-hydrotalcite (89%, E:Z = 6:94), while both product yield and selectivity were low using the MS-system (entry 3).[10] Although the reason for this high catalytic activity and selectivity arising from immobilisation of a palladium(II) salt on hydrotalcite is not yet clear,[10] this catalyst is shown to be especially effective for the oxidation of unsaturated alcohols.

The catalyst could be easily separated from the reaction mixture by simple filtration and recycled. For example, Pd(II)-hydrotalcite could be recycled at least three times in the oxidation of benzyl alcohol **1a** although the catalytic activity decreased with the third use (1st: 98%, 2nd: 93%, 3rd: 77%).

In summary, we have demonstrated that a novel Pd(II)-supported hydrotalcite worked as an efficient catalyst for the oxidation of alcohols under oxygen. Especially, in the oxidation of geometrically isomerizable allylic alcohols such as geraniol and nerol, the corresponding aldehydes were obtained in high yield without any isomerization. The catalyst can be easily separated and recycled. Further characterization of this catalyst and application to other reactions are now in progress.

We gratefully thank Kyowa Chemical Ind., Ltd. for the gift of hydrotalcite [$Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, brand name ALCAMAC < L > ®]. T. N. gratefully thanks a Fellowship of the Japan Society for the Promotion of Science for Young Scientists.

Notes and references

† *Procedure for the preparation 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 during which the brown suspension turned yellowish white. Then, hydrotalcite (ALCAMAC < L > ®, 10.0 g) was added and the mixture was stirred vigorously for 1 h at 80 °C. The obtained slurry was cooled to 0 °C, followed by filtration and washing with diethyl ether (20 mL × 2). The resulting solid was dried *in vacuo* at room temp. to give a yellowish white powder of Pd(II)-hydrotalcite. Elemental analysis; found: N, 0.35% [calc. N, 0.44% assuming that $Pd(OAc)_2 \cdot 2C_5H_5N$ formed *in situ* was completely adsorbed].

‡ *Procedure for Pd(II)-hydrotalcite catalysed oxidation of alcohols using molecular oxygen*: to a suspension of Pd(II)-hydrotalcite (300 mg, 0.05 mmol Pd) in toluene (6 mL) in a 20 mL two-necked flask was added pyridine (0.2–5.0 mmol) and the resulting mixture was stirred. Oxygen was then introduced into the flask from an O$_2$ balloon under atmospheric pressure and the mixture was heated to 80 °C for *ca.* 10 min with stirring. Then, an alcohol (1.0 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 reduced pressure left an oily residue which was subjected to column chromatography (Merck silica gel 60; hexane–diethyl ether as eluent) to give the product.

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10 Low catalytic activity of the MS-system might be due to strong complexation of palladium by the olefin. In Pd(II)-hydrotalcite, however, such complexation may be inhibited because of the steric bulk of hydrotalcite surface and this may be a reason for very low geometric isomerizations observed with the Pd(II)-hydrotalcite system.