Creation of a high-valent manganese species on hydrotalcite and its application to the catalytic aerobic oxidation of alcohols†

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A high-valent Mn oxide species is successfully synthesized on the surface of hydrotalcite (Mn/HT-*Ox*), and is found to act as an efficient heterogeneous catalyst for the oxidation of alcohols using molecular oxygen as an oxidant.

The oxidation of alcohols is currently a significant issue in many important fields[1] such as organic synthesis, hydrogen storage/release, and transformation of renewable biomass resources. For this purpose, manganese compounds have long been used as oxidizing reagents due to their high oxidation ability.[2] While these compounds are extremely useful, stoichiometric amounts are necessary to achieve the oxidations, which results in vast amounts of unrecoverable Mn compounds as waste. From environmental and practical standpoints, these stoichiometric methods should be replaced by catalytic ones. Recently, several successful catalytic approaches using various kinds of oxidizing reagents have been reported.[3] Among these systems, a methodology using molecular oxygen as a 'green' re-oxidizing agent would be the most attractive approach leading to a minimum amount of waste. However, there are few reports on the construction of a catalytic cycle involving Mn species combined with O_2 for oxidation of alcohols.[4]

Hydrotalcite [HT; $Mg_6Al_2(OH)_{16}CO_3$] is a layered anionic clay consisting of positively charged two-dimensional brucite layers with anionic species such as hydroxide and carbonate located in the interlayer. It has attracted considerable interest as a catalyst because of its multifunctional potential, which is due to its alternating cationic and anionic layers, tunable surface-basicity, and metal-adsorption capacity. The metal-adsorption ability of HT offers strong potential to create various metal species on the surface. Immobilized metals on HT can act as efficient heterogeneous catalysts for various organic reactions.[5] Herein, a high-valent Mn oxide species (Mn/HT-*Ox*) was successfully synthesized on the surface of HT, and found to oxidize alcohols. Interestingly, the resulting reduced Mn compounds could be reversibly re-oxidized by O_2, and Mn/HT-*Ox* was applicable for the efficient aerobic oxidation of alcohols as a heterogeneous catalyst.

HT was synthesized according to the literature procedure.[6] HT (1.0 g) was added to 50 mL of an aqueous solution of $MnCl_2 \cdot 4H_2O$ (0.3 mM), and then the heterogeneous mixture was stirred at 40 °C for 1 h under air, affording HT-containing Mn species (Mn/HT). Next, the pH of the solution was adjusted to 12 by adding 5 mL of an aqueous solution of KOH (1.0 M), and the resulting slurry was further stirred for 1 h. Finally, the obtained solid was isolated by filtration, washed with deionized water until the filtrate changed to neutrality, and dried at room temperature *in vacuo*, yielding Mn/HT-*Ox* as a brown powder. Elemental analysis of Mn/HT-*Ox* showed that the chemical composition of the Mn species was 1.6 wt%, and potassium ions were not detected. The XRD pattern of Mn/HT-*Ox* was similar to that of the parent HT.

Oxidation states of Mn/HT and Mn/HT-*Ox* were investigated using X-ray absorption fine structure (XAFS) analysis and comparison with Mn reference compounds (Mn foil, MnO, Mn_2O_3 and MnO_2).[7] The results are summarized in Fig. 1. The energy shift of the edge in the (X-ray absorption near-edge structure) XANES spectrum indicated the average oxidation state of the Mn species in Mn/HT was 3.1 (Fig. 1B, filled blue triangles). On the other hand, Mn in Mn/HT-*Ox* was oxidized up to a valency of 6 (Fig. 1B, filled green circles).[8]

These results reveal that adding KOH raises the oxidation state of the Mn species on HT to afford high-valent Mn species. It is said that basic compounds are effective additives for the formation of stable high-valent Mn species.[9] Both KOH and the surface basicity of HT may stabilize the high-valent Mn species generated on HT.

Mn/HT and Mn/HT-*Ox* were treated with benzyl alcohol (**1**) in toluene at 100 °C under an Ar atmosphere. Mn/HT-*Ox* oxidized **1** to give benzaldehyde (**2**) stoichiometrically, together with the formation of a reduced Mn/HT-*Ox* (Fig. 1B, open green circles, and Fig. 2b), while Mn/HT resulted in an extremely low yield of **2**. Notably, when the reduced Mn/HT-Ox was treated under air, the reduced Mn species was easily re-oxidized to the original high-valent Mn species (Fig. 1B, filled red squares, and Fig. 2c). Moreover, the regenerated high-valent Mn species on Mn/HT-*Ox* could oxidize **1** again, affording **2** and the reduced Mn species (Fig. 1B, open red squares, and Fig. 2d). These phenomena indicate that the high-valent Mn species on the HT surface can oxidize **1**, and then, reduced Mn/HT-*Ox* can be re-oxidized by O_2 reversibly. The redox property of Mn/HT-*Ox* during the above treatment was also confirmed by EXAFS analysis: the peak intensity of Mn–O in FT increased then decreased when treatment with O_2 followed by **1** was conducted (Fig. 1S).

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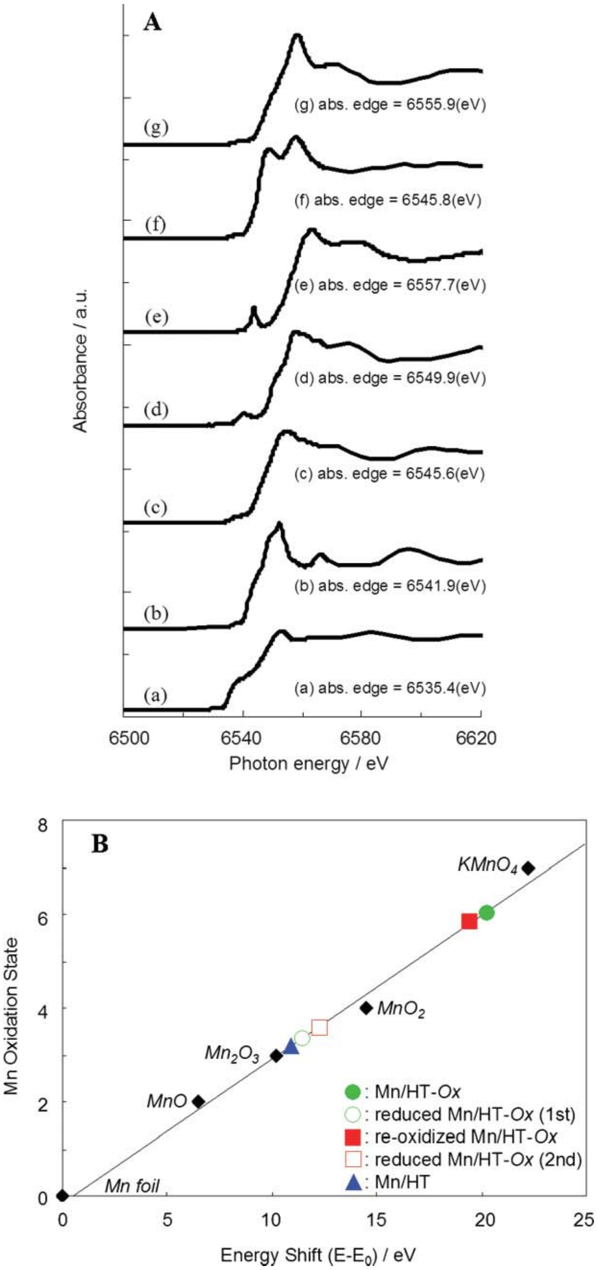


Fig. 1 (A) Mn K-edge XANES spectra of (a) Mn foil, (b) MnO, (c) Mn_2O_3, (d) β-MnO_2, (e) $KMnO_4$, (f) Mn/HT and (g) Mn/HT-*Ox* and (B) Mn valence *vs.* Mn K-edge position of experimental samples for reference Mn model compounds.

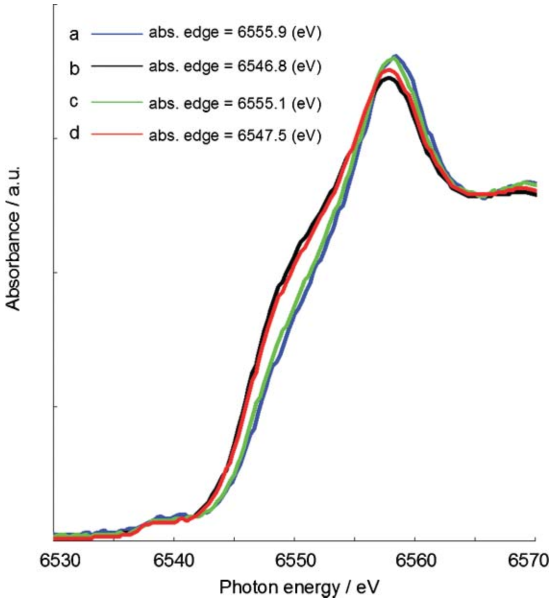


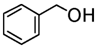
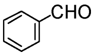
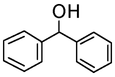
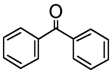
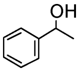
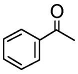
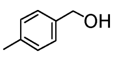
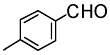
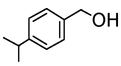
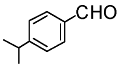
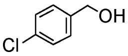
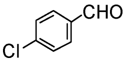
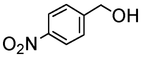
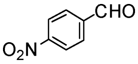
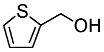
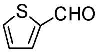
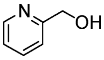
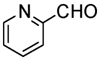
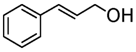
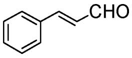
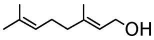
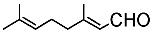
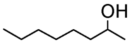
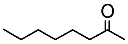
Fig. 2 Mn K-edge XANES spectra for the redox experiments. (a) Mn/HT-*Ox*, (b) after reduction of Mn/HT-*Ox* with alcohol under Ar, (c) re-oxidation of reduced Mn/HT-*Ox* under air, and (d) reduction of re-oxidized Mn/HT-*Ox* under the same conditions as in (b).

Encouraged by the above results, we next investigated the catalytic potential of Mn/HT-*Ox* for the aerobic oxidation of various alcohols. The results are shown in Table 1.[10] Mn/HT-*Ox* showed a high catalytic activity for the oxidation of benzylic alcohols under an atmospheric pressure of O_2 (Table 1, entries 1, 6–14).[11] For example, various benzylic alcohols with functional groups such as chlorine, nitro, and methyl at the *para* positions were converted to the corresponding aldehydes in excellent yields (entries 8–11). Heterocyclic alcohols also exhibited high reactivities (entries 12 and 13). In addition, cinnamyl alcohol gave the corresponding cinnamaldehyde as the sole product, while the C═C double bond was not affected by the reaction. Aliphatic and allylic alcohols such as 2-octanol and geraniol gave low yields of products (entries 15 and 16). The obtained results reveal that Mn/HT-*Ox* shows high catalytic activity for benzylic and cinnamyl alcohols, and low activity for aliphatic alcohols. The above substrate scope of Mn/HT-*Ox* is similar to those of stoichiometric Mn reagents such as $BaMnO_4$[12] and active MnO_2.[13] The great advantage of our newly developed Mn/HT-*Ox* is that catalytic amounts of Mn are sufficient to achieve the oxidation, while the conventional Mn reagents are needed in more than stoichiometric amounts.

Because of the heterogeneous character of the present oxidation, the Mn/HT-*Ox* catalyst was readily separated from the reaction mixture by simple filtration. In the aerobic oxidation of **1**, the recovered catalyst could be reused without any appreciable loss of its high activity or selectivity in three recycling experiments (Table 11, entries 2–4). During the above recycles, no leaching of Mn species in the filtrate was detected by an ICP method (detection limit 24 ppb). In addition, the recovered catalyst maintained its original high-valent Mn structure, as confirmed by XAFS.

In conclusion, high-valent Mn species could be created on the HT surface by treatment with KOH. The Mn compounds, which possessed redox properties when combined with alcohols and molecular oxygen, acted as efficient heterogeneous catalysts for the aerobic oxidation of various benzylic alcohols. The present preparation method is therefore a powerful protocol for the creation of high-valent Mn species on the surface of inorganic materials, and we hope that these Mn species may be versatile in catalyzing other oxidations.

Table 1 Aerobic oxidations of alcohols by Mn/HT-*Ox* catalyst[a]

Entry	Substrate	Product	Time (h)	Conv. (%)[b]	Yield (%)[b]
1			12	99	99
2[c]			12	99	99
3[d]			12	97	97
4[e]			12	99	99
5[f]			12	<1	<1
6			11	>99	>99
7			10	>99	98
8			11	>99	>99
9			16	>99	98
10			8	99	90
11			16	99	82
12			10	99	88
13			18	99	76
14			11	>99	>99
15			24	18	17
16			24	11	10

[a] Reaction conditions: Substrate (1 mmol), catalyst (Mn: 6 mol%), toluene (8 mL), O_2 atmosphere, 100 °C. [b] Determined by GC using an internal standard technique. [c] Cycle 1. [d] Cycle 2. [e] Cycle 3. [f] HT was used as catalyst.

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8 Extended X-ray absorption fine structure (EXAFS) studies showed that Mn/HT-*Ox* had no peak at 1.9 Å from a Mn–O shell which appeared in Mn/HT, and the magnitudes of two prominent peaks attributed to Mn–O and Mn–Mn shells around 1–3 Å in Mn/HT-*Ox* were greater than those in Mn/HT (Fig. 1S†). The inverse FT of these two peaks around 1–3 Å was well fitted using a Mn–O bond (1.9 Å) and a Mn–Mn bond (2.9 Å) with coordination numbers (CN) of 6.0 and 3.6, respectively. The above results suggest that highly dispersed planar manganese oxide clusters consisting of approximately seven Mn atoms are formed on the surface of Mn/HT-*Ox* (Table 1S†).

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11 To confirm whether the oxidation of alcohol occurred at the Mn species on the hydrotalcite solid, the Mn/HT-*Ox*, in the case of the aerobic oxidation of benzyl alcohol, was removed by filtration after *ca.* 50% conversion of benzyl alcohol at the reaction temperature. Further treatment of the filtrate under similar reaction conditions did not afford any product.

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