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COMMUNICATION

Nano-sized Mn oxide as a true catalyst for alcohol oxidation by a mononuclear manganese(II) complex†

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Herein new findings for alcohol-oxidizing activity of a mononuclear manganese(II) complex are reported. We propose that nano-sized Mn oxide is a true catalyst for the oxidation of some alcohols to aldehydes in the presence of Oxone (2KHSO₅·KHSO₄·K₂SO₄) as an oxidant.

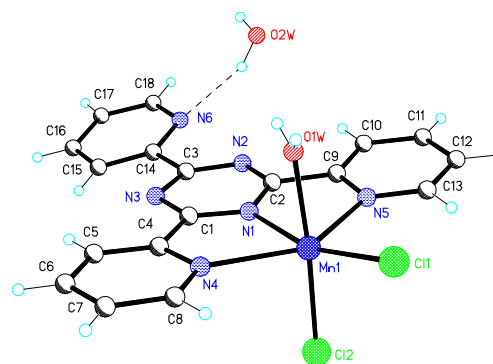
Efficient and stable catalysts toward the selective oxidation of various chemicals into useful products are necessary for industrial applications. Mn is low-cost, abundant, and environmentally friendly, and thus trying to find efficient Mn based catalysts for many reactions is very promising.¹⁻⁶ For example, Costas et al. reported a Mn catalyst with a tetradentate ligand derived from triazacyclononane with high catalytic activity toward epoxidation reactions using peracetic acid as oxidant.^{6b} The catalyst is selective toward aliphatic cis-olefins.^{6b} Comba et al. reported that mononuclear nonheme Mn(IV)=O complexes with two isomers of a bispidine ligand show reactivity toward hydrogen-atom abstraction and sulfoxidation reactions.^{6c} Goldberg et al. considered hydrogen-atom transfer to a Mn(V)=O corrolazine complex.^{6d} Enantioselective epoxidation of unfunctionalized olefins with Mn Schiff base complexes were also considered by Jacobsen's group.^{6e} It is interesting to note that K. N. Parida et al. reported the oxidation of benzyl alcohols, benzyl halides, and alkylbenzenes to their corresponding oxidation products by stirring/heating of the reactants and Oxone in acetonitrile/water (1:1, v/v).^{6f} Although such procedure is limited to substrates that do not contain sensitive functionalities and heteroaromatic rings, the method without catalyst is promising, simple and practical.^{6f}

On the other hand, numerous Mn complexes with terpyridine and oligopyridines ligands have been investigated because of their interesting structural, redox, photochemical, catalytic, and water oxidation properties.^{1,7-9}

Recently, the ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) is used as a potential spacer, which functions as a bis-bidentate or as a tridentate and a bidentate bridging unit. The ligand is stable towards nucleophilic attack and has been used as an analytical reagent for various metal ions. This tridentate ligand forms hepta-coordinate complexes with Mn(II) with small chelate bite angles.¹⁰⁻¹⁴

The oxidation of alcohols to carbonyl compounds is among important reactions. The usual oxidants for the reaction are

permanganate and dichromate salts. However, these oxidants are moderately expensive, toxic, corrosive, unstable, and show no selectivity, and require dangerous procedures for preparation as well as over-oxidation to carboxylic acids and moisture-sensitivity. In 2010, the efficient and selective oxidation of alcohols to aldehydes and ketones using a mononuclear Mn complex (**1**) (Scheme 1) with tptz ligand under mild and biphasic conditions (CH₂Cl₂/H₂O) at room temperature with Oxone as oxidant was reported.¹³ To design and synthesize more efficient catalysts for alcohol oxidation, findings on the mechanism of oxidation and the true catalyst for this reaction is necessary. Molecular mechanisms are usually proposed for these complexes and a dinuclear Mn₂^{III,IV} was observed by EPR as an intermediate to oxidize alcohols.¹³

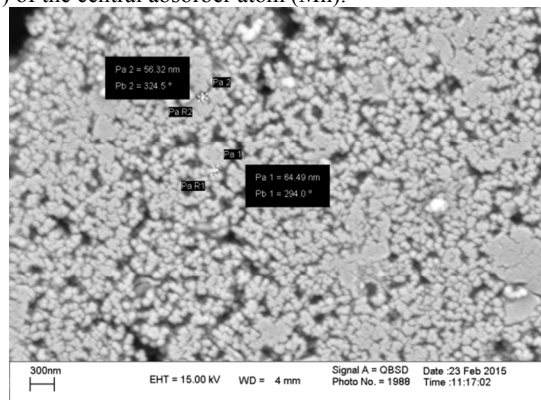


Scheme 1 The structure of Mn(II)(tptz)Cl₂(H₂O). Image and caption is from ref. 13. Adapted with permission from ref. 13. Copyright (2010) by Springer.

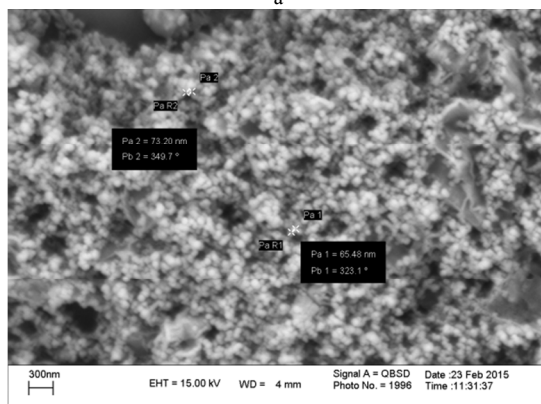
However, using dynamic light scattering, we found that immediately (2-3 seconds) after the reaction of Mn(II)(tptz)Cl₂(H₂O) with Oxone (see ref. 13 for experimental condition), large amounts of nanoparticles are formed. Dynamic light scattering (DLS) from the mixing **1** and Oxone shows that agglomerated particles (ca. 1 μm) form after a few minutes (Fig. S1 and S2, ESI†). Such particles were observed even when we performed the experiments in acetonitrile using Oxone® tetrabutylammonium salt and in the absence of water (Fig. S3, ESI†). SEM images showed that the

morphologies of particles significantly depend on the conditions of the reaction such as the concentration of oxidant, complex, and also solvent (Fig. 1 and Fig. S4-S7, ESI†).

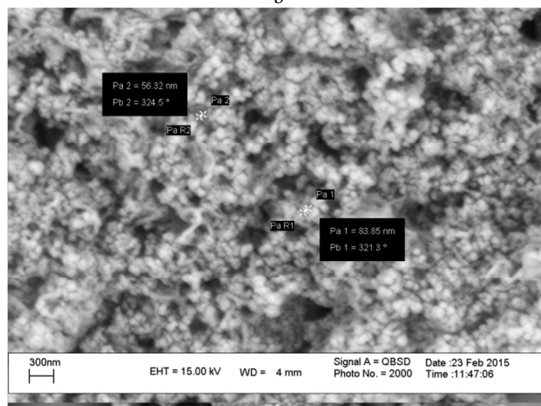
The solid is too amorphous to be detected by X-ray diffraction (XRD). To further characterize the solid, X-ray absorption near edge structure (XANES) spectra were used (Fig. 2). The results show two major peaks; the main intense peak is the rising edge or edge peak (E_0) which contains information about the average oxidation state (AOS) of the central absorber atom (Mn).



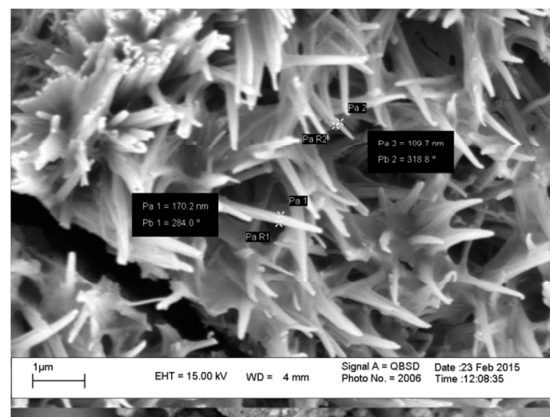
a



b



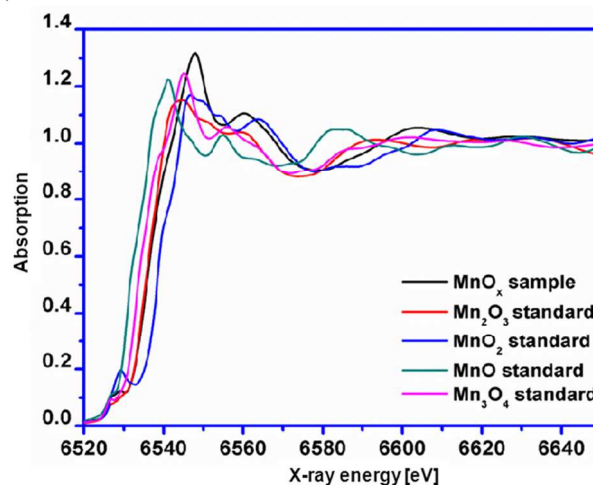
c



d

Fig. 1 SEM image from mixing **1** (1 mL, 4.21 mM), benzyl alcohol (0.25 mL) and Oxone (2 mL, 81 mM) in water after 10 minutes (a). SEM image from mixing **1** (2 mL, 4.21 mM), benzyl alcohol (0.25 mL) and Oxone (1 mL, 81 mM) in water after 10 minutes (b). SEM image from mixing **1** (4 mL, 4.21 mM), benzyl alcohol (0.25 mL) and Oxone (0.5 mL, 81 mM) in water after 10 minutes (c). SEM image from mixing **1** (4 mL, 4.21 mM), benzyl alcohol (0.25 mL) and Oxone® tetrabutylammonium (0.5 mL, 26 mM) in acetonitrile after 10 minutes. The centrifuged particles were washed carefully with solvent before considering by SEM.

In order to obtain the average oxidation state of Mn we ran a series of Mn oxide standards. By plotting the E_0 values versus oxidation states of these standards, we obtained the standard calibration curve as shown in Fig. 2c. Data of Fig. 2c shows that the MnO_x sample has an AOS value of 3.19. This sample has mixed valencies of Mn(III) and Mn(IV) but the Mn(III) is more predominant than Mn(IV). One possible structure for Mn_2O_3 is the cubic bixbyite structure which can undergo a phase transition to an orthorhombic phase. The second peak is the pre-edge peak which is the peak before the most intense one. By comparing the MnO_x sample with standards (especially the Mn_2O_3 and MnO_2) we observed the presence of the Mn(IV) pre-edge peak in the range of energy of 6525-6530 eV for the MnO_x sample which is considered as evidence for the presence of Mn(IV) in the structure (Fig. 2). Such structure is different from the phase proposed by Pourbaix diagram¹⁴⁻¹⁹ because high concentrations of organic compounds from solvents or substrate under this condition inhibit the formation of high valent Mn oxides (such as layered Mn oxide).



a

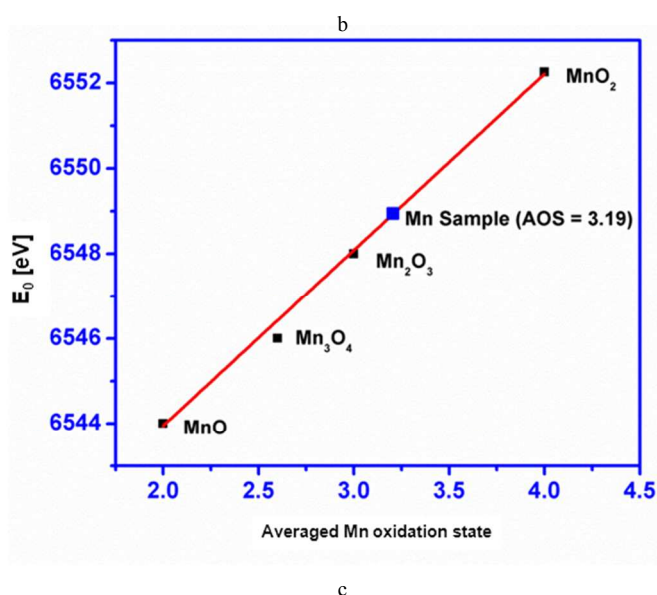
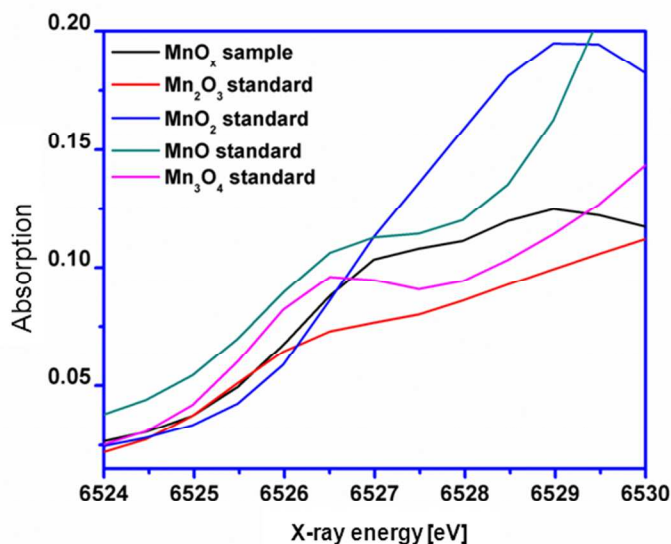


Fig. 2 X-ray adsorption spectra for the sample from mixing **1** (1 mL, 4.21 mM), benzyl alcohol (0.25 mL) and Oxone (2 mL, 81 mM) in water after 10 minutes compared to MnO_x standards (a). The pre-edge peak of the MnO_x sample as compared to MnO_x standards (b). Standard calibration curve for the average oxidation state of MnO_x sample value is 3.19 (c).

The Fourier transform of the extended X-Ray absorption fine structure (EXAFS) data of the MnO_x sample showed the most intense peak for Mn-O and Mn-Mn bond distances (**Fig. 3**). The position of the Mn-O bond in the MnO_x sample is the same for the standard Mn₂O₃ but we observed a shift to smaller Mn-Mn bond distances, which might be due to strain of the Mn-O-Mn bonds by incorporation of Mn(IV) in the bixbyite structure (**Fig. 3**).

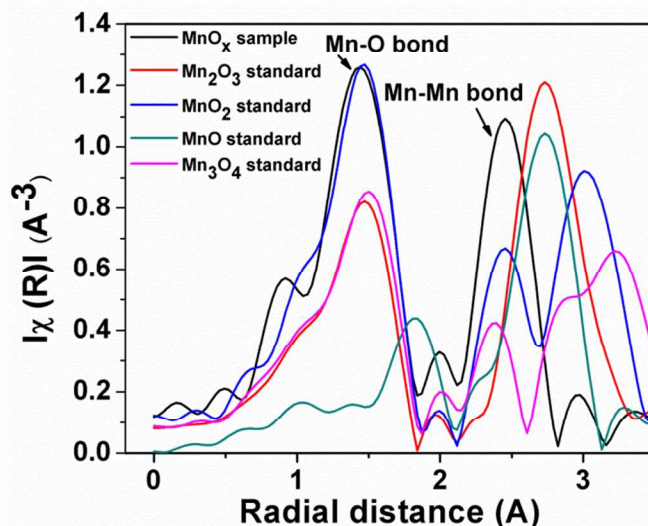
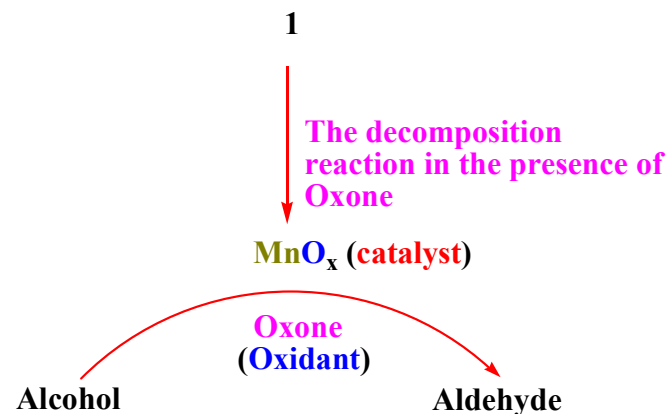


Fig. 3 Fourier transform of the EXAFS with possible bonding interactions for the most intense peaks from mixing **1** (1 mL, 4.21 mM), benzyl alcohol (0.25 mL) and Oxone (2 mL, 81 mM) in water after 10 minutes.

The mechanism of Mn oxide formation by **1** is not known but in according to EPR spectroscopy¹³ before Mn oxide formation, accumulation of mononuclear complexes such as a Mn₂^{III,IV} occurs. In the next step we tried to answer to the question whether this nano-sized Mn oxide is a true catalyst or is one of the products of the decomposition reaction. In this regard, we used the centrifuged particles from the reaction of Oxone and **1** as a catalyst toward alcohol oxidation under a condition similar to previously reported conditions¹³ by **1**. The results show that these nano-sized Mn oxides have efficiency and selectivity for alcohol oxidation (**Table 1**).

Table 1

Thus, at least a few seconds after mixing Oxone and the complex, one of the true catalysts for alcohol oxidation is nano-sized Mn oxides (**Scheme 2**). Interestingly, alcohol-oxidation reactions with typical active Mn oxide²⁰ in the absence of organic ligand compounds show higher activities but lower selectivity (**Table 1**). We propose that the ligand around Mn oxide particles has an important effect on formation of Mn oxide not only from a morphological view but also activity and selectivity towards alcohol oxidation. The detection of such nanoparticles is not easy in low concentrations by the naked eye especially in the first seconds of the reaction.



Scheme 2 The proposed mechanism for the oxidation of some alcohols to aldehydes in the presence of Oxone (2KHSO₅·KHSO₄·K₂SO₄) as an oxidant and **1**.

In conclusion, we considered the alcohol oxidation of a Mn complex with 2,4,6-tris(2-pyridyl)-1,3,5-triazine ligand in the presence of Oxone. After a few seconds, we observed a solid in solution. Characterization of the solid show this material is a nano-structured Mn oxide. The Mn oxide also shows alcohol activity and selectivity to **1**. We propose that in the reaction of metal complex with strong oxidants, the true catalyst should be carefully checked because usually oxidizing agents can decompose ligands and release metal ions, which could form metal oxide as an efficient catalyst for related reactions. These results are also important to design and synthesis of metal oxides with high selectivity.

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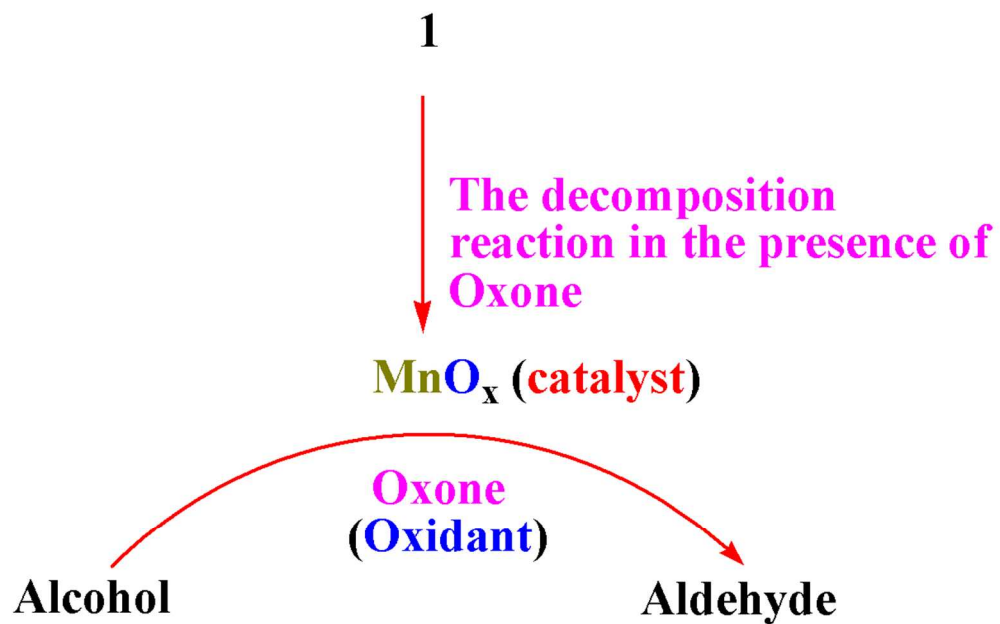
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†Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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We propose that nano-sized Mn oxide is a true catalyst for the oxidation of some alcohols to aldehydes in the presence of a mononuclear manganese(II) complex, and Oxone as an oxidant.