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Catalytic O_2 Evolution from Water Induced by Adsorption of $[(OH_2)(Terpy)Mn(\mu\text{-}O)_2Mn(Terpy)(OH_2)]^{3+}$ Complex onto Clay Compounds

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Water oxidation to evolve O_2 (eq 1) is an important and fundamental chemical reaction in photosynthesis. This reaction is catalyzed by a unique manganese enzyme referred to as oxygen-evolving complex (OEC), whose active site is comprised of an oxo-bridged tetramanganese cluster.[1−4] Though synthetic manganese−oxo complexes have guided thoughts on the chemical and electronic structures of the OEC,[1,2] most of the structural models have not catalyzed water oxidation to evolve O_2 in a homogeneous aqueous solution so far.[5,6]

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{1}$$

Limburg et al. reported O_2 evolution from water by the reaction of $[(OH_2)(terpy)Mn^{III}(\mu\text{-}O)_2Mn^{IV}(terpy)(OH_2)]^{3+}$ (terpy = 2,2′:6′,2″-terpyridine) (**1**) with NaClO or $KHSO_5$.[7,8] However, the mechanism of the O_2 formation is completely unclear, including even disproportionation of $2ClO^- \rightarrow O_2 + 2Cl^-$, which is known to be catalyzed by Mn^{II} and other Lewis acids.[5] To exclude this possibility, O_2 evolution experiments should be conducted using oxidizing agents that do not contain any oxygen atoms.

We reported that in water oxidation by $[Ru(NH_3)_5Cl]^{2+}$, a favorable intermolecular interaction is provided for the cooperative catalysis in a solid polymer matrix relative to a homogeneous solution to increase the catalytic activity.[9] This result encouraged us to design a heterogeneous catalysis system as a strategy for realizing catalytic O_2 evolution from water by manganese−oxo complexes. The adsorption of **1** onto clay compounds yielded a successful functional mimic for OEC. Herein we report that the reaction of **1** with a Ce^{IV} oxidant leads to decomposition of **1** to MnO_4^- without O_2 evolution in an aqueous solution but catalytically produces O_2 from water when **1** is adsorbed on clay compounds.

Water oxidation by **1** was investigated in a solution using a Ce^{IV} oxidant. Figure 1a shows the time course of the amount of O_2 involved in the aqueous solution containing 0.42 mM **1** and a large excess of Ce^{IV} ion (50 mM) measured by a Clark-type oxygen electrode. O_2 evolution was not observed compared with a blank experiment without **1** (Figure 1b), nor was O_2 evolved using a 10-fold larger concentration of **1** (5 mM **1**, 100mM Ce^{IV}). It was concluded that the reaction of **1** with a Ce^{IV} oxidant evolves no O_2,[10] which contrasts markedly with the catalytic O_2 evolution reported previously using **1** and either NaClO or $KHSO_5$ as oxidants.[7,8] A detailed re-examination of the proposed O_2 evolution mechanism should be required in the previous system.

Surprisingly, when a comparable amount (0.72 μmol) of **1** as used in solution was adsorbed onto Kaolin clay, the addition of a large excess of Ce^{IV} ion to its aqueous suspension produced a significant amount of O_2, as shown in Figure 1c. The control experiment using the same amount of Kaolin clay without **1** did not exhibit any O_2 evolution (Figure 1d). A prolonged experiment over 7 days using a gas chromatograph for O_2 detection gave a turnover number (TN) of 13.5 ± 1.1 (average for three trials) under the following conditions: 0.46 μmol of **1**/50 mg of clay, 100 mM Ce^{IV}, 10 mL. These results evidently reveal that adsorbed **1** catalyzes O_2 evolution.

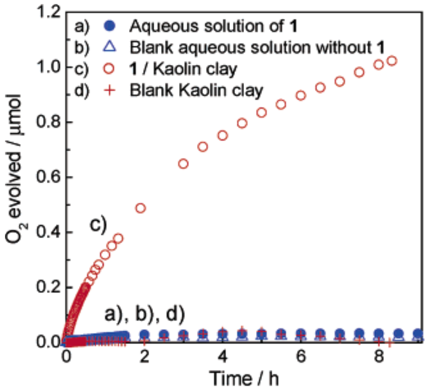

Figure 1. Time courses of the amount of O_2 evolved in reaction of **1** and a 50 mM Ce^{IV} oxidant. (a) Aqueous solution of **1** (0.84 μmol; 0.42 mM). (b) Aqueous solution without **1** for a blank experiment. (c) Aqueous suspension of Kaolin clay (75 mg) adsorbing **1** (0.72 μmol (0.46 mg); 9.6 μmol (6.2 mg)/clay g). (d) Aqueous suspension of Kaolin clay (75 mg) without **1** for a control experiment; liquid volume, 2.0 mL; pH = 1.0.

To identify an oxygen atom source for O_2 evolution, ^{18}O-labeling experiments were conducted using $H_2{}^{18}O$. The evolved gas was analyzed on an electron-impact-ionization mass (EIMS) spectrometer. The experiments in $H_2{}^{18}O$ media gave peaks at $m/z = 34$ and 36, corresponding to $^{16}O^{18}O$ and $(^{18}O)_2$, in addition to the peak for $(^{16}O)_2$ at $m/z = 32$, in contrast to no peaks at $m/z = 34$ and 36 for natural abundance water (Figure S1). The content fraction of ^{18}O atom in O_2 evolved is consistent with the ^{18}O content in the water. (The content fractions are 23 and 42 for 23.8 and 47.5 v/v % $H_2{}^{18}O$, respectively; see Table S1.) The O_2 evolution was thus confirmed to come exclusively from water.

To define the catalysis by **1** adsorbed on the clay, similar O_2 evolution experiments were extended to various manganese species, including manganese oxides (MnO_2 and Mn_2O_3), Mn^{2+}, Mn^{3+}, and MnO_4^- ions in solutions, as well as adsorbed Mn^{2+}, Mn^{3+}, and $terpyH_n{}^{n+}$ on Kaolin clay. In none of the trials using these species was O_2 evolution detected. These results show the uniqueness of the catalysis by **1** adsorbed on the clay.

UV−visible diffuse reflectance and X-ray absorption spectroscopic measurements were carried out to characterize **1** adsorbed on clay (Figures S2−S6). The diffuse reflectance spectrum of the **1**/clay adsorbate was similar to the absorption spectrum of the $Mn^{IV}-Mn^{IV}$ state in water rather than the $Mn^{III}-Mn^{IV}$ state. The oxidation to $Mn^{IV}-Mn^{IV}$ was supported by Mn K-edge X-ray absorption near-edge structure (XANES) spectroscopic data in which the Mn K-edge shifted to a higher energy region by 3.2 eV at the peak versus that for **1** as a powder. Mn K-edge extended X-ray absorption fine structure (EXAFS) spectrum of the **1**/clay adsorbate did not show an appreciable change compared with that

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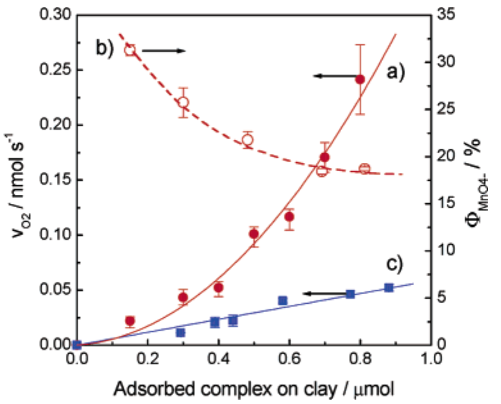

Figure 2. Plots of initial rate (v_{O_2} (mol s^{-1})) of O_2 evolution and yield ($\Phi_{MnO_4^-}$) of MnO_4^- formation versus the amount of the adsorbed complex on clay; (a) v_{O_2} for **1** (closed red circle), (b) $\Phi_{MnO_4^-}$ for **1** (open red circle), and **(**c) v_{O_2} for **2** (closed blue square). Kaolin clay amount was 75 mg. The conditions are indicated in Figure 1.

for **1** as a powder. These data could suggest that **1** is autoxidized to the $Mn^{IV}-Mn^{IV}$ state on the clay possibly by a silicate layer without a significant change in its original coordination structure. Preliminary X-ray absorption spectroscopic data of the **1**/clay adsorbate treated with an Ce^{IV} oxidant indicated that the $Mn^{IV}-Mn^{IV}$ species exists before and after the catalysis for 30 min, in contrast to the further oxidized species suggested by the corresponding data for **1** with a Ce^{IV} solution.

The visible absorption spectral change of the aqueous solution containing **1** and a large excess of Ce^{IV} ion was followed to see what reactions are happening in solution. The spectral change indicated the formation of MnO_4^- from **1**. The kinetic analysis showed that a bimolecular reaction of **1** is involved in a rate-determining step of the MnO_4^- formation (Figures S7 and S8). It is possibly formed by disproportionation of the high oxidation state. The yield ($\Phi_{MnO_4^-}$) of MnO_4^- formed during a 30 min reaction was 30−86% (0.05−2 mM **1**, 50 mM Ce^{IV}, 2.0 mL) in the solution. For the **1**/clay adsorbate, MnO_4^- formation was also observed in the liquid phase after the removal of the **1**/clay adsorbate by centrifugation. However, $\Phi_{MnO_4^-}$ (18−32%; 0.15−0.81 µmol **1**/75 mg clay, 2.0 mL) is much less than in the homogeneous solution,[11] showing that adsorption of **1** onto the clay significantly suppresses their disproportionation to form MnO_4^-.

The plots of the initial O_2 evolution rates (v_{O_2} (mol s^{-1})) vs the amount of **1** adsorbed on the clay gave upward curvature in Figure 2a, showing that the specific O_2 evolution rate increases as the amount of **1** on the clay increases. The kinetic analysis of v_{O_2} suggests that the predominant O_2 evolution is produced by a bimolecular reaction of adsorbed **1** (see Supporting Information). Most likely, two molecules of **1** cooperatively catalyze O_2 evolution between complexes adsorbed in close proximity to each other on the clay. In contrast, $\Phi_{MnO_4^-}$ decreased with the amount of **1**, as illustrated in Figure 2b. There could be local adsorption equilibria of **1** at the interface between the clay and liquid phase. MnO_4^- prefers to be formed in the liquid-phase rather than on the clay since the MnO_4^- formation is suppressed by the adsorption of **1** on the clay (vide supra). As the amount of adsorbed **1** increases, the fraction of **1** subject to MnO_4^- formation decreases in competition with facilitated bimolecular O_2 evolution.[12] The MnO_4^- formation might still occur on the clay, but it could be much slower relative to the O_2 evolution.

To evaluate the mechanism of the O_2 evolution by **1**, $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3+}$ (**2**), which has a structure comparable with **1** but no terminal water ligands, was used for similar experiments in both solution and on Kaolin clay. O_2 was evolved for **2**/clay, but not at all for the solution. However, the saturated amount of O_2 was 0.51 µmol at 99 h for **2**/clay, and the TN (0.63) of **2** is less than unity. The v_{O2} for **2** (Figure 2c) is much lower than that for **1** comparing the same amount of the adsorbed complex under the conditions employed.[13] These results suggest that the terminal water ligands are involved in the catalysis. It may take place by intermolecular coupling of $Mn^V=O$ that could be formed by successive oxidation of a terminal water ligand on **1**. However, no evidence for involvement of $Mn^V=O$ in the catalysis is obtained. The adsorption of **1** onto the clay suppressed the decomposition to form MnO_4^- and results in a highly concentrated condition compared with solutions, thus facilitating the cooperative catalysis to form O_2. This could account for the adsorption-induced catalytic activity.

The adsorption of **1** on Montmorillonite MK10 clay also produced catalytic O_2 evolution from water, extending the generality of the adsorption-induced catalytic activity of **1**. The plots of v_{O_2} vs the amount of adsorbed **1** on Montmorillonite also provided an upward curvature (Figure S9). The observed catalytic activity depends on the degree of the concentration onto clays, and the intrinsic catalytic activity of **1** is basically the same between both clays. These results support the cooperative interaction proposed in the adsorption-induced catalytic activity of **1**. The present paper illustrates that the adsorption of **1** onto a heterogeneous matrix is required for catalytic O_2 evolution from water.

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Supporting Information Available: Detailed experimental procedures for catalysis, spectroscopic data (UV−vis, XANES, and EXAFS) of **1**/clay adsorbate, kinetic analysis for MnO_4^- formation, and v_{O_2} data for **1** or **2**/Montmorillonite (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) A similar experiment using the aqueous solution containing 0.42 mM **1** and 50 mM Ce^{IV} at pH = 3.0 did not yield O_2 evolution at all, though **1** is intact at pH = 3−6 in the solution.
(11) MnO_4^- formed in the clay should come out of the anionic clay to the bulk solution. We confirmed that MnO_4^- cannot be adsorbed on clay at all.
(12) Without the catalytic activity of **1** adsorbed on clay, the $\Phi_{MnO_4^-}$ could increase linearly with the adsorption amount of **1** by the increased bimolecular decomposition of **1**. The $\Phi_{MnO_4^-}$ decrease suggests that the O_2 evolution is correlated to MnO_4^- formation. This could be explained by the O_2 evolution by adsorbed **1** that competes with the bimolecular decomposition to form MnO_4^-.
(13) v_{O_2} increased linearly with the amount of **2** on Kaolin (Figure 2c), indicating unimolecular O_2 evolution in contrast with bimolecular catalysis of **1**. The unimolecular O_2 evolution might be explained by either O−O coupling of di-µ-O bridges or attack of outer-sphere water onto a µ-O bridge in high oxidation species, probably including µ-O^- radical bridges. A coupling of di-µ-O^- radical bridges in a $Mn(\mu\text{-}O)_2Mn$ unit was proposed by Yachandara et al. as a possible mechanism of O_2 production in OEC based on EXAFS results.

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