

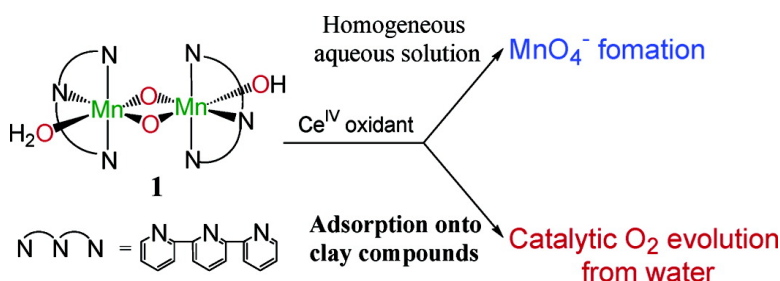
Communication

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Masayuki Yagi, and Komei Narita

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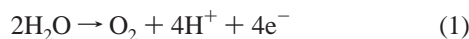
Catalytic O₂ Evolution from Water Induced by Adsorption of [(OH)₂(Terpy)Mn(μ-O)₂Mn(Terpy)(OH)₂]³⁺ Complex onto Clay Compounds

Masayuki Yagi* and Komei Narita

Faculty of Education and Human Sciences, and Center for Transdisciplinary Research, Niigata University, 8050 Ikarashi-2, Niigata 950-2181, Japan

Received November 25, 2003; E-mail: yagi@ed.niigata-u.ac.jp

Water oxidation to evolve O₂ (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 O₂ in a homogeneous aqueous solution so far.^{5,6}



Limburg et al. reported O₂ evolution from water by the reaction of [(OH)₂(terpy)Mn^{III}(μ-O)₂Mn^{IV}(terpy)(OH)₂]³⁺ (terpy = 2,2':6',2''-terpyridine) (**1**) with NaClO or KHSO₅.^{7,8} However, the mechanism of the O₂ formation is completely unclear, including even disproportionation of 2ClO[–] → O₂ + 2Cl[–], which is known to be catalyzed by Mn^{II} and other Lewis acids.⁵ To exclude this possibility, O₂ evolution experiments should be conducted using oxidizing agents that do not contain any oxygen atoms.

We reported that in water oxidation by [Ru(NH₃)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 O₂ 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 MnO₄[–] without O₂ evolution in an aqueous solution but catalytically produces O₂ 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 O₂ evolved 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. O₂ evolution was not observed compared with a blank experiment without **1** (Figure 1b), nor was O₂ evolved using a 10-fold larger concentration of **1** (5 mM **1**, 100 mM Ce^{IV}). It was concluded that the reaction of **1** with a Ce^{IV} oxidant evolves no O₂,¹⁰ which contrasts markedly with the catalytic O₂ evolution reported previously using **1** and either NaClO or KHSO₅ as oxidants.^{7,8} A detailed re-examination of the proposed O₂ 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 O₂, as shown in Figure 1c. The control experiment using the same amount of Kaolin clay without **1** did not exhibit any O₂ evolution (Figure 1d). A prolonged experiment over 7 days using a gas chromatograph for O₂ detection gave a turnover number (TN) of 13.5 ± 1.1 (average for three trials) under the

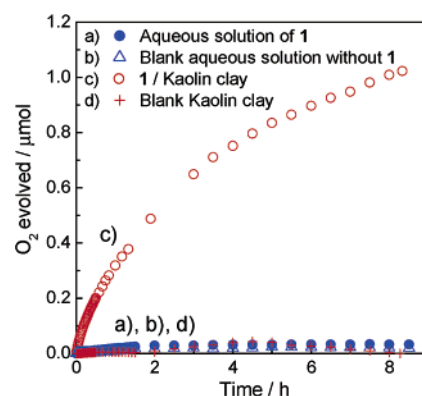


Figure 1. Time courses of the amount of O₂ evolved in reaction of **1** and a 50 mM Ce^{IV} oxidant. (a) Aqueous solution of **1** (0.84 μmol; 0.42 mM). (b) Aqueous solution without **1** for a blank experiment. (c) Aqueous suspension of Kaolin clay (75 mg) adsorbing **1** (0.72 μmol (0.46 mg); 9.6 μmol (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.

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 O₂ evolution.

To identify an oxygen atom source for O₂ evolution, ¹⁸O-labeling experiments were conducted using H₂¹⁸O. The evolved gas was analyzed on an electron-impact-ionization mass (EIMS) spectrometer. The experiments in H₂¹⁸O media gave peaks at *m/z* = 34 and 36, corresponding to ¹⁶O¹⁸O and (¹⁸O)₂, in addition to the peak for (¹⁶O)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 ¹⁸O atom in O₂ evolved is consistent with the ¹⁸O content in the water. (The content fractions are 23 and 42 for 23.8 and 47.5 v/v % H₂¹⁸O, respectively; see Table S1.) The O₂ evolution was thus confirmed to come exclusively from water.

To define the catalysis by **1** adsorbed on the clay, similar O₂ evolution experiments were extended to various manganese species, including manganese oxides (MnO₂ and Mn₂O₃), Mn²⁺, Mn³⁺, and MnO₄[–] ions in solutions, as well as adsorbed Mn²⁺, Mn³⁺, and terpyH_{*n*}^{*n+*} on Kaolin clay. In none of the trials using these species was O₂ 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

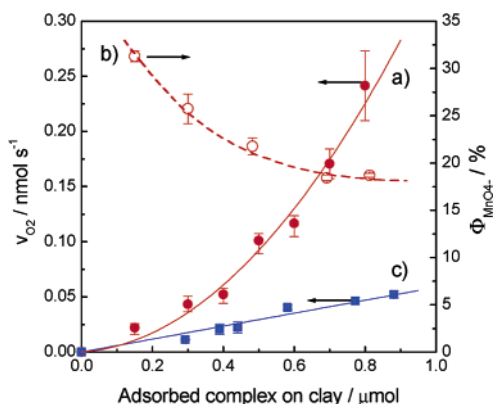


Figure 2. Plots of initial rate (v_{O_2} (mol s⁻¹)) of O₂ evolution and yield ($\Phi_{\text{MnO}_4^-}$) of MnO₄⁻ formation versus the amount of the adsorbed complex on clay; (a) v_{O_2} for **1** (closed red circle), (b) $\Phi_{\text{MnO}_4^-}$ for **1** (open red circle), and (c) v_{O_2} for **2** (closed 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 MnO₄⁻ from **1**. The kinetic analysis showed that a bimolecular reaction of **1** is involved in a rate-determining step of the MnO₄⁻ formation (Figures S7 and S8). It is possibly formed by disproportionation of the high oxidation state. The yield ($\Phi_{\text{MnO}_4^-}$) of MnO₄⁻ 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, MnO₄⁻ formation was also observed in the liquid phase after the removal of the **1**/clay adsorbate by centrifugation. However, $\Phi_{\text{MnO}_4^-}$ (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 MnO₄⁻.

The plots of the initial O₂ 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 O₂ evolution rate increases as the amount of **1** on the clay increases. The kinetic analysis of v_{O_2} suggests that the predominant O₂ evolution is produced by a bimolecular reaction of adsorbed **1** (see Supporting Information). Most likely, two molecules of **1** cooperatively catalyze O₂ evolution between complexes adsorbed in close proximity to each other on the clay. In contrast, $\Phi_{\text{MnO}_4^-}$ 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. MnO₄⁻ prefers to be formed in the liquid-phase rather than on the clay since the MnO₄⁻ 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 MnO₄⁻ formation decreases in competition with facilitated bimolecular O₂ evolution.¹² The MnO₄⁻ formation might still occur on the clay, but it could be much slower relative to the O₂ evolution.

To evaluate the mechanism of the O₂ evolution by **1**, [(bpy)₂-Mn^{III}(μ-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. O₂ was evolved

for **2**/clay, but not at all for the solution. However, the saturated amount of O₂ was 0.51 μmol at 99 h for **2**/clay, and the TN (0.63) of **2** is less than unity. The v_{O_2} 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 MnO₄⁻ and results in a highly concentrated condition compared with solutions, thus facilitating the cooperative catalysis to form O₂. This could account for the adsorption-induced catalytic activity.

The adsorption of **1** on Montmorillonite MK10 clay also produced catalytic O₂ 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 O₂ 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 MnO₄⁻ 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 O₂ evolution at all, though **1** is intact at pH = 3–6 in the solution.
- (11) MnO₄⁻ formed in the clay should come out of the anionic clay to the bulk solution. We confirmed that MnO₄⁻ cannot be adsorbed on clay at all.
- (12) Without the catalytic activity of **1** adsorbed on clay, the $\Phi_{\text{MnO}_4^-}$ could increase linearly with the adsorption amount of **1** by the increased bimolecular decomposition of **1**. The $\Phi_{\text{MnO}_4^-}$ decrease suggests that the O₂ evolution is correlated to MnO₄⁻ formation. This could be explained by the O₂ evolution by adsorbed **1** that competes with the bimolecular decomposition to form MnO₄⁻.
- (13) v_{O_2} increased linearly with the amount of **2** on Kaolin (Figure 2c), indicating unimolecular O₂ evolution in contrast with bimolecular catalysis of **1**. The unimolecular O₂ 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(μ-O)₂Mn unit was proposed by Yachandara et al. as a possible mechanism of O₂ production in OEC based on EXAFS results.

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