Distribution of manganese species in an oxidative dimerization reaction of a bis-terpyridine mononuclear manganese (II) complex and their heterogeneous water oxidation activities

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Abstract

Heterogeneous water oxidation catalyses were studied as a synthetic model of *oxygen evolving complex* (OEC) in photosynthesis using mica adsorbing various manganese species. Distribution of manganese species formed in the oxidative dimerization reaction of $[\text{Mn}^{\text{II}}(\text{terpy})_2]^{2+}$ (terpy = 2,2':6',2''-terpyridine) (**1'**) with various oxidants in water was revealed. **1'** was stoichiometrically oxidized to form di- μ -oxo dinuclear manganese complex, $[(\text{OH}_2)(\text{terpy})\text{Mn}^{\text{III}}(\mu\text{-O})_2\text{Mn}^{\text{IV}}(\text{terpy})(\text{OH}_2)]^{3+}$ (**1**) by KMnO_4 as an oxidant. When Oxone and Ce(IV) oxidants were used, the further oxidation of **1** to $[(\text{OH}_2)(\text{terpy})\text{Mn}^{\text{IV}}(\mu\text{-O})_2\text{Mn}^{\text{IV}}(\text{terpy})(\text{OH}_2)]^{4+}$ (**2**) was observed after the oxidative dimerization reaction of **1'**. The mica adsorbates with various composition of **1'**, **1** and **2** were prepared by adding mica suspension to the various oxidant-treated solutions followed by filtration. The heterogeneous water oxidation catalysis by the mica adsorbates was examined using a Ce(IV) oxidant. The observed catalytic activity of the mica adsorbates corresponded to a content of **1** (**1_{ads}**) adsorbed on mica for KMnO_4 - and Oxone-treated systems, indicating that **1'** (**1'_{ads}**) and **2** (**2_{ads}**) adsorbed on mica do not work for the catalysis. The kinetic analysis suggested that **1_{ads}** works for the catalysis through cooperation with adjacent **1_{ads}** or **2_{ads}**, meaning that **2_{ads}** assists the cooperative catalysis by **1_{ads}** though **2_{ads}** is not able to work for the catalysis alone. For the Ce(IV)-treated system, O_2 evolution was hardly observed although the sufficient amount of **1_{ads}** was contained in the mica adsorbates. This was explained by the impeded penetration of Ce(IV) ions (as an oxidant for water oxidation) into mica by Ce^{3+} cations (generated in oxidative dimerization of **1'**) co-adsorbed with **1_{ads}**.

Introduction

For photosynthesis in nature, O₂ evolution from water is catalyzed by OEC composed of a tetranuclear manganese cluster. Recent X-ray diffraction[1-5] and extended X-ray absorption fine structure (EXAFS)[6, 7] studies have revealed the detailed structure of OEC. The crystal structure of PS II at a resolution of 1.9 Å displayed that the tetramanganese cluster (Mn₄CaO₅) containing an asymmetric Mn₃CaO₄ cubane core is located together with all of their ligands in the OEC center,[5] and very recently the core structure was refined based on a ‘radiation-damage-free’ structure of PSII determined using femtosecond X-ray pulses [8].

Many synthetic manganese complexes as an OEC model have been synthesized for X-ray crystallography, EXAFS, electron paramagnetic resonance (EPR), and magnetic susceptibility studies to provide important insights into the structure of OEC in PS II.[9-21] Although manganese complexes have thus made significant contributions to the structure and the oxidation states of OEC, very limited manganese complexes act as a functional model that is capable of catalyzing water oxidation.[22-37] Molecular aspects and activities of synthetic catalysts for water oxidation have generally been investigated in a homogeneous solution system to gain essential aspects of the catalysts, although the OEC center is confined in heterogeneous protein matrixes. Kaneko *et al* reported pioneering works on heterogeneous water oxidation catalysis by manganese and ruthenium complexes on layer compounds in the late 1980s.[38, 39]

O₂ evolution by **1** in reactions with oxygen donor agents in a homogeneous solution were first reported.[22, 23] We reported the heterogeneous water oxidation catalysis of **1**_{ads} on layer compounds such as kaolin, mica and montmorillonite (Mt).[26, 40-42] The kinetic analysis of O₂ evolution suggested that the catalysis requires cooperation of two

equivalents of $\mathbf{1}_{\text{ads}}$ on layer compounds. The heterogeneous catalytic activity of the derivatives with R-terpy ligands (R= butoxy, propoxy, ethoxy, methoxy, methyl, methylthio, chloro and pyridyl) are quite different, showing that the catalytic activity strongly depends on the structure of complexes adsorbed [43]. We reported that UV-visible diffuse reflectance (DR) spectra, Mn K-edge X-ray absorption near edge structure (XANES) and EXAFS spectra of $\mathbf{1}_{\text{ads}}$ on Mt in supporting information of the literature [26]. Although the DR spectrum changed when $\mathbf{1}$ was adsorbed on Mt, the EXAFS spectral data showed that Mn $\cdots$ O (1.67 Å) and Mn $\cdots$ Mn (2.43 Å) distance did not considerably change. The Mn K-edge for $\mathbf{1}_{\text{ads}}$ on Mt shifted to a higher energy region versus that for $\mathbf{1}$ as a powder[26], suggesting that $\mathbf{1}$ is partially oxidized when adsorbed on Mt. We further demonstrated that the XANES spectra of $\mathbf{1}_{\text{ads}}$ on Mt hardly changed before and after water oxidation catalysis for 30 min using Ce(IV). Very recently, Najafpour et al also reported that the XANES and XAFS data of $\mathbf{1}_{\text{ads}}$ on Mt [44], which are inconsistent with our results reported earlier [26]. Their XANES data suggested that a mean oxidation state (3.5) of $\mathbf{1}$ was reduced to 2.6 (of $\mathbf{1}_{\text{ads}}$) when $\mathbf{1}$ was adsorbed on Mt from the lower energy shift of the Mn K-edge for $\mathbf{1}_{\text{ads}}$ on Mt. Their XAFS data provided the longer Mn $\cdots$ O/N (1.80 and 2.03 Å) and Mn $\cdots$ Mn (2.72 Å) distances for $\mathbf{1}_{\text{ads}}$ on Mt, compared with those reported earlier[26]. By treatment with Ce(IV) $\mathbf{1}_{\text{ads}}$ on Mt was re-oxidized to 3.5 of the mean oxidation state and the Mn $\cdots$ O (1.87 Å) and Mn $\cdots$ Mn (2.86, 3.10, 3.81, 4.99 Å) distance were lengthened in their report. Najafpour et al also mentioned that manganese clay adsorbates with similar water oxidation activity can be obtained starting (not from $\mathbf{1}$) from simple Mn salts, e.g., Mn(NO₃)₂, despite being treated with MnO₄⁻ in basic conditions[44, 45]. This result is quite different from our previous

report that layer compounds containing Mn^{2+} or Mn^{3+} ions does not work for water oxidation at all.[26, 40-42] They suggested from their X-ray absorption spectroscopic and O_2 evolution data that **1** is transformed on Mt into layered type manganese-oxide particles which are the actual water oxidation catalyst. The manganese-based Mt adsorbate samples prepared by Najafpour et al are different from those prepared in our group, possibly due to difference of a sort in a method. Thus, the mechanism of water oxidation by **1**_{ads} on the layer compounds is still interesting issue.

1 can be synthesized by oxidative dimerization of $\text{Mn}(\text{terpy})_2^{2+}$ (**1'**) or $\text{Mn}(\text{terpy})\text{Cl}_2$ precursor.[46, 47] The oxidative dimerization of **1'** in an aqueous solution involves initial one-electron oxidation to form $\text{Mn}(\text{terpy})_2^{3+}$ intermediate and subsequent and rapid disproportionation of $\text{Mn}(\text{terpy})_2^{3+}$ to form **1** [48]. However, there is no report on quantitatively-determined oxidative dimerization reactions of **1'** by chemical oxidants. Herein we investigate oxidative dimerization reactions of **1'** using different kinds of oxidants (KMnO_4 , Oxone, Ce^{IV}) in water to quantitatively determine the solution composition of manganese species formed in the reactions. The solutions with different composition of manganese species are useful to easily prepare a large variety of manganese species-based adsorbates of layer compounds. We examine the heterogeneous water oxidation activity of mica adsorbates with different composition of manganese species.

Experimental Section

Materials. Oxone ($\text{KHSO}_5 \cdot 0.5\text{KHSO}_4 \cdot 0.5\text{K}_2\text{SO}_4$), KMnO_4 and $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ (Wako Pure Chemical Industries, Ltd.), terpy (Aldrich Co., Inc.) were purchased. Somasif (ME-100) of mica was given from Co-op Chemical Co., Inc., Japan. All the chemicals are

used as received. $\mathbf{1}'(\text{NO}_3)_2$ was prepared according to the literatures.[48]

Preparation of mica adsorbing manganese species.

An aqueous solution (1 mM, 10 ml. pH = 3.0) containing $\mathbf{1}'(\text{NO}_3)_2$ and various amounts of the oxidants was added to an aqueous mica suspension (50 mg mica, 5 ml, pH = 3.0) to adsorb manganese species from the solution onto mica. The suspension was filtrated after stirring for 30 min, and then dried under vacuum to yield mica adsorbing manganese species. The amount of manganese species adsorbed was calculated by the UV-visible absorption spectral change of the solution before and after adding mica.

Measurements.

The titration of the aqueous $\mathbf{1}'(\text{NO}_3)_2$ solution with various oxidants (Oxone, KMnO_4 , $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$) was performed as follows. An adequate small portion of an aqueous solution (0.1 M) of an aqueous oxidant solution was added to an aqueous $\mathbf{1}'$ solution (1 mM, 4.0 ml, pH = 3.0). The UV-visible absorption spectral change of the solution was measured in a quartz cell using a photodiode array spectrophotometer (Shimadzu, Multispec-1500). UV-vis diffuse reflectance (DR) spectra were measured using a spectrophotometer (JASCO Inc., V-670) with an integrating sphere (ISN-723). The flow electrolysis was performed using a flow electrolysis system (HX-201, Hokuto Denko Co., Ltd.). Electrolysis was conducted at 1.2 V vs Ag/AgCl using an electrolyte solution of 0.1 M KNO_3 . O_2 evolution experiments were performed as follows. An aqueous solution (0.1 M, 100 μl) of $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ was added to the aqueous suspension (1.9 ml, pH = 1.0) containing 10 mg of mica adsorbing manganese species.

The amount of O₂ evolved was measured in a liquid phase using a Clark type O₂ analyzer (Hansatech Instruments, Oxygraph OXYG1 and DW1/AD unit).

Results and discussion

Titration of a **1'** solution with a KMnO₄ oxidant.

The UV-visible absorption spectral change in the reaction of **1'** with KMnO₄ is shown in Figure 1. **1'** does not exhibit any absorption band over 500 nm (red spectrum in Figure 1A). The absorption bands at 552 and 655 nm appeared by addition of KMnO₄ (shown by green spectra), indicating formation of **1**. The absorption bands at 552 nm and 655 nm are assigned to d-d transition and oxygen-to-manganese charge-transfer bands for the Mn^{III}(μ-O)₂Mn^{IV} core, respectively.[49-51] As the amount of KMnO₄ added increased from 0 to 0.5 equivalent (eq) vs the **1'** amount, both the absorbances at 552 nm and 655 nm increased linearly, as shown in Figure 1B. The slopes of the linear plots for 552 nm and 655 nm are consistent with the molar absorption coefficients of 605 and 600 M⁻¹ cm⁻¹ at the wavelength of **1**, respectively [43]. Above 0.5 eq of KMnO₄, the slopes of the absorbance change at 552 and 655 nm changed. The difference spectrum between 0.5 eq and 1.0 eq is agreement with the UV-visible absorption spectrum of MnO₄⁻ ion, showing that the absorption spectral change (shown by purple in Figure 1A) above 0.5 eq is due to a mere concentration increase of KMnO₄.

The titration experiment shows that formation of **1** was saturated at 0.5 eq of KMnO₄ and that **1** is not further oxidized under the excess KMnO₄ conditions. The maximum *in situ* formation yield of **1** at 0.5 eq of KMnO₄ was calculated using the molar absorption coefficient (600 M⁻¹ cm⁻¹) at 655 nm to be 145% based on **1'**. This overproduction (over

100%) was explained by regeneration of **1'** from the liberated terpy ligands and Mn^{2+} formed by reduction of KMnO_4 , as shown by eqn 1 ~ 4.

The oxidative dimerization of **1'** to **1** is 3-electron process with liberation of an equivalent of the terpy ligand per **1'** (eqn 1). KMnO_4 is known to act as a 5-electron oxidant to give a Mn^{2+} ion (eqn 2). The terpy ligands liberated in eqn 1 are immediately coordinated by Mn^{2+} ions to form **1'** (eqn 3), which is also oxidized to **1**. The total oxidative dimerization reaction of **1'** by KMnO_4 is represented by eqn 4 from eqns 1 ~ 3. The theoretical formation yield of **1** based on **1'** is 143 % according to eq 4. The present yield (145%) of **1** suggests that all the reactions (eqns 1 ~ 3) involved in the oxidative dimerization of **1'** to **1** proceeds stoichiometrically.

The distribution of manganese species formed in the dimerization reaction versus the KMnO_4 amount was calculated from the UV-visible absorption spectral change in the KMnO_4 titration (Figure 2). The concentrations (c_1 / M) of **1** were calculated from the absorbance and the molar absorption coefficient ($600 \text{ M}^{-1} \text{ cm}^{-1}$) at 655 nm. The concentrations ($c_{1'}$ / M) of **1'** were calculated by the initial concentration ($c_{1'}^{\text{initial}} = 1.0$ mM) of **1'** and c_1 according to $c_{1'}^{\text{initial}} - 7/5c_1$ based on eqn 4. c_1 increased linearly with $c_{1'}$ decreased as the amount of KMnO_4 increased up to 0.5 eq, and thereafter c_1 became constant (0.75 mM) up to 1.0 eq.

Titration of a **1**' solution with an Oxone oxidant.

The UV-visible absorption spectral change in the reaction of **1**' with Oxone is shown in Figure 3A. The absorption bands at 552 and 655 nm of a sign of formation of **1** increased linearly by addition of 0 ~ 0.4 eq Oxone (Figure 3B), as it is for the KMnO_4 titration. However, the absorbance above 655 nm decreased by further addition of Oxone with an isosbestic point at 608 nm. The absorbance decrease at 655 nm could be attributed to the further oxidation of **1** to **2**. It is reported that oxidation of **1** to **2** is followed by formation of the tetranuclear manganese(IV) complex of dimer-to-dimer.[52] For this reason, the accurate UV-visible absorption spectrum of **2** has not been reported so far. However, the formation of the tetranuclear manganese(IV) complex is relatively slow [53]. In order to identify the UV visible absorption spectrum of **2**, we set up a flow spectroelectrochemical system connected with a photodiode array spectrophotometer to take the UV visible absorption spectrum of fresh electrochemical products quickly (order of second) compared with a bulk electrolysis system (order of minute or hour). For the flow spectroelectrochemical measurement, the applied potential of 1.2 V vs Ag/AgCl was employed because the oxidation wave from **1** to **2** is 0.977 V vs Ag/AgCl on the CV of **1** in 0.1 M KNO_3 electrolyte solution [43]. The flow rate is important for the flow spectroelectrochemical measurement. In the case of the slow flow rate (0.1 ml min^{-1}), the absorption due to tetranuclear manganese(IV) complex was observed in the UV-visible absorption spectrum after electrolysis of the **1** solution, whereas it was not observed when the flow rate is faster than 20.0 ml min^{-1} . The UV-visible absorption spectra before and after electrolysis at 1.2 V vs Ag/AgCl (flow rate 20.0 ml min^{-1}) are shown in Figure 4.

The spectrum after electrolysis is almost identical with the spectrum of the titration solution at 0.7 eq Oxone (Figure 3A), suggesting that **2** was subsequently formed by oxidation of **1** that is formed by oxidative dimerization of **1'** with Oxone, in contrast to no further reaction of **1** in the KMnO_4 system.

The distribution of manganese species formed in the dimerization reaction versus the Oxone amount was calculated from the UV-visible absorption spectral change in Oxone titration (Figure 5). c_1 and the concentrations (c_2 / M) of **2** were calculated from the absorbance change using the molar absorption coefficients of **1** ($(\epsilon_{552})_1 = 605$, $(\epsilon_{655})_1 = 600$, $(\epsilon_{730})_1 = 498 \text{ M}^{-1} \text{ cm}^{-1}$) and **2** ($(\epsilon_{552})_2 = 1180$, $(\epsilon_{655})_2 = 492$, $(\epsilon_{730})_2 = 306 \text{ M}^{-1} \text{ cm}^{-1}$) at respective wavelength (indicated in subscript notations of ϵ) given by the spectroelectrochemical measurement (Figure 5). c_1 was calculated by $c_1^{\text{initial}} = 1.0 \text{ mM}$, c_1 and c_2 according to $c_1^{\text{initial}} - 2(c_1 + c_2)$. c_1 increased linearly with c_1 decreased as the amount of Oxone up to 0.4 eq, and thereafter c_1 decrease with c_2 increased up to 1.0 eq. The maximum *in situ* formation yields of **1** and **2** were 87% (at 0.8 eq) and 91% (1.4 eq), respectively. The calculated c_1 value includes ~9% of the other manganese species particularly at the higher Oxone amounts.

Titration of a **1' solution with a Ce(IV) oxidant.**

When a Ce(IV) oxidant was used for titration of the **1'** solution, the similar UV-visible absorption spectral change to that in the Oxone titration was observed (Figure 6); **1** was formed followed by **2** formation as the Ce(IV) amount increased. The distribution of manganese species formed in the dimerization reaction versus the Ce(IV) amount was calculated in the same manner as the Oxone system (Figure 7). c_1 increased

with the amount of Ce(IV) from 0 to 5.2 eq. c_1 decreased with c_2 increased in the further addition (5.2 ~ 10 eq) of Ce(IV), and c_1 and c_2 became zero and constant value of 0.74 mM over 9.4 eq Ce(IV), respectively. The maximum *in situ* formation yield of **1** and **2** was 67% at 5.2 eq and 74% at 9.4 eq, respectively.

The maximum yields of **1** and **2** in the oxidative dimerization reaction of **1'** using various oxidants are summarized in Table 1. For the yield of **1**, KMnO₄ (145% at 0.5 eq) is a favorable oxidant because 1) **1** is stoichiometrically formed, 2) the liberated terpy ligands are reused for formation of **1'** through complexation with Mn²⁺ (*via* KMnO₄), and 3) the further oxidation of **1** to **2** does not proceed. When Oxone was used, **1** and **2** were obtained in nearly quantitative yields of 87% at 0.8 eq and 91.4% at 1.4 eq, respectively. When Ce(IV) was used, the maximum yields (67% and 74%) of **1** and **2** are lower than those for Oxone, and the much larger amount (5.2 eq and 9.4 eq) of Ce(IV) was required for the maximum yields of **1** and **2**. The electron oxidant of Ce(IV) is relatively unsuitable for **1** and **2** formations to oxygen atom donating agents of Oxone.

Preparation and characterization of mica adsorbates.

To investigate influence of manganese species adsorbed onto mica on the heterogeneous catalytic activity, the various mica adsorbates were prepared by adding mica suspensions to the solutions with different manganese composition of **1'**, **1** and **2** formed by various oxidant-treatments. For the solution treated using KMnO₄ or Oxone, all the manganese complexes were adsorbed onto mica by cation exchange with Na⁺ under the conditions employed. For the Ce(IV)-treated solution, Ce³⁺ cations generated by reduction of Ce(IV) are co-adsorbed with the manganese complexes. The UV-visible DR

spectrum of the mica adsorbate prepared from the solution mainly containing **1** (treated with 0.8 eq Oxone) exhibited an intense shoulder at 410 nm (green line in Figure 8), which is very similar to that of the mica adsorbate prepared using isolated **1** [40]. The similar DR spectra were observed for the KMnO₄ (0.5 eq) and Ce(IV) (5.2 eq) systems. However, **1**_{ads} on mica is not intact as reported earlier [40]. The DR spectrum of the mica adsorbate prepared from the solution mainly containing **2** (treated with 1.4 eq Oxone) showed a shoulder at 550 nm (blue line in Figure 8). It is considerably different from the absorption spectrum of **2** in water (Figure 3A and 4), suggesting that **2**_{ads} on mica is not intact although it is not fully characterized yet. The different DR spectrum between **1**_{ads} and **2**_{ads} in Figure 8 suggests that the manganese species on mica is certainly different between the cases prepared from **1** and **2** solutions.

Heterogeneous water oxidation by mica adsorbates.

The heterogeneous catalytic activities of various mica adsorbates for water oxidation were examined using a Ce(IV) oxidant. The time courses of the amount of O₂ evolved by water oxidation for the mica adsorbates prepared from the KMnO₄-treated solutions are shown in Figure 9. The amount of O₂ evolved increased with an increase (0 ~ 0.5 eq) of the amount of KMnO₄ added for oxidative dimerization of **1**'. The initial O₂ evolution rates (v_{O_2} / mol s⁻¹) were calculated from the initial slopes of the O₂ evolution time courses. The plots of v_{O_2} vs the amount of KMnO₄ are shown in Figure 2 together with distribution of manganese species in the KMnO₄-treated solution. The v_{O_2} data gave an upward curve in a KMnO₄ amount range of 0 ~ 0.5 eq where c_1 increased linearly with the amount of KMnO₄, and the v_{O_2} value became constant coincident with c_1 above 0.5 eq.

To reveal the catalytic activity per one equivalent of $\mathbf{1}_{\text{ads}}$, v_{O_2} was normalized by the amount of $\mathbf{1}_{\text{ads}}$ (n_1 / mol) to define the apparent turnover frequency (k_{app} / s^{-1}) as $k_{\text{app}} = v_{\text{O}_2} / n_1$. The plots of k_{app} vs n_1 gave a straight line with the significant slope passing through the near origin (Figure 10A). The significant slope and the almost zero intercept suggest that O_2 evolution is a second order with respect to $\mathbf{1}_{\text{ads}}$. This result is consistent with the cooperative catalysis by two equivalences of $\mathbf{1}_{\text{ads}}$, as reported previously [26, 40]. The v_{O_2} data clearly show that $\mathbf{1}_{\text{ads}}$ works for water oxidation catalysis, whereas $\mathbf{1}'$ ($\mathbf{1}'_{\text{ads}}$) adsorbed on mica does not do so.

For the Oxone-treated system, the plots of v_{O_2} vs the amount of Oxone was shown in Figure 5 together with distribution of manganese species. The v_{O_2} data changed significantly although the total manganese amount adsorbed onto mica is the same. The v_{O_2} data gave upward curve in an Oxone amount range of 0 ~ 0.8 eq, and thereafter passing the maximum value at 0.4 eq, v_{O_2} decreased with the Oxone amount to be zero above 0.7 eq. The amount (0.8 eq) of Oxone for the maximum v_{O_2} is in agreement with that for the maximum c_1 , supporting that $\mathbf{1}_{\text{ads}}$ works for water oxidation catalysis. It also suggests that $\mathbf{2}_{\text{ads}}$ does not work for the catalysis, as is the case for $\mathbf{1}'_{\text{ads}}$. The reason for inactivity of $\mathbf{2}_{\text{ads}}$ might be explained by conversion of $\mathbf{2}_{\text{ads}}$ to inactive species, as $\mathbf{2}$ is gradually converted to the tetranuclear manganese(IV) complex in solution [52, 53]. The UV-visible DR spectrum of the mica adsorbate prepared from the solution mainly containing $\mathbf{2}$ (blue line in Figure 8) could rather be that of inactive species converted from $\mathbf{2}_{\text{ads}}$, than of $\mathbf{2}_{\text{ads}}$ itself.

The plots of k_{app} vs n_1 gave a straight line with the significant slope passing through the near origin at 0 ~ 0.8 eq of Oxone. This suggests that O_2 evolution is second order with respect to $\mathbf{1}_{\text{ads}}$ (Figure 10B), being similar to the KMnO_4 -treated system. At 0.8 ~ 1.4

eq of Oxone, k_{app} was independent with n_1 , suggesting that O_2 evolution is a first order with respect to adsorbed 1_{ads} . Under these conditions, 1_{ads} and 2_{ads} co-exist on mica because the mica adsorbate was prepared from the solution containing **1** and **2**. The first order O_2 evolution with respect to 1_{ads} could be explained by cooperative catalysis of 1_{ads} with 2_{ads} . This means that 1_{ads} can work for the catalysis cooperatively with not only 1_{ads} but also 2_{ads} , although 2_{ads} does not induce the catalytic activity alone. During the catalysis, 1_{ads} is oxidized to 2_{ads} , which could predominantly work for cooperative catalysis prior to relatively slow conversion to inactive species.

For the Ce(IV)-treated system, the plots of v_{O_2} vs the amount of Ce(IV) are added in Figure 7. The v_{O_2} is very low under the conditions employed ($0.64\ \mu\text{mol } 1_{ads}$ on 10 mg mica) although the significant amount of O_2 was observed under the similar 1_{ads} concentration conditions for KMnO_4 - and Oxone-treated systems. Penetration of Ce(IV) ions (as an oxidant for water oxidation) into mica could be impeded by Ce^{3+} cations (generated in oxidative dimerization of **1'**) co-adsorbed with 1_{ads} in the mica adsorbates to give low v_{O_2} for the Ce(IV)-treated system. This is supported by our earlier report in which v_{O_2} for mica adsorbates containing 1_{ads} (prepared using isolated **1**) drastically decreased when trications such as Al^{3+} or Ce^{3+} are co-adsorbed (or post-adsorbed), although v_{O_2} did not change when Mg^{2+} or Ba^{2+} dications are co-adsorbed.

Conclusions.

The oxidative dimerization reaction **1'** stoichiometrically proceeded to from **1** when a KMnO_4 oxidant was used. The subsequent oxidation of formed **1** to **2** following oxidative dimerization reaction of **1'** was observed when Oxone and Ce(IV) oxidants are used. KMnO_4 is a favorable oxidant for high yield (145%) of **1** formation. The

heterogeneous water oxidation catalyses by the mica adsorbates containing different composition of manganese species were examined. **1'** and **2_{ads}** did not induce the catalysis activity alone, whereas **1_{ads}** worked for the catalysis through cooperation with adjacent **1_{ads}** or **2_{ads}**. The recent X-ray absorption spectroscopic study of montmorillonite adsorbing **1** remind us the possibility of conversion of **1_{ads}** to the manganese oxides as active catalysts during the catalysis[44]. However, the significantly dependent catalytic activity of manganese complex-based mica adsorbates on manganese species adsorbed could be difficult to be explained by simple formation of manganese oxides. It is most likely that **1_{ads}** on works as the manganese cluster-based catalyst for water oxidation rather than manganese oxide.

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Table 1 Summary of *in situ* formation yields of **1** and **2** from a **1'** solution (1.0 mM, pH = 3.0) and amounts (expressed as equivalence (eq)) of oxidant using various oxidants.

Oxidant	1 yield (oxidant eq)	2 yield (oxidant eq)
KMnO ₄	145% (0.5 eq)	-
Oxone	87% (0.8 eq)	91.4% (1.4 eq)
Ce(IV)	67% (5.2 eq)	74% (9.4 eq)

Figure captions

Figure 1A UV-Visible adsorption spectral change of a **1'** solution (1.0 mM, pH = 3.0) in titration with a KMnO₄ solution. The red spectrum is for the **1'** solution. The green and purple spectral changes are due to formation of **1** and KMnO₄ concentration increase, respectively.

Figure 1B Absorbance changes at 552 (○) and 655 (■) nm in titration of **1'** solution (1.0 mM, pH = 3.0) with a KMnO₄ solution.

Figure 2 Distribution of manganese species (**1'** (□) and **1** (●)) in an oxidative dimerization reaction of **1'** (1.0 mM, pH = 3.0), and initial rate (v_{O_2} (mol s⁻¹)) of O₂ evolution versus the amount of added KMnO₄ for the KMnO₄-treated system. The conditions for O₂ evolution experiments are 50 mM Ce(IV), 2.0 mol (total Mn amount) / 10 mg mica, 2.0 ml liquid volume, pH = 1.0.

Figure 3A UV-Visible adsorption spectral change of **1'** solution (1.0 mM, pH = 3.0) in titration with an Oxone solution. The red spectrum is for the **1'** solution. The green and brown spectral changes are due to formation of **1** and **2**, respectively.

Figure 3B Absorbance changes at 552 (○) and 655 (■) nm in titration of **1'** solution (1.0 mM, pH = 3.0) with an Oxone solution.

Figure 4 UV-Visible adsorption spectra of the **1** solution (0.5 mM, pH = 3.0) before (green dot line) and after (red line) flow electrolysis (800 s) of (a) at 1.2 V vs Ag/AgCl and 20.0 ml min⁻¹ of the flow rate.

Figure 5 Distribution of manganese species (**1'** (□), **1** (●) and **2** (◐)) in an oxidative dimerization reaction of **1'** (1.0 mM, pH = 3.0), and initial rate (v_{O_2} (mol s⁻¹)) of O₂ evolution versus the amount of added Oxone for the Oxone-treated system. The conditions for O₂ evolution experiments are 50 mM Ce(IV), 2.0 mol (total Mn amount) / 10 mg mica, 2.0 ml liquid volume, pH = 1.0. The calculated $c_{1'}$ value includes ~9% of the other manganese species particularly at the higher Oxone amounts.

Figure 6 UV-Visible adsorption spectral change of **1'** solution (1.0 mM, pH = 3.0) in titration with a Ce(IV) solution. The red spectrum is for the **1'** solution. The green and brown spectral changes are due to formation of **1** and **2**, respectively.

Figure 7 Distribution of manganese species (**1'** (□), **1** (●) and **2** (◐)) in an oxidative dimerization reaction of **1'** (1.0 mM, pH = 3.0), and initial rate (v_{O_2} (mol s⁻¹)) of O₂ evolution versus the amount of added Ce(IV) for the Ce(IV)-treated system. The conditions for O₂ evolution experiments are 50 mM Ce(IV), 2.0 mol (total Mn amount) / 10 mg mica, 2.0 ml liquid volume, pH = 1.0. The calculated $c_{1'}$ value includes at most 26% of the other manganese species particularly at the higher Ce(IV) amounts.

Figure 8 UV-visible diffuse reflectance (DR) of the mica adsorbates prepared from the solution mainly containing **1** (treated with 0.8 eq Oxone) (green line) and prepared from the solution mainly containing **2** (treated with 1.4 eq Oxone) (blue line)

Figure 9 Plots of k_{app} vs. the amount (n_1) of complex **1** ($\mathbf{1}_{ads}$) adsorbed onto mica for $KMnO_4$ -treated system (A) and Oxone-treated system (B). The amounts of oxidants added are indicated on figures.

Figure 1A

Figure 1B

Figure 2

Figure 3A

Figure 3B

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10A

Figure 10B

Graphical Abstract