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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A B S T R A C T

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 $[Mn^{II}(terpy)_2]^{2+}$ (terpy = 2,2′:6′,2″-terpyridine) ($\mathbf{1}'$) with various oxidants in water was revealed. $\mathbf{1}'$ was stoichiometrically oxidized to form di-μ-oxo dinuclear manganese complex, $[(OH_2)(terpy)Mn^{III}(\mu\text{-}O)_2Mn^{IV}(terpy)(OH_2)]^{3+}$ (1) by $KMnO_4$ as an oxidant. When Oxone and Ce(IV) oxidants were used, the further oxidation of 1 to $[(OH_2)(terpy)Mn^{IV}(\mu\text{-}O)_2Mn^{IV}(terpy)(OH_2)]^{4+}$ (2) was observed after the oxidative dimerization reaction of $\mathbf{1}'$. The mica adsorbates with various composition of $\mathbf{1}'$, 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 ($\mathbf{1}_{ads}$) adsorbed on mica for $KMnO_4$- and Oxone-treated systems, indicating that $\mathbf{1}'$ ($\mathbf{1}'_{ads}$) and 2 ($\mathbf{2}_{ads}$) adsorbed on mica do not work for the catalysis. The kinetic analysis suggested that $\mathbf{1}_{ads}$ works for the catalysis through cooperation with adjacent $\mathbf{1}_{ads}$ or $\mathbf{2}_{ads}$, meaning that $\mathbf{2}_{ads}$ assists the cooperative catalysis by $\mathbf{1}_{ads}$ though $\mathbf{2}_{ads}$ 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 $\mathbf{1}_{ads}$ 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 $\mathbf{1}'$) co-adsorbed with $\mathbf{1}_{ads}$.

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1. Introduction

For photosynthesis in nature, O_2 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 (Mn_4CaO_5) containing an asymmetric Mn_3CaO_4 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].

O_2 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 O_2 evolution suggested that the catalysis requires cooperation of two equivalents of 1_{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 1_{ads} on Mt in supporting information of the literature [26]. Although the DR spectrum changed when **1** was adsorbed on Mt, the EXAFS spectral data showed that Mn...O (1.67 Å) and Mn...Mn (2.43 Å) distance did not considerably change. The Mn K-edge for 1_{ads} on Mt shifted to a higher energy region versus that for **1** as a powder [26], suggesting that **1** is partially oxidized when adsorbed on Mt. We further demonstrated that the XANES spectra of 1_{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 1_{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 **1** was reduced to 2.6 (of 1_{ads}) when **1** was adsorbed on Mt from the lower energy shift of the Mn K-edge for 1_{ads} on Mt. Their XAFS data provided the longer Mn...O/N (1.80 and 2.03 Å) and Mn...Mn (2.72 Å) distances for 1_{ads} on Mt, compared with those reported earlier [26]. By treatment with Ce(IV) 1_{ads} on Mt was re-oxidized to 3.5 of the mean oxidation state and the Mn...O (1.87 Å) and Mn...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 **1**) from simple Mn salts, e.g., $Mn(NO_3)_2$, despite being treated with MnO_4^- 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 $Mn(terpy)_2^{2+}$ (**1**′) or $Mn(terpy)Cl_2$ precursor [46,47]. The oxidative dimerization of **1**′ in an aqueous solution involves initial one-electron oxidation to form $Mn(terpy)_2^{3+}$ intermediate and subsequent and rapid disproportionation of $Mn(terpy)_2^{3+}$ 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 (KMnO₄, 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.

2. Experimental section

2.1. Materials

Oxone ($KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$), KMnO₄ and $Ce(NH_4)_2(NO_3)_6$ (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. **1**′$(NO_3)_2$ was prepared according to the literatures [48].

2.2. Preparation of mica adsorbing manganese species

An aqueous solution (1 mM, 10 ml, pH = 3.0) containing **1**′$(NO_3)_2$ 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.

2.3. Measurements

The titration of the aqueous **1**′$(NO_3)_2$ solution with various oxidants (Oxone, KMnO₄, $Ce(NH_4)_2(NO_3)_6$) 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 **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 KNO₃. O_2 evolution experiments were performed as follows. An aqueous solution (0.1 M, 100 μl) of $Ce(NH_4)_2(NO_3)_6$ was added to the aqueous suspension (1.9 ml, pH = 1.0) containing 10 mg of mica adsorbing manganese species. The amount of O_2 evolved was measured in a liquid phase using a Clark type O_2 analyzer (Hansatech Instruments, Oxygraph OXYG1 and DW1/AD unit).

3. Results and discussion

3.1. 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 Fig. 1. **1**′ does not exhibit any absorption band over 500 nm (red spectrum in Fig. 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 $Mn^{III}(\mu-O)_2Mn^{IV}$ 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 Fig. 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 MnO_4^- ion, showing that the absorption spectral change (shown by purple in Fig. 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