

## Heterogeneous Water Oxidation by a Dinuclear Manganese Complex

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The di- $\mu$ -oxo-tetrakis(2,2'-bipyridine)dimanganese complex was used as a heterogeneous phase catalyst for water oxidation by adsorbing into Kaolin clay. The oxygen evolved was analyzed by gas chromatography and mass spectrometry. The water oxidation reaction involving the four-electron process in a heterogeneous phase was discussed.

Manganese is the essential metal ion in the charge accumulation center of the oxygen evolving protein complex of the photosynthesis in green plants<sup>1)</sup> where a loosely bound pool of manganese acts as a multicentered catalyst for the oxidation of water to oxygen. However, the number of metal ions involved in the water oxidation process, the chemical environments around the manganese ions, and their oxidation state are not clear. Calvin<sup>2)</sup> and Porter<sup>3)</sup> proposed a model in their attempts to decompose water with manganese porphyrin and phthalocyanine, but Calvin's initial claims to success in photolytic dioxygen evolution were subsequently withdrawn.<sup>4)</sup> So far, there have been no substantiated reports in which a metalloporphyrin was used to oxidize water to oxygen. Several compounds of non-biological metal oxides have been reported to catalyze the oxidation of water to oxygen by strong one-electron oxidants.<sup>7-9)</sup> More recently it has been reported that polynuclear ruthenium and manganese complexes are capable of oxidizing water to oxygen in the presence of Ce(IV).<sup>10-14)</sup> In this paper, we report successful construction of a heterogeneous water oxidation system using clay as an adsorbent of the di- $\mu$ -oxo-bridged dinuclear manganese complex which is believed to be a model catalyst for the photosynthetic water oxidation.<sup>2,3)</sup>

Di- $\mu$ -oxo-tetrakis(2,2'-bipyridine)dimanganese (III,IV) perchlorate,  $[(\text{bpy})_2\text{Mn}(\text{O})_2\text{Mn}(\text{bpy})_2](\text{ClO}_4)_3$  (1), was prepared according to the reported method<sup>15)</sup> and characterized by UV-VIS and IR spectroscopy and elemental analyses. The heterogeneous catalyst was prepared by mixing the dinuclear manganese complex 1 and commercially available Kaolin clay (Nakarai Chemicals Ltd) in deionized water. The mixture was stirred until complete adsorption was noticed. The catalyst adsorbed clay was filtered, washed with deionized water, and dried in air. The cyclic voltammogram was recorded for 1 in an aqueous solution using a Basal Plane Pyrrolytic Graphite (BPG) working electrode, platinum wire auxiliary and a saturated calomel reference electrode (SCE). The cyclic voltammogram of 1 exhibits two electrochemically reversible redox reactions at 1.14 V and 0.98 V vs. SCE corresponding to the manganese (IV,IV/III,IV) and (III,IV/III,III) couples. The electrochemical property of 1 has mainly been studied in acetonitrile,<sup>15,16)</sup> and it was reported that the anodic electrolysis of 1 in this medium at 1.45 V vs. SCE caused decomposition. However, in the present study, the anodic electrolysis in water at 1.45 V vs. SCE did not bring about any noticeable decomposition of 1.

Water oxidation experiments were carried out with complex 1 in the presence of ammonium cerium (IV) nitrate. When complex 1 was used in a homogeneous aqueous solution, no gas evolution was observed and analysis of the gas phase showed that no oxygen was formed. However, when complex 1 was used in a clay adsorbed heterogeneous state, the formation of gas bubbles on the clay surface was observed. The evolved gas was analyzed chromatographically (Shimadzu GC 4C gas chromatography) using a 1.5 m column of molecular sieve 5 A and argon carrier. The amount of oxygen evolved was calculated by subtracting the oxygen content due to the residual air that was contained in the reaction vessel from the total oxygen observed. Mass spectral studies were carried out (Ulvac MSQ-150A quadrupole mass spectrometer) for the gas evolved from water containing 1.9%  $\text{H}_2^{18}\text{O}$ . The ratio of  $^{18}\text{O}^{16}\text{O}^+ / ^{16}\text{O}_2^+$  was found to be 2.16% in comparison with the value of 0.3% of the oxygen from air. The deviation of the experimental value 2.16% from the theoretical value 3.87% would be due to the residual air accompanying the measurement by the mass spectrometer. During the water oxidation catalyzed by Kaolin adsorbed 1, complex 1 undergoes decomposition depending on its concentration in clay. The amount of oxygen evolved and the stability of 1 during the catalysis were shown in Tables 1 and 2.

Table 1. Oxygen evolution by heterogeneous water oxidation using Kaolin clay adsorbed 1 at 25 °C

Kaolin clay = 150 mg

1 : Ce(IV) = 1 : 100 (molar ratio), Reaction time = 3 h

| <u>1</u><br>( $\mu\text{mol}$ ) | $\text{O}_2$<br>( $\mu\text{l}$ ) | $\text{O}_2$<br>( $\mu\text{mol}$ ) | Decomposition<br>of catalyst |
|---------------------------------|-----------------------------------|-------------------------------------|------------------------------|
| 0.9                             | 19                                | 0.79                                | No                           |
| 1.8                             | 22                                | 0.91                                | No                           |
| 3.6                             | 35                                | 1.44                                | Yes                          |
| 4.5                             | 56                                | 2.32                                | Yes                          |

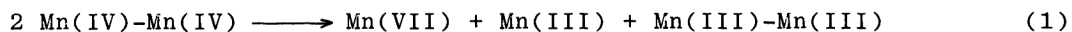
Table 2. Effect of reaction conditions on the oxygen evolution catalyzed by Kaolin clay adsorbed 1 at 25 °C

1 : Ce(IV) = 1 : 100 (molar ratio)

Reaction time = 3 h (M = mol dm<sup>-3</sup>)

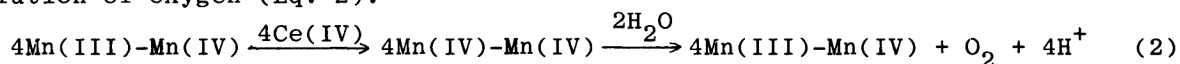
| Kaolin <u>1</u><br>(mg) | Condition<br>( $\mu\text{mol}$ ) | $\text{O}_2$<br>( $\mu\text{l}$ ) | $\text{O}_2$<br>( $\mu\text{mol}$ ) | Decomposition<br>of catalyst |
|-------------------------|----------------------------------|-----------------------------------|-------------------------------------|------------------------------|
| 150                     | 2.7 10mM HNO <sub>3</sub>        | 33                                | 1.35                                | No                           |
| 150                     | 4.5 10mM HNO <sub>3</sub>        | 57                                | 2.34                                | Yes                          |
| 150                     | 2.7 10mM NaOH                    | 36                                | 1.49                                | No                           |
| 150                     | 4.5 10mM NaOH                    | 41                                | 1.69                                | Yes                          |
| 300                     | 4.5 Water                        | 57                                | 2.37                                | No                           |
| 500                     | 4.5 Water                        | 84                                | 3.44                                | No                           |

Table 1 shows that the increase in the catalyst concentration in Kaolin clay gives more oxygen. However, when the catalyst concentration exceeds 3.6  $\mu\text{mol}/150$  mg Kaolin, complex 1 was found to undergo decomposition. Table 2 shows that the addition of acids or alkalis does not affect much the water oxidation. The oxygen evolved can increase without decomposition of the complex when the amount of the clay is increased while keeping the amount of the complex constant. The results of Tables 1 and 2 clearly show that when the catalyst concentration exceeds a critical limit, the decomposition of complex 1 occurs. The decomposition product was found to be  $\text{MnO}_4^-$  from the six absorption peaks in the region 600 to 670 nm of the spectrum of the solution after the reaction. The decomposition probably occurs due to the disproportionation reaction of the higher oxidation state of the Mn complex (Eq. 1).



The redox potential of 1 described before shows that it can be used as a one-electron oxidant for water oxidation, and therefore the one-electron process must be coupled to the four-electron process in order to achieve oxygen evolution by water oxidation. In a solid state, the heterogeneity of the complex could materialize four-electron water oxidation. In a homogeneous solution, however, realization of such a coupled reaction would be impossible. The probable role of the

heterogeneity is to bring oxygen atoms of two water molecules into close proximity to form an O-O bond which will lead to the generation of dioxygen. A model postulates a dinuclear manganese complex where water ligands are the source of an O-O bond at the level of the bound peroxide that is binuclearly complexed.<sup>17)</sup> It has already been suggested<sup>1,17,18)</sup> that the microheterogeneous environment around manganese and the close proximity of manganese atoms to one another are responsible for water-splitting in the photosynthesis. It is conceivable that four molecules of 1 may be oxidized by four Ce(IV) ions to produce a four-electron depletion center on the surface of the solid. The oxidizing center would realize four-electron oxidation of two molecules of weakly bound water with subsequent evolution of oxygen (Eq. 2).



The O-O bond formation prior to the oxygen evolution in catalytic water oxidation has already been proposed by the previous works.<sup>11-14)</sup>

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