

Effect of immobilization and activity analysis of water oxidation catalysts adsorbed into clay

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Abstract

The catalytic activity of a trinuclear Ru complex; $[(\text{NH}_3)_5\text{Ru}-\text{O}-\text{Ru}(\text{NH}_3)_4-\text{O}-\text{Ru}(\text{NH}_3)_5]^{6+}$ (Ru-red) for water oxidation was investigated both in a homogeneous aqueous solution system (AS) and a heterogeneous montmorillonite adsorbed system (clay). It was shown that water oxidation by the catalyst in the clay to evolve O_2 is a competitive reaction with bimolecular decomposition of the catalyst. The bimolecular decomposition was remarkably suppressed in the clay as compared with the aqueous solution, and the catalytic activity was maintained under higher concentration conditions. This was ascribed to the immobilization and isolation of the complex in the clay. The catalytic activity was analyzed by a model equation based on intermolecular distance distribution of the complex. The catalytic activity (k_{O_2}) and the critical decomposition distance (r_d) were obtained as $1.7 \times 10^{-2} \text{ s}^{-1}$ and 2.39 nm, respectively. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Utilization of a functional molecule in a heterogeneous matrix such as polymer membranes [1,2], ion-exchange resins [3–5], cellulose [6] and intercalation compounds [7] is recently receiving much attention in relation to its application to electric and photoelectric functional devices. It is important to optimize the function of

the molecule in such systems. In our previous reports [8–10], it was found that a water oxidation catalyst is remarkably stabilized in a heterogeneous Nafion polymer membrane. Water oxidation is the most fundamental and important process toward construction of an artificial photosynthetic system in relevant to solar energy conversion and storage to create a new energy resource [2]. In order to construct an active and stable water oxidation catalyst, utilization of a heterogeneous phase is crucial. We have utilized heterogeneous Nafion membrane incorporating active water oxidation catalyst such as $[(\text{NH}_3)_5\text{Ru}-\text{O}-\text{Ru}(\text{NH}_3)_4-\text{O}-\text{Ru}(\text{NH}_3)_5]^{6+}$ (Ru-red) [2,8], $[(\text{NH}_3)_3\text{Ru}-\text{O}-\text{Ru}(\text{NH}_3)_5]^{4+}$ [9] and

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$[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$ [10,11]. These ruthenium complexes undergo bimolecular decomposition due to diffusion and collision at high concentration conditions in an aqueous solution. Such catalyst can be stabilized by immobilization in a polymer membrane [2,8–11]. In a Nafion membrane system where cationic complex is electrostatically attached to the anionic sulfonate groups, the ruthenium complex was almost immobilized in the matrix. Consequently, the bimolecular decomposition was remarkably suppressed in the membrane and catalytic activity was maintained even under high concentration conditions.

In the present paper, the effect of immobilization and catalytic activity of Ru-red in a clay (montmorillonite; abbreviated to clay) were investigated. Cation exchange occurring between the inorganic layers and the substrates depends on the size of the exchanged cation [12]. The interlayer space is separated by the inorganic layer, so that it is expected that the interaction between the adsorbed substrates is minimum. In the present clay system, catalytic activity analysis will be carried out by a model equation based on intermolecular distance distribution.

2. Experimental

2.1. Materials

Ru-red and cerium (IV) diammonium nitrate were purchased from Wako Pure Chemical Ind. Clay was purchased from Kunimine Ind. The reagents were used without further purification.

2.2. Preparation of clay adsorbing Ru-red

A mixture of Ru-red and clay (0.2 g) in water was vigorously stirred for ca. 5 h. The amount of the adsorbed complex was estimated from the absorption spectral change of Ru-red (532 nm)

in the solution before and after adsorption of the complex into clay. The clay was centrifuged after adsorption and washed repeatedly by distilled water. The volume of clay was estimated using its density value of $4.0 \times 10^{-4} \text{ dm}^3 \text{ g}^{-1}$

2.3. Measurement of oxygen evolved

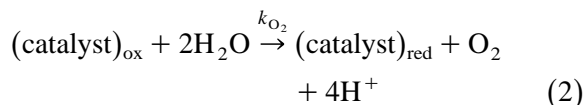
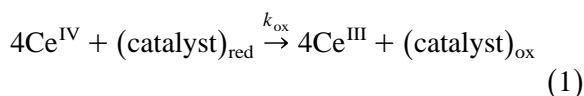
Excess Ce(IV) diammonium nitrate powder was added as oxidant quickly into water containing suspended clay which adsorbed the catalyst. The atmosphere in the reaction vessel was replaced with argon gas before adding the Ce(IV) oxidant. For all the experiments, the vessel was kept at 25°C in the dark by cutting off the ambient light. The O_2 evolved was analyzed by a gas chromatograph equipped with a 5-Å molecular sieve column using argon carrier gas (flow rate is 40 ml min^{-1}) at 50°C. The amount of the O_2 evolved was calculated by subtracting the amount of O_2 detected for blank experiment without the complex.

3. Results and discussion

It is well-known that clay markedly swells in water. The interlayer spacing of clay is ca. 0.66 nm under dry conditions and expands to ca. 1.25 nm under swollen conditions [13]. The clay has an interesting inorganic layer structure assembled by SiO_4 tetrahedral and AlO_6 octahedral sheets. Since the size of Ru-red (a kind of cylinder with 0.75 nm diameter and 1.40 nm length) is smaller than the size between the layers, the complex can be adsorbed among the layers. Cationic complexes are adsorbed into the space (called as exchangeable space) between the inorganic layers by cationic exchange.

Chemical catalytic water oxidation using oxidant consists of two steps. In the first step, the catalyst is oxidized by oxidant to a high oxidation state as shown by Eq. (1). In the second step, two water molecules were oxidized by the

high oxidation state catalyst to evolve oxygen as shown by Eq. (2):



where k_{ox} and k_{O_2} represent the reaction rate constants of Eqs. (1) and (2), respectively.

Fig. 1 shows a typical time dependence of oxygen evolved by the Ru-red in a heterogeneous clay under the excess Ce (IV) oxidant. The O_2 evolved increased almost linearly with time at the initial stage (up to 20 min). The O_2 evolution rate (V_{O_2} (mol s^{-1})) was obtained from the initial slope. The oxygen evolution stopped after ca. 2 h. This saturation is considered to be due to inactivation by bimolecular decomposition between the adjacent catalysts as reported previously [8] because a large excess of the Ce(IV) oxidant remained even after 2 h.

The plot of the initial oxygen evolution rate (V_{O_2}) vs. the Ce(IV) concentration for the clay system is shown in Fig. 2. Under low concentration the V_{O_2} value is first-order with respect to the cerium concentration, showing that oxygen evolution can be treated as a pseudo-first-order rate vs. Ce(IV) concentration. The V_{O_2} value is saturated beyond the molar ratio of Ce(IV)/Ru-red (= 900, at 4.0×10^{-2} M Ce(IV)). All the

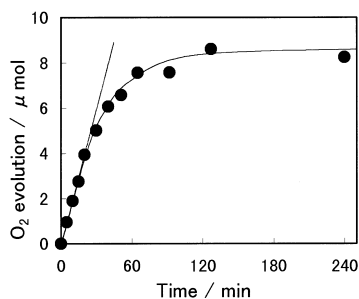


Fig. 1. Time dependence of the amount of O_2 evolved for the clay. The dotted line indicates the slope of the straight line at the initial stage. The amount of complex and Ce(IV) oxidant are 2×10^{-7} and 2×10^{-3} mol, respectively; clay, 0.3 g; liquid volume, 10 cm^3 .

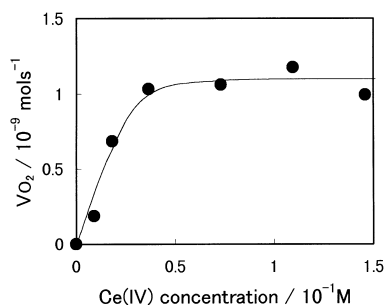


Fig. 2. Dependence of O_2 evolution rate (V_{O_2} (mol^{-1})) on Ce(IV) concentration for the clay. The amount of complex, 4.1×10^{-7} mol; clay, 0.2 g; liquid volume, 10 cm^3 .

experiments were conducted beyond this cerium concentration where V_{O_2} is independent of the Ce(IV) concentration.

Fig. 3 shows the relationship between the V_{O_2} and catalyst concentration in clay. The V_{O_2} value increased linearly with the increase of the Ru-red concentration at low concentration conditions as shown in the inset of Fig. 3. This linear relationship shows that the water oxidation reaction by Ru-red can be treated as a pseudo-first-order process with respect to the Ru-red concentration. The first-order rate constant of O_2 evolution was estimated as $1.7 \times 10^{-2} \text{ s}^{-1}$ from the slope of the straight line in the inset of Fig. 3. However, under high concentration conditions, the V_{O_2} value decreased with the increase of the Ru-red concentration, showing that a bimolecular decomposition takes place between adjacent complexes. We have reported [8] that the cat-

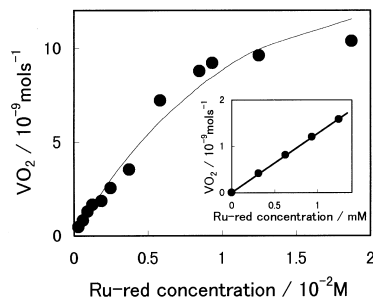
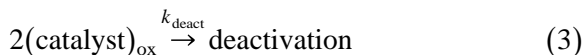


Fig. 3. Dependence of V_{O_2} on Ru-red concentrations in the clay. The amount of Ce(IV) oxidant, 2.0×10^{-3} mol; clay, 0.2 g; liquid volume, 10 cm^3 . The inset illustrates the plots at low concentrations.

alytic activity of Ru-red at high concentrations in an aqueous solution system (AS) decreased drastically by oxidation of the ammine ligands evolving N_2 as shown in Eq. (3).



This k_{deact} represents the second-order rate constant of the bimolecular decomposition. In the present heterogeneous clay, the bimolecular decomposition also should take place between the complexes; however, no N_2 was detected because of the small amount of the catalyst. In order to compare the catalyses for the AS and heterogeneous clay, the apparent catalytic activity (k_{app} (s^{-1})) is defined as

$$k_{\text{app}} = V_{\text{O}_2} / m_{\text{Ru}} \quad (4)$$

where m_{Ru} represents the amount of the catalyst present. The relationship between k_{app} and the Ru-red concentration in AS and clay is shown in Fig. 4. The k_{app} value in the AS decreased drastically with the increase of the Ru-red concentration. However, it was maintained even at high concentrations in the clay. This shows that the bimolecular decomposition was inhibited by immobilization of the cationic complex in the clay, and that the complexes adsorbed in different interlayer spaces are isolated to suppress the bimolecular decomposition.

The water oxidation by a high oxidation state catalyst would compete with a second-order bimolecular decomposition between the cata-

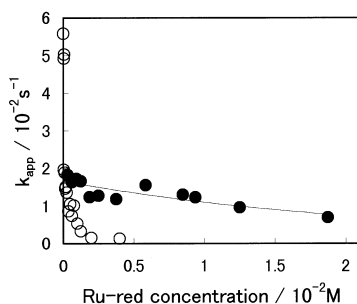


Fig. 4. Relationship between k_{app} and complex concentration in the AS (○) and in the clay (●). The dashed line is the calculated curve based on Eq. (12).

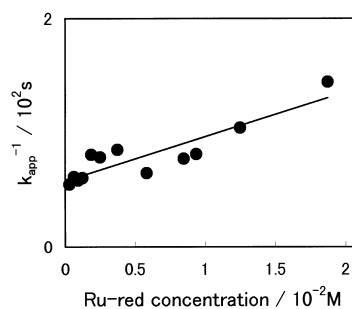


Fig. 5. Plots of k_{app}^{-1} vs. complex concentration in the clay.

lysts. Based on this, k_{app} is represented by Eq. (5).

$$k_{\text{app}} = k_{\text{O}_2} \Phi_{\text{O}_2} \quad (5)$$

where Φ_{O_2} is the yield of the O_2 evolution defined by the following equation:

$$\Phi_{\text{O}_2} = k_{\text{O}_2} [\text{catalyst}] / (k_{\text{O}_2} [\text{catalyst}] + k_{\text{deact}} [\text{catalyst}]^2) \quad (6)$$

where k_{deact} ($M^{-1} s^{-1}$) is a second-order rate constant for the inactivation by the bimolecular decomposition in Eq. (3), and $[\text{catalyst}]$ represents the Ru-red concentration in clay. Eq. (7) is given from Eqs. (5) and (6).

$$k_{\text{app}}^{-1} = 1/k_{\text{O}_2} + (k_{\text{deact}}/k_{\text{O}_2}^2) [\text{catalyst}] \quad (7)$$

The plots of k_{app}^{-1} vs. the Ru-red concentration for clay are shown in Fig. 5. Since these plots almost fall on a straight line in accord with Eq. (7), it is reasonable that the catalytic first-order O_2 evolution is a competitive reaction with the second-order bimolecular decomposition. The values of k_{O_2} and k_{deact} in clay were obtained from the intercept and the slope of the straight line as $1.7 \times 10^{-2} s^{-1}$ and $1.2 M^{-1} s^{-1}$, respectively. The k_{O_2} and k_{deact} values in AS and

Table 1

Summary of the rate constants for O_2 evolution and bimolecular decomposition

	k_{O_2} ($10^{-2} s^{-1}$)	k_{deact} ($M^{-1} s^{-1}$)
AS	5.1	5.2×10^2
Clay system	1.7	1.2

clay are listed in Table 1. The k_{O_2} value thus obtained agreed with that obtained from the slope in the inset of Fig. 3. This shows that Eq. (7) based on the kinetic treatment is reasonable, and that the water oxidation can be treated as a pseudo-first-order reaction with respect to the Ru-red concentration. Although the catalytic activity in clay is one third of that in AS, it is noteworthy that the k_{deact} value in clay is suppressed by 400 times as in AS, indicating that the inorganic layer structure is advantageous to construct a stable water oxidation catalyst system. In the clay where the cationic complex is electrostatically attached to the exchangeable site, the complex would be almost fixed, and a free diffusion of the complex would be prohibited. The catalysis and the bimolecular decomposition could, therefore, be analyzed by a static mechanism rather than a dynamic one that involves diffusion and collision of the complex. In our previous studies, a catalytic activity analysis based on the static mechanism considering intermolecular distance distribution was carried out [8–10]. The intermolecular distance between the molecules dispersed into such a heterogeneous matrix has a distribution depending on their concentration (Fig. 6). The probability density ($P(r)$ (nm^{-1})) of the nearest neighbor intermolecular distance (r (nm), center-to-center distance) of the catalyst molecule can be represented by Eq. (8) [8,14–19];

$$P(r) = 4\pi r^2 N_A \alpha c \times 10^{-24} \times \exp[-4\pi(r^3 - s^3)N_A \alpha c \times 10^{-24}/3] \quad (8)$$

where N_A (mol^{-1}) and c (mol dm^{-3}) are Avogadro's number and apparent average complex concentration in the clay, respectively; s represents the contact distance between the complexes. The s value was obtained as 1.06 nm from a diameter of a sphere that has the same volume as the Ru-red molecular volume [8]. α represents the degree of localization of the complex in the clay [18]. When the complex is localized in the interlayer region of the clay, the α value is necessary to calculate the real local

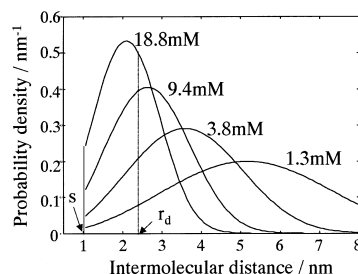


Fig. 6. Intermolecular distance distribution between the nearest-neighbor complexes in the clay at various complex concentrations.

complex concentration in the clay. For the clay, the Ru-red is adsorbed into only interlayer space. The α value in the clay was obtained from the volume fraction of the interlayer space in the clay. The thickness of the inorganic layer is ca. 0.66 nm, and the thickness of the interlayer space expands to ca. 1.25 nm under the conditions of the present experiment. Therefore, the α value in the clay system was estimated as 1.53. Fig. 5 shows intermolecular distance distribution for various Ru-red concentrations according to Eq. (8). Assuming that the catalysts existing within a critical decomposition distance r_d (nm) undergo a bimolecular decomposition to deactivate, the fraction (R_{dec}) of the decomposing catalyst is expressed as follows;

$$R_{dec} = \int_s^{r_d} P(r) dr. \quad (9)$$

The fraction of the effective catalyst for water oxidation is represented by $1 - R_{dec}$ as Eq. (10).

$$1 - R_{dec} = 1 - \int_s^{r_d} P(r) dr = \exp\{-4\pi(r_d^3 - s^3)\alpha c N_A \times 10^{-24}/3\} \quad (10)$$

The k_{app} should be proportional to $1 - R_{dec}$, so that it can be expressed as follows;

$$k_{app} = k(1 - R_{dec}) \quad (11)$$

where k is a constant to represent the intrinsic activity of the catalyst without bimolecular decomposition. Eq. (12) can be derived from Eqs. (10) and (11).

$$k_{app} = k \exp\{-4\pi(r_d^3 - s^3)\alpha c N_A \times 10^{-24}/3\} \quad (12)$$

Eq. (12) was applied to the plots of Fig. 4 for the clay using a nonlinear least-square method, and the best fitting was obtained when the k and r_d value were $1.7 \times 10^{-2} \text{ s}^{-1}$ and 2.39 nm, respectively. The k value is the same as the k_{O_2} ($1.7 \times 10^{-2} \text{ s}^{-1}$) value that was obtained from the intercept of the straight line in Fig. 3 according to Eq. (7). The r_d value is much larger than the molecular size of the Ru-red (1.06 nm), suggesting that the bimolecular decomposition can occur only by diffusion of the complex in the interlayer space. In order to construct a stable catalyst system, the immobilization of the catalyst in the clay was thus very effective.

4. Conclusion

Chemical catalytic water oxidation by Ru-red adsorbed into a clay was studied using Ce(IV) oxidant. The activity analysis was carried out by model equations considering kinetics and an intermolecular distance distribution. As the result, the first-order rate constant of water oxidation (k_{O_2}) and the second-order bimolecular decomposition rate constant (k_{deact}) as well as a critical decomposition distance (r_d (nm)) were obtained. It was shown that the deactivation rate constant k_{deact} in the clay decreased remarkably as compared with that in an AS, indicating that the bimolecular decomposition was suppressed to a great extent in the clay due to isolation and immobilization of the complexes by the inorganic layer. The decomposition distance r_d was estimated as 2.39 nm. In order to construct a stable and an active artificial water oxidation catalyst system, it is very effective to use a heterogeneous clay matrix to immobilize the catalyst.

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