

Cooperative Catalysis and Critical Decomposition Distances in Water Oxidation by the Mononuclear Ammineruthenium(III) Complex in a Nafion Membrane

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Activity of hexaammineruthenium(III) complex ($[\text{Ru}(\text{NH}_3)_6]^{3+}$) as a water oxidation catalyst was investigated in a homogeneous aqueous solution (AS) as well as in a heterogeneous Nafion membrane (HM). In the AS, the apparent catalytic activity ($k_{\text{app}}/\text{s}^{-1}$) decreased monotonically with the concentration, which was ascribed to a bimolecular decomposition of the complex at high concentrations. The bimolecular decomposition was suppressed remarkably by incorporating the complex into the membrane. It was shown that 4-electron water oxidation is cooperatively catalyzed by two molecules of the complex in the membrane. The k_{app} in the HM was much higher than that in the AS at the whole concentration range, which was ascribed both to a favorable interaction for the cooperative catalysis and to the suppression of the bimolecular decomposition by immobilization of the complex. The k_{app} was analyzed in terms of an intrinsic activity ($k_{\text{O}_2}/\text{s}^{-1}$) of the complex, cooperative catalysis distance (r_{co}/nm) and critical decomposition distance (r_{d}/nm) between them based on the intermolecular distance distribution to give $k_{\text{O}_2} = 3.5 \times 10^{-5} \text{ s}^{-1}$, $r_{\text{co}} = 1.21 \text{ nm}$, and $r_{\text{d}} = 0.82 \text{ nm}$. These values were discussed and compared with those obtained in the pentaamminechlororuthenium(III) complex ($[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$) system.

Introduction

Activity of a molecule-based catalyst immobilized into heterogeneous matrixes such as clays,¹ ion-exchange resins,^{2–4} intercalation compounds,⁵ inorganic particles,⁶ and polymer membranes^{7–10} has been studied in view of a fundamental research in photochemistry and electrochemistry as well as for its application to practical use. To optimize the catalysis, it is important to study factors affecting the activity and stability and to establish activity models involving these factors. Many heterogeneous systems of water oxidation catalyst that are important for construction of an artificial photosynthetic system¹¹ have been reported.^{12–14} However, there has been no report on an activity model in a heterogeneous water oxidation catalysis except our earlier works on molecule-based water oxidation catalyst confined onto Pt black⁶ or in a Nafion membrane.^{7,8}

We have studied the catalytic activity of pentaamminechlororuthenium(III) complex ($[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$) in a Nafion membrane for water oxidation using Ce(IV) oxidant and found that two molecules of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$ catalyzed cooperatively 4-electron water oxidation in the membrane.⁹ We have reported that hexaammineruthenium(III) complex ($[\text{Ru}(\text{NH}_3)_6]^{3+}$) is an active water oxidation catalyst.¹⁵ However, detailed studies on its activity and catalysis mechanism have remained open. The effect of a coordination structure for active water oxidation catalyst on its activity, as well as the catalysis mechanism, can be elucidated by analyzing and comparing the catalytic activity of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ with that of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$. In the present paper, the catalytic activity of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ in a Nafion membrane as a water oxidation catalyst is studied, and its

activity is analyzed in terms of an intrinsic activity ($k_{\text{O}_2}/\text{s}^{-1}$), a cooperative catalysis distance (r_{co}/nm), and a critical decomposition distance (r_{d}/nm) based on the intermolecular distance distribution. The catalysis by $[\text{Ru}(\text{NH}_3)_6]^{3+}$ will be discussed and compared with that by $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$.⁹

Experimental Section

Materials. Hexaammineruthenium(III) chloride, $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$, and a Nafion 117 membrane (thickness 180 μm) were purchased from Aldrich Chemical Co. Inc. Cerium(IV) diammonium nitrate, $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$, was purchased from Wako Pure Chemical Industries Ltd. All the materials were of commercially available purest grade and used as received.

Preparation of a Nafion Membrane Incorporating $[\text{Ru}(\text{NH}_3)_6]^{3+}$. Nafion membrane was swollen sufficiently by soaking in pure water for ca. 24 h. The swollen membrane was immersed in a 2.4×10^{-4} to $8.0 \times 10^{-3} \text{ mol dm}^{-3}$ (M) complex aqueous solution (5 mL) for ca. 5 h so that the complex is incorporated into the membrane by cation exchange. The complex amount in the membrane was estimated from the absorbance change (at 320 nm) of the aqueous solution before and after adsorption of the complex. The membrane volume was estimated from the area and thickness (180 μm), and the complex concentration in the membrane calculated from the complex amount and the membrane volume.

Dioxygen Evolution. In a homogeneous aqueous solution (AS) system, excess $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ oxidant ($6.0 \times 10^{-3} \text{ mol}$) was added quickly to 1.0×10^{-3} to $1.2 \times 10^{-2} \text{ M}$ complex aqueous solution (5.0 mL) in a reaction vessel. In a heterogeneous Nafion membrane (HM) system, the membrane (volume: $2.0 \times 10^{-4} \text{ dm}^3$) that incorporated 2.0×10^{-6} to $4.0 \times 10^{-5} \text{ mol}$ of complex was put into pure water in a reaction vessel, and excess Ce^{IV} oxidant ($6.0 \times 10^{-3} \text{ mol}$) was added

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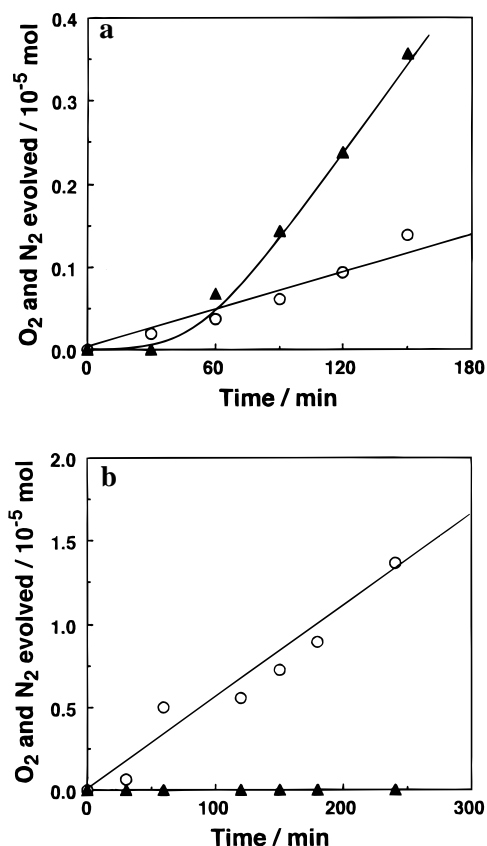


Figure 1. (a) Plots of O₂ (○) and N₂ (▲) evolved vs time in the AS: amount of the complex, 4.0×10^{-5} mol; amount of Ce^{IV} oxidant, 6.0×10^{-3} mol; solution volume, 5.0×10^{-3} dm³. (b) Plots of O₂ (○) and N₂ (▲) evolved vs time in the HM: amount of the complex, 4.0×10^{-5} mol; amount of Ce^{IV} oxidant, 6.0×10^{-3} mol; membrane volume, 2.0×10^{-4} dm³; solution volume, 5.0×10^{-3} dm³.

quickly. In both the systems, 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. The pH was 0.43 without any buffer under the whole complex concentration range, and the pH change was less than 0.03 before and after the O₂ evolution experiment. The O₂ evolved was analyzed on 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.

Results and Discussion

The plots of the amount of O₂ evolved vs reaction time in AS and HM are shown in Figure 1a,b, respectively. The amount of O₂ evolved increased with time, and dinitrogen (N₂) was detected after 1 h only in AS. This N₂ can result only from oxidation of the ammine ligands of the complex since no N₂ was detected without [Ru(NH₃)₆]³⁺. The O₂ evolution continued for ca. 4 h in AS, but for more than 10 h in HM. The amount of O₂ evolved in HM was much higher (by about 6 times) than that in AS under the same amount of the complex in the reaction system.

The initial O₂ evolution rate ($V_{O_2}/\text{mol s}^{-1}$), which was obtained from the slope at time zero of the plots of O₂ evolved vs time, was plotted against the complex concentration in the AS, as shown in Figure 2a. V_{O_2} increased with the complex concentration and then decreased after passing a maximum V_{O_2} at 3.0×10^{-3} M. The initial N₂ evolution rate, $V_{N_2}/\text{mol s}^{-1}$, is second order with respect to the complex concentration,

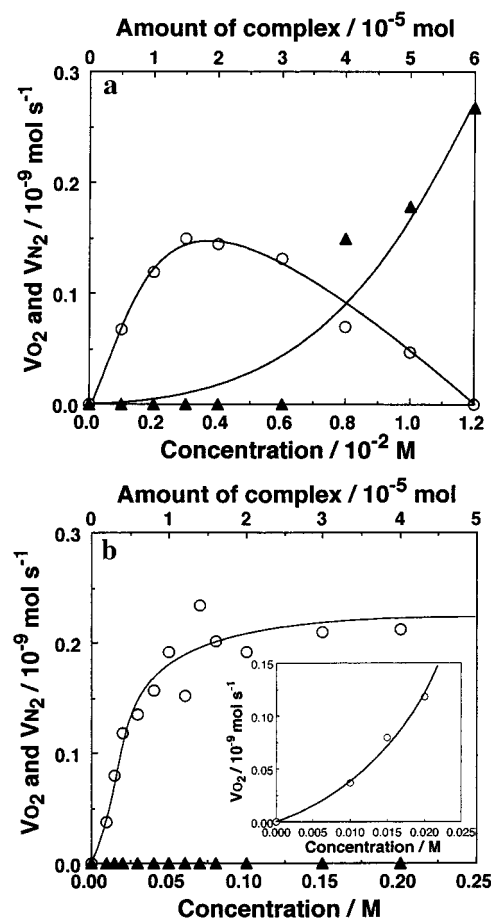


Figure 2. (a) Plots of the rates of gas evolution (V_{O_2} (○) and V_{N_2} (▲)) versus complex concentration and complex amount for the AS: amount of Ce^{IV} oxidant, 6.0×10^{-3} mol; solution volume, 5.0×10^{-3} dm³. (b) Plots of the rates of gas evolution (V_{O_2} (○) and V_{N_2} (▲)) versus complex concentration and complex amount for the HM; The inset illustrates the plots at low concentrations.

indicating that decomposition of the complexes to yield N₂ is a bimolecular process. The V_{O_2} decrease at higher concentrations is ascribable to the bimolecular decomposition.

Figure 2b shows the plots of V_{O_2} vs complex concentration in the HM. The V_{O_2} increase was second-order with respect to the complex concentration at low concentrations, as shown in the inset of Figure 2b, which indicates that O₂ evolution is a bimolecular reaction of the complex. The complex [Ru(NH₃)₆]³⁺ can work only as a 2-electron oxidation catalyst, and we have actually observed two oxidation waves at 1.04 and 1.32 V vs SCE in the cyclic voltammogram (CV) of a Nafion-coated graphite electrode incorporating [Ru(NH₃)₆]³⁺.¹⁵ Therefore, two molecules of [Ru(NH₃)₆]³⁺ are required for a 4-electron water oxidation catalysis and work cooperatively.

The V_{O_2} increase was saturated at high concentrations (more than 0.10 M) in the HM (Figure 2b), which is also ascribed to a bimolecular decomposition of the complex. However, no N₂ was evolved, and V_{O_2} did not decrease even when the complex concentration (0.20 M) in the HM is ca. 70 times as high as that (3.0×10^{-3} M) for the maximum V_{O_2} in the AS. The saturation of the V_{O_2} increase in Figure 2b cannot be explained by the deactivation of the complex due to the release of NH₃ ligands, because [Ru(NH₃)₆]³⁺ is stable in the aqueous solution as well as the Nafion membrane and the concentration (2.4 M) of NH₄⁺ resulting from the large excess (6.0×10^{-3} mol) of a Ce(NH₄)₂(NO₃)₆ oxidant is high in the liquid phase. We consider

that some slow processes exist between the bimolecular decomposition to deactivate and N_2 evolution in the Nafion membrane.

To study the catalysis in the present system, the apparent catalyst activity (k_{app}/s^{-1}), which means turnover number of the catalyst, was defined as $k_{app} = V_{O_2}/m_{Ru}$ where m_{Ru}/mol is the amount of the complex present in the reaction system either in the AS or HM. The dependencies of k_{app} on the complex concentration for the AS and HM are shown in Figure 3a,b, respectively. In the AS, k_{app} decreased monotonically with the concentration, which is ascribed to a bimolecular decomposition of the complex. On the other hand, in the HM, k_{app} increased with the concentration when the concentration is low and then decreased with the concentration after passing a maximum value at 2.0×10^{-2} M. The increase of k_{app} at the low concentration region (less than 2.0×10^{-2} M) can be explained by a cooperative catalysis by two molecules of the complex. An isolated complex in the membrane could not work for this cooperative catalysis. As the complex concentration increases, the fraction of the adjacent complexes capable of cooperative catalysis increases to result in the k_{app} increase. When the concentration increases further, the fraction of the complex that undergoes a bimolecular decomposition would increase to result in the k_{app} decrease. Such a k_{app} behavior has been found only in the case of mononuclear complexes that work as a 2-electron oxidation catalyst. In the trinuclear complex, $[(NH_3)_5Ru-O-Ru(NH_3)_4-O-Ru(NH_3)_5]^{6+}$,⁷ which works as a 4-electron oxidation catalyst, 4-electron water oxidation is catalyzed by one catalyst molecule, but bimolecular decomposition of the catalyst takes place at high concentrations, so that k_{app} in the HM decreased monotonically with the concentration.

The k_{app} values in the HM were much higher than those in the AS at the whole concentration range (compare Figure 3a,b); for instance the k_{app} value ($1.8 \times 10^{-5} s^{-1}$) at 1.0×10^{-2} M in the HM was 20 times higher than that ($9.4 \times 10^{-7} s^{-1}$) in the AS. The diffusion of the complex is suppressed by incorporating it into the membrane, which favors a cooperative catalysis as well as suppresses the bimolecular decomposition, leading to the higher k_{app} values in the HM. The complex concentration in the HM under the present conditions is much higher than that in the AS so that most complexes are close to each other, making cooperative catalysis possible. Complexes interacting via two water molecules would form an intermediate in this cooperative catalysis. The intermediate would be stabilized thermodynamically by immobilization of the complex in the membrane to increase the catalytic activity.

In our earlier paper on a $[Ru(NH_3)_5Cl]^{2+}$ system,⁹ the k_{app} in the HM is 140 times higher than that in the AS at the same complex concentration (1.0×10^{-2} M), which was also explained by a favorable interaction for the cooperative catalysis and by the suppression of the bimolecular decomposition by immobilization of the complex. The higher degree (140 times) of the k_{app} increase for the $[Ru(NH_3)_5Cl]^{2+}$ system by its incorporation in the membrane than that (20 times) for the $[Ru(NH_3)_6]^{3+}$ system would be caused by a much more bimolecular decomposition in the AS for the former than the latter system. (V_{N_2} values in the AS (at 8.0×10^{-3} M of the complex concentration) are $4.1 \times 10^{-9} mol s^{-1}$ ⁹) and less than $1.0 \times 10^{-11} mol s^{-1}$ in the $[Ru(NH_3)_5Cl]^{2+}$ and $[Ru(NH_3)_6]^{3+}$ systems, respectively.)

The reversible redox wave at -0.22 V vs SCE due to $Ru^{III/II}$ in the cyclic voltammogram (CV) of Nafion-coated ITO electrode incorporating $[Ru(NH_3)_6]^{3+}$ did not decrease in repetitive cyclic potential sweeps, showing that the complexes

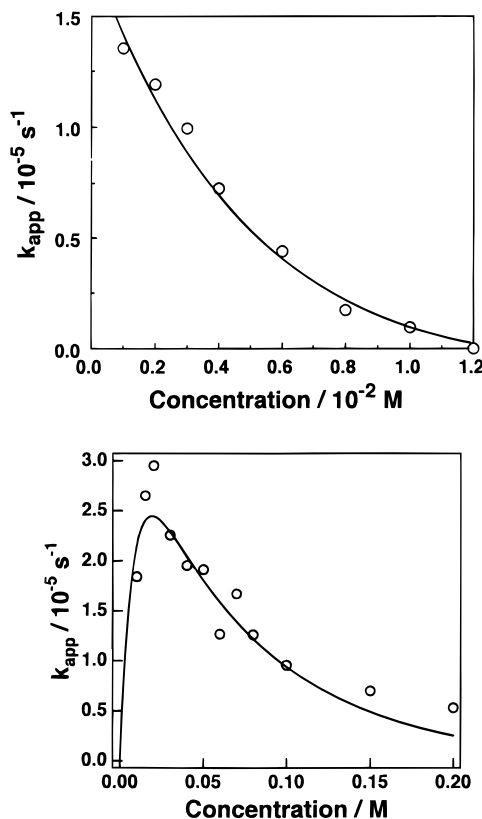


Figure 3. (a) Relationship between the apparent catalyst activity (k_{app}) and complex concentration in the AS. (b) Relationship between the apparent catalyst activity (k_{app}) and complex concentration in the HM. The curve shows a calculated value based on eq 1.

are immobilized stably in the membrane without the dissolution of the complexes from the membrane to bulk electrolyte solution. Both the cooperative catalysis and the bimolecular decomposition in the membrane depend on the intermolecular distance between the complexes in the present system where the complexes are immobilized in the membrane. It is important to take intermolecular distance distribution into account rather than average intermolecular distance. k_{app} can be expressed by eq 1⁹ on the basis of intermolecular distance distribution:

$$k_{app} = k_{O_2} [\exp\{-4\pi(r_d^3 - s^3)\alpha c N_A \times 10^{-24}/3\} - \exp\{-4\pi(r_{co}^3 - s^3)\alpha c N_A \times 10^{-24}/3\}] \quad (1)$$

where k_{O_2}/h^{-1} is a constant to express an intrinsic activity of the catalyst, r_d/nm is a critical decomposition distance within which the bimolecular decomposition of complexes takes place, r_{co}/nm is a cooperative catalysis distance (r_{co}/nm) within which the complexes can work for cooperative catalysis, and s/nm , $\alpha, c/mol dm^{-3}$, and N_A/mol^{-1} are the contact distance ($s = 0.75 nm$)¹⁶ between the complexes, the degree ($\alpha = 40$)⁷ of localization of the complex in the membrane, the complex concentration in the membrane, and Avogadro's number, respectively. The first exponential term in parentheses of eq 1 represents the fraction of the complex that does not undergo the bimolecular decomposition (intermolecular distance between the nearest-neighbor complexes, r , is longer than r_d), and the second one represents the fraction of the complex that cannot work for cooperative catalysis (r is longer than r_{co}).

Eq 1 was applied to the relationship between k_{app} and concentration in Figure 3b using the nonlinear least-squares method. The best fitting was obtained as shown in the curve of

TABLE 1: Summary of k_{O_2} , s , r_{co} , and r_d Values in Water Oxidation Catalysis by Ammine-Coordinate Mononuclear Ruthenium Complexes in a Nafion Membrane

system	k_{O_2}/s^{-1}	s/nm	r_{co}/nm	r_d/nm
Nafion/[Ru(NH ₃) ₆] ³⁺	3.5×10^{-5}	0.75	1.21	0.82
Nafion/[Ru(NH ₃) ₅ Cl] ²⁺ ^a	2.7×10^{-3}	0.75	1.21	0.84

^a Ref 9.

Figure 3b when $k_{O_2} = 3.5 \times 10^{-5} s^{-1}$, $r_d = 0.82$ nm, and $r_{co} = 1.21$ nm. This good fitting of eq 1 supports that this treatment is reasonable. The fitting parameters obtained are summarized in Table 1 together with the earlier analysis results in the [Ru(NH₃)₅Cl]²⁺ system.⁹ The k_{O_2} in the [Ru(NH₃)₅Cl]²⁺ system is higher than that in the [Ru(NH₃)₆]³⁺ system by 2 orders of magnitude. The k_{O_2} increased remarkably on substitution of an ammine ligand by a chloro ligand though the redox potentials of both the complexes in the membrane are almost the same: $E^{III/II} = -0.25$ V, $E^{IV/III} = 1.06$ V, $E^{V/IV} = 1.28$ V (vs SCE) for [Ru(NH₃)₅Cl]²⁺,¹⁷ $E^{III/II} = -0.22$ V, $E^{IV/III} = 1.04$ V, $E^{V/IV} = 1.32$ V (vs SCE) for [Ru(NH₃)₆]³⁺.¹⁵

The r_d value (0.82 nm) is very close to that (0.84 nm) of [Ru(NH₃)₅Cl]²⁺ and reasonable when considering the molecular size (0.75 nm) of [Ru(NH₃)₆]³⁺, showing that the bimolecular decomposition takes place between the complexes in close proximity with each other for both the complexes.

The r_{co} values (1.21 nm) for both the complexes were longer than the calculated distance (0.58 nm) between the Ru centers in a presumed Ru—O—O—Ru intermediate binding (Ru—O, 0.214 nm;¹⁸ O—O, 0.148 nm¹⁹). We have proposed in our earlier paper on the [Ru(NH₃)₅Cl]²⁺ system⁹ that two kinds of interpretations might be possible for this. One is that water-coordinated high oxidation state complexes move from their anchored positions in the membrane^{20,21} (so-called bounded motion) to make the real interacted distance much shorter (~0.58 nm). Another interpretation is possible by considering a new mechanism for water coordination; i.e., an intermediate is formed through hydrogen bonds between water and its ammine ligands (Ru—N—H···O—O···H—N—Ru). The same r_{co} values (1.21 nm) for both [Ru(NH₃)₆]³⁺ and [Ru(NH₃)₅Cl]²⁺ might support the possibility of such an intermediate mechanism.

Conclusion

The activity of hexaammineruthenium(III) complex ([Ru(NH₃)₆]³⁺) as water oxidation catalyst was studied in a homogeneous aqueous solution (AS) and a heterogeneous Nafion membrane (HM). In the AS, the apparent catalytic activity (k_{app}/s^{-1}) decreased monotonically with the concentration by a bimolecular decomposition of the complexes at high concentrations. This bimolecular decomposition was remarkably suppressed by incorporating into a Nafion membrane. An optimum complex concentration for k_{app}/s^{-1} in the HM was exhibited, which was explained by both a cooperative catalysis by two complex molecules and a bimolecular decomposition. The k_{app} was remarkably higher in the HM than in the AS, which is ascribed to a favorable interaction for the cooperative catalysis

and to a suppression of a bimolecular decomposition by immobilization of the complex. The k_{app} in the HM was analyzed in terms of an intrinsic catalytic activity (k_{O_2}/s^{-1}) of the complex, a cooperative catalysis distance (r_{co}/nm), and a critical decomposition distance (r_d/nm) between them based on the intermolecular distance distribution, and the $k_{O_2} = 3.5 \times 10^{-5} s^{-1}$, $r_d = 0.84$ nm, and $r_{co} = 1.21$ nm were obtained. The k_{O_2} in the [Ru(NH₃)₅Cl]²⁺ system was higher than that in the [Ru(NH₃)₆]³⁺ system by 2 orders of magnitude. This remarkable increase of k_{O_2} on substitution of an ammine ligand by a chloro one gives an important suggestion for designing more active molecular catalyst and encourages us to investigate the catalysis by a tetraamminedichlororuthenium(III) complex. The r_{co} value obtained suggested that the cooperative catalysis by the ammine-coordinated mononuclear ruthenium complexes takes place through hydrogen bonds between water and ammine ligands.

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References and Notes

- (1) *Chemistry of Clays and Clay Minerals*; Newman, A. C. D., Ed.; Wiley: New York, 1987.
- (2) Thornton, A. T.; Laurence, G. S. *J. Chem. Soc., Chem. Commun.* **1987**, 408.
- (3) Slamo-Schwok, A.; Feitelson, Y.; Rabani, J. *J. Phys. Chem.* **1981**, 85, 2222.
- (4) Kurimura, Y.; Nagashima, M.; Takato, K.; Tsuchida, E.; Kaneko, M. Yamada, A. *J. Phys. Chem.* **1982**, 86, 2432.
- (5) Makoto, O.; Kazuyuki, J. *Chem. Rev.* **1995**, 95, 399.
- (6) Ogino, I.; Nagoshi, K.; Yagi, M.; Kaneko, M. *J. Chem. Soc., Faraday Trans.* **1996**, 92, 3431.
- (7) Yagi, M.; Tokita, S.; Nagoshi, K.; Ogino, I.; Kaneko, M. *J. Chem. Soc. Faraday Trans.* **1996**, 92, 2457.
- (8) Buttry, D. A.; Anson, F. C. *J. Am. Chem. Soc.* **1984**, 106, 59.
- (9) Yagi, M.; Nagoshi, K.; Kaneko, M. *J. Phys. Chem. B* **1997**, 101, 5143.
- (10) Sharp, M.; Montgomery, D. D.; Anson, F. C. *J. Electroanal. Chem.* **1985**, 194, 247.
- (11) (a) Kaneko, M. *Macromolecular Complexes: Dynamic Interaction and Electronic Processes*; Tsuchida, E., Ed.; VCH Publishers: New York, 1991; p 353–377. (b) Bard, A. J.; Fox, M. A. *Acc. Chem. Res.* **1995**, 24, 141. (c) Graetzel, M.; Kalyanasundaram, K. *Curr. Sci.* **1994**, 66, 706.
- (12) Thampi, K. R.; Graetzel, M. *J. Mol. Catal.* **1990**, 60, 31.
- (13) Harriman, A.; Pickering, J.; Thomas, J. M.; Christensen, P. A. *J. Chem. Soc., Faraday Trans. 1* **1988**, 84, 2795.
- (14) Mills, A.; Davies, H. L. *Inorg. Chim. Acta* **1991**, 189, 149.
- (15) Rmaraji, R.; Kaneko, M.; Kira, A. *Bull. Chem. Soc. Jpn.* **1991**, 64, 1028.
- (16) The complexes were approximated as a sphere, and its diameter ($s = 0.75$ nm) was calculated from the distance and the angle of the atoms (Ru—N, 0.210 nm; N—H, 0.101 nm, \angle H—N—Ru, 110°) as well as the van der Waals radius (0.12 nm) of hydrogen.
- (17) Ramaraj, R.; Kira, A.; Kaneko, M. *J. Chem. Soc., Chem. Commun.* **1987**, 227.
- (18) Gilbert, J. A.; Eggleston, D. S.; Murphy, W. R., Jr.; Geselowitz, D. A.; Gersten, S. W.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, 107, 3855.
- (19) *CRC Handbook of Chemical and Physics*, 73th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1992.
- (20) Yagi, M.; Nagai, K.; Onikubo, T.; Kaneko, M. *J. Electroanal. Chem.* **1995**, 383, 61.
- (21) Blauch, D. N.; Saveant, J.-M. *J. Am. Chem. Soc.* **1992**, 114, 3323.