

Catalytic water oxidation using chemically generated $\text{Ru}(\text{bpy})_3^{3+}$ oxidant

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Abstract

Catalytic water oxidation to evolve O_2 was studied using chemically generated $\text{Ru}(\text{bpy})_3^{3+}$ (bpy; 2,2'-bipyridine) oxidant. $\text{Ru}(\text{bpy})_2^{2+}$ was oxidized to $\text{Ru}(\text{bpy})_3^{3+}$ by suspension of PbO_2 powders. In the catalytic water oxidation system composed of the $\text{Ru}(\text{bpy})_3^{3+}$ and RuO_2 adsorbing Ru-red ($[(\text{NH}_3)_5\text{Ru}-\text{O}-\text{Ru}(\text{NH}_3)_4-\text{O}-\text{Ru}(\text{NH}_3)_5]\text{Cl}_6$), much higher amount of O_2 evolved than in a homogeneous $\text{Ru}(\text{bpy})_3^{3+}$ /Ru-red system. This was ascribed to the suppression of the bimolecular decomposition of Ru-red in the RuO_2 matrix. The amount of the O_2 evolved increased with the adsorbed amount of the Ru-red into RuO_2 , whereas higher amount of the adsorbed Ru-red resulted in the decrease of the O_2 evolution, which was ascribed to bimolecular decomposition of Ru-red in the RuO_2 at higher concentrations. The activity of Ru-red in the RuO_2 matrix was analyzed considering a static distance distribution between the nearest-neighboring molecules. The decomposition distance (r_d) was obtained as 1.25 nm showing that contacting Ru-red molecules undergo bimolecular decomposition without catalysis. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ru-red; $\text{Ru}(\text{bpy})_3^{3+}$; Water oxidation

1. Introduction

Constructing an artificial photosynthetic system such as a water photolysis to obtain H_2 and O_2 is of importance to develop a new energy resource instead of the fossil fuels. Tris(2,2'-bipyridine) ruthenium ($\text{Ru}(\text{bpy})_3^{2+}$) is one of the most well-known photocatalysts capable of theoretical water splitting into O_2 and H_2 . How-

ever, there has been so far no example of water splitting by using $\text{Ru}(\text{bpy})_3^{2+}$ as a photosensitizer. As an approach to this goal, photochemical water oxidation composed of $\text{Ru}(\text{bpy})_3^{2+}$ and sensitizer has been studied in the presence of electron acceptor (Fe^{3+} , $\text{S}_2\text{O}_8^{2-}$, Co^{3+} complex etc.) and water oxidation catalyst (RuO_2 , etc.) [1–3], which can be regarded as a Photosystem II model. Although water oxidation is an important reaction to provide electrons to an artificial photosynthetic system, the number of reports on water oxidation has not been many in comparison with a photochemical H^+ reduction. Since $\text{Ru}(\text{bpy})_3^{3+}$ is a 1-electron oxidant for water oxidation, it is impossible to oxidize water to

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evolve O_2 (4-electron process) without catalyst. In order to establish an efficient water oxidation site, it is necessary to combine the $Ru(bpy)_3^{3+}$ with an active water oxidation catalyst capable of 4-electron oxidation. The present authors have found active molecule-based catalysts for water oxidation [4–10]. Trinuclear Ru complex called Ru-red ($[(NH_3)_5Ru-O-Ru(NH_3)_4-O-Ru(NH_3)_5]Cl_6$) was found to catalyze water oxidation in the presence of Ce(IV) oxidant [7–10] showing much higher activity than the conventional catalyst such as RuO_2 . However, it has been difficult to realize water oxidation by Ru-red catalyst with $Ru(bpy)_3^{3+}$ oxidant. Now we have found that if the Ru-red is used in combination with RuO_2 , it shows high activity in water oxidation, and the results will be reported.

2. Experimental

2.1. Material and catalyst preparation

Both tris(2,2'-bipyridine) ruthenium(II) perchlorate ($Ru(bpy)_3^{2+}$) [11] and μ -oxo-bis[aqua-bis(2,2'-bipyridine)ruthenium] ($Ru-O-Ru, [(bpy)_2(H_2O)Ru-O-Ru(bpy)_2(H_2O)]^{6+}$) [12] were synthesized according to previous procedures. PbO_2 , RuO_2 and Ru-red were purchased from Kanto Chemical, Aldrich Chemical and Wako, respectively.

RuO_2 adsorbing one of the molecule-based catalysts was prepared in an aqueous solution of the complex containing suspended RuO_2 by sonication for 6 h. The adsorbed amount of the complex into RuO_2 was estimated from the visible absorption spectral change of the complex solution before and after the adsorption. The catalyst obtained is denoted as, e.g., $RuO_2[Ru-red]$. It was confirmed that no desorption of Ru-red from the RuO_2 matrix takes place if once Ru-red was adsorbed into RuO_2 matrix. The adsorbed Ru-red did not go out of the RuO_2 throughout the catalytic water oxidation.

2.2. Water oxidation

In a catalytic water oxidation system, excess of PbO_2 powders were added to a pH 2.15 aqueous solution (reaction volume, 10 ml; pH 2.15, HNO_3 – KNO_3 buffer) containing the known amounts of $Ru(bpy)_3^{2+}$ and catalyst (e.g., $RuO_2[Ru-red]$). All the water oxidation reactions were run under argon atmosphere. The O_2 produced was analyzed by a gas chromatograph (Hitachi, 165) with a molecular sieve 5 A column and argon carrier gas. The net amount of O_2 evolved was obtained by subtracting a blank amount of O_2 coming from air. In the present study the experimental errors were $\pm 10\%$.

3. Results and discussion

It has been reported previously that stability of $Ru(bpy)_3^{3+}$ depended on the pH conditions [3]. At $pH > 5$, nucleophilic substitution of the bpy ligand by hydroxide ion was assumed to take place competitively with the O_2 evolution. Therefore, catalytic water oxidation with $Ru(bpy)_3^{3+}$ oxidant was carried out in a pH 2.15 aqueous solution in the present study.

Formal potentials of $Pb^{4+}(PbO_2)/Pb^{2+}$ and $Ru(bpy)_3^{3+/2+}$ couples are present at +1.46 V [13] and +1.27 V (vs. NHE) [14], respectively, so that PbO_2 can work as an oxidant to generate $Ru(bpy)_3^{3+}$ from $Ru(bpy)_3^{2+}$. Fig. 1 shows the typical absorption spectra of a $Ru(bpy)_3^{2+}$ aqueous solution before and after the addition of PbO_2 oxidant. When PbO_2 oxidant of 0.24 g (0.1 M/10 ml) was added into a 0.1 mM/10 ml $Ru(bpy)_3^{2+}$ solution, the absorption peak of $Ru(bpy)_3^{2+}$ at 454 nm ($\epsilon = 1.46 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) [15] almost disappeared and a new peak appeared at 420 nm ($\epsilon = 3.3 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) [16] due to the formation of $Ru(bpy)_3^{3+}$. In the present condition (the molar ratio of $[PbO_2]/[Ru(bpy)_3^{2+}] > 1000$), almost all the $Ru(bpy)_3^{2+}$ were converted to $Ru(bpy)_3^{3+}$.

Catalytic water oxidation was carried out in the presence of $Ru(bpy)_3^{2+}$, RuO_2 as a water

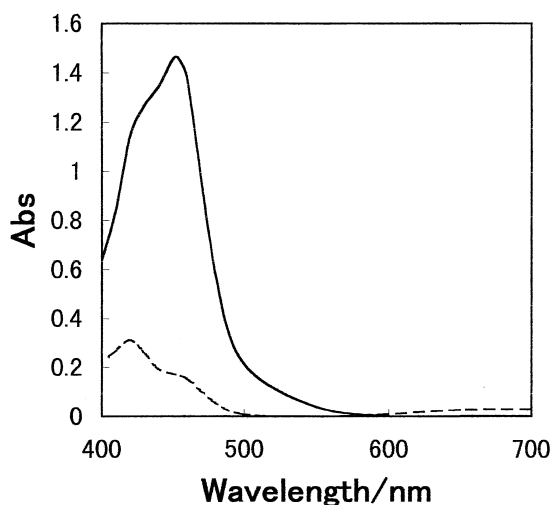
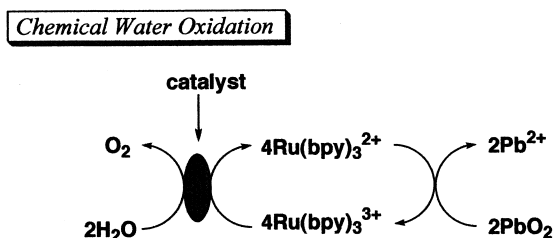


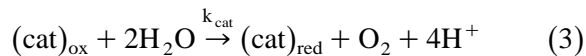
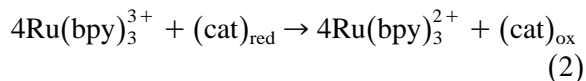
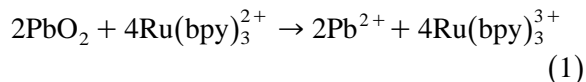
Fig. 1. Visible absorption spectra of a $\text{Ru}(\text{bpy})_3^{2+}$ solution before (solid line) and after (dashed line) adding PbO_2 oxidant. $[\text{Ru}(\text{bpy})_3^{2+}]$, 0.1 mmol dm^{-3} ; $[\text{PbO}_2]$, 0.1 mol dm^{-3} ; pH 2.15 (HCl– KNO_3 buffer).

oxidation catalyst and PbO_2 oxidant to generate $\text{Ru}(\text{bpy})_3^{3+}$ (see Scheme 1). The present authors have reported a catalytic water oxidation by molecule-based catalysts with Ce(IV) oxidant. Although the redox potential of Ce(IV)/Ce(III) couple (+1.71 V vs. NHE) [13] is more positive than that of $\text{Pb}^{4+}/\text{Pb}^{2+}$, $\text{Ru}(\text{bpy})_3^{2+}$ cannot be oxidized by Ce(IV) oxidant as reported previously [17]. Therefore, PbO_2 instead of Ce(IV) oxidant was applied in the present work. Fig. 2 shows the relationship between the apparent rate of the O_2 evolution (V_{O_2} , mol s^{-1}) and the added PbO_2 amount. In a blank experiment without $\text{Ru}(\text{bpy})_3^{2+}$, no O_2 evolution took place. In addition, it was confirmed that PbO_2 itself cannot oxidize water to evolve O_2 . The V_{O_2} increased with the added amount of PbO_2 , and



Scheme 1.

then was saturated beyond $1.0 \times 10^{-3} \text{ mol}$ (0.24 g) of the PbO_2 amount (molar ratio, $[\text{PbO}_2]/[\text{Ru}(\text{bpy})_3^{2+}] > 1000$). The present catalytic water oxidation consists of three reaction processes as follows.



where $(\text{cat})_{\text{red}}$ and $(\text{cat})_{\text{ox}}$ are the reduced species of the catalyst and the oxidized ones, respectively. In the excess water conditions the catalytic water oxidation is represented by the pseudo first-order rate with respect to the catalyst concentration (Eq. (3)), where the rate constant is k_{cat} (s^{-1}). When large excess of PbO_2 more than 0.24 g (PbO_2 concentration higher than 0.1 M and $[\text{PbO}_2]/[\text{Ru}(\text{bpy})_3^{2+}] > 1000$, see Fig. 2) was used, V_{O_2} was independent of the PbO_2 amount because excess and steady concentration of $\text{Ru}(\text{bpy})_3^{3+}$ was present during the water oxidation catalysis. This indicates that the formation of $\text{Ru}(\text{bpy})_3^{3+}$ by PbO_2 oxidant is

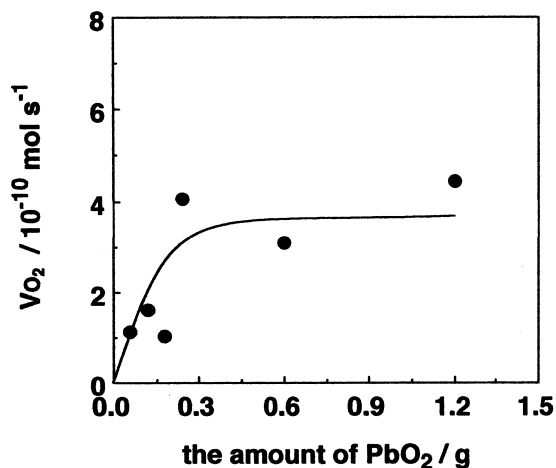


Fig. 2. Relationship between the rate of O_2 evolution and the amount of PbO_2 , oxidizing reagent of $\text{Ru}(\text{bpy})_3^{2+}$ in the catalytic water oxidation. $[\text{RuO}_2]$, 0.1 mmol dm^{-3} ; $[\text{Ru}(\text{bpy})_3^{2+}]$, 0.1 mmol dm^{-3} ; pH 2.15 (HNO_3 – KNO_3 buffer); reaction time, 1 h.

not rate-determining step (Eq. (1)). It was confirmed that when the concentration of PbO_2 and $\text{Ru}(\text{bpy})_3^{2+}$ are fixed, the rate of O_2 evolution is proportional to the catalyst (RuO_2) concentration, so that it is given by Eq. (4).

$$\begin{aligned} d[\text{O}_2]/dt &= (V_{\text{O}_2}/v) \\ &= k_{\text{cat}}[\text{cat}]_{\text{T}} \end{aligned} \quad (4)$$

where v (dm^3) is the reaction volume and $[\text{cat}]_{\text{T}}$ is the total concentration of the catalyst. The following study for the catalytic water oxidation was carried out under the conditions of $[\text{PbO}_2]/[\text{Ru}(\text{bpy})_3^{2+}] = 1000$ where the Eq. (4) is applicable.

Catalytic water oxidation according to Scheme 1 was studied using various kinds of catalyst to oxidize water. Typical data are shown in Table 1. Almost no O_2 production took place when the molecule-based catalysts such as Ru–O–Ru and Ru-red instead of RuO_2 were employed as a homogeneous catalyst. It has been reported by Gilbert et al. [12] that Ru–O–Ru ($(\text{H}_2\text{O})(\text{bpy})_2\text{Ru}-\text{O}-\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})^{6+}$) shows an activity for water oxidation. The present authors have also studied the catalytic water oxidation by a homogeneous Ru–O–Ru catalyst with Ce(IV) oxidant, and confirmed that the catalytic activity of Ru–O–Ru is much smaller than that of Ru-red (the turnover number (TN) of molecular catalyst to oxidize water: Ru–O–Ru, $\sim 4 \text{ h}^{-1}$; Ru-red, 50 h^{-1}) [18]. We concluded that the low activity of Ru–O–Ru is due

to the decomposition via high oxidation state of Ru–O–Ru into the monomeric complex. However, it was found (Table 1) that adsorption of the molecule-based catalyst into RuO_2 results in a drastic enhancement of the catalytic activity much more than a merely additive effect. When the TN of the molecule-based catalyst adsorbed into RuO_2 matrix was estimated by considering the net O_2 evolution via the adsorbed complex after subtracting the O_2 evolution from the RuO_2 blank (run 3), the TN of the adsorbed molecular catalyst is 2–3 order of magnitude higher than that of the RuO_2 catalyst.

In order to understand the catalysis by the Ru-red adsorbed into RuO_2 matrix ($\text{RuO}_2[\text{Ru-red}]$), the catalytic water oxidation was studied with respect to the adsorbed amount of the Ru-red into RuO_2 (the employed amount of RuO_2 is constant), and the result is shown in Fig. 3. The amount of O_2 evolved increased with the adsorbed amount of Ru-red when its amount is low, whereas on increasing the adsorbed amount of Ru-red O_2 production was suppressed after passing an optimum point. The present authors have reported recently the catalytic water oxidation with Ce(IV) oxidant and heterogeneous catalyst systems where Ru-red is incorporated into a solid matrix [7]. The catalytic water oxidation by the Ru-red takes place monomolecularly, but a bimolecular decomposition occurs competitively with the water oxidation. In a homogeneous catalyst system by the Ru-red with Ce(IV) oxidant, bimolecular de-

Table 1
Typical data of catalytic water oxidation by catalyst/ $\text{Ru}(\text{bpy})_3^{2+}$ / PbO_2 system^{a,b}

Run	Catalyst	O_2 produced (μl)	Turnover number (TN) (h^{-1})
1	Ru–O–Ru (1.0×10^{-6} mol) (homogeneous system)	~ 0	~ 0
2	Ru-red (1.0×10^{-6} mol) (homogeneous system)	4.2	0.17
3	RuO_2 (1.0×10^{-6} mol)	35.5	1.5
4	RuO_2 (1.0×10^{-6} mol) [Ru–O–Ru] (8.3×10^{-10} mol) ^c	42.9	365 ^d
5	RuO_2 (1.0×10^{-6} mol) [Ru-red (8.3×10^{-10} mol)] ^c	66.9	1550 ^d

^aReaction time, 1 h; reaction volume, 10 ml.

^b $[\text{Ru}(\text{bpy})_3^{2+}]$, 0.1 mmol dm^{-3} ; PbO_2 , 0.24 g (corresponding to 0.1 mol dm^{-3}).

^cThe molecule-based catalyst was adsorbed on RuO_2 particle.

^dThe net amount of O_2 evolved coming from the molecule-based catalyst in both runs 4 and 5 was calculated by subtracting a blank O_2 evolved by RuO_2 (run 3), and the turnover number was estimated based on the adsorbed amount of the complex on RuO_2 .

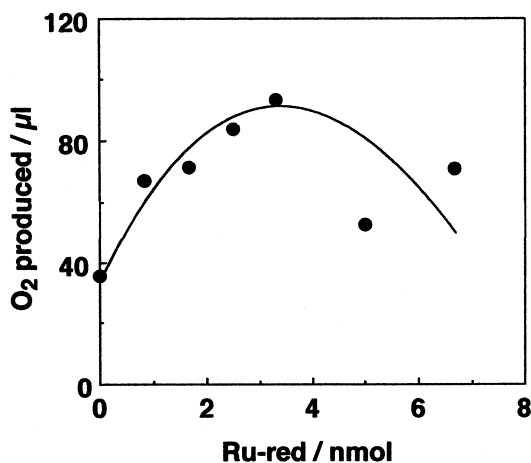


Fig. 3. Dependence of the O₂ evolution on the adsorbed amount of Ru-red into RuO₂. RuO₂ amount was constant in each run, and only the adsorbed amount of Ru-red onto RuO₂ was varied. [PbO₂], 0.1 mol dm⁻³/10 ml; [RuO₂], 0.1 mmol dm⁻³/10 ml; [Ru(bpy)₃]²⁺, 0.1 mmol dm⁻³/10 ml; pH 2.15 (HNO₃-KNO₃ buffer); reaction time, 1 h.

composition was observed remarkably even in a dilute concentration below 1 mM. However, it was found that the fixation of the catalyst into a solid matrix results in the suppression of the catalyst decomposition, and that the catalytic activity of the Ru-red is maintained under highly concentrated condition in the matrix. The enhanced activity of RuO₂[Ru-O-Ru] in Table 1 could also be the same as mentioned above. The present catalysis by RuO₂[Ru-complex] as shown in Table 1 as well as in Fig. 3 is similar to our previous results.

Although the fixation of the Ru-red into RuO₂ matrix results in much higher activity than a homogeneous Ru-red system, the decomposition of the Ru-red would also takes place as shown by the decrease of the evolved O₂ in increasing the adsorbed amount of Ru-red. Such bimolecular decomposition of Ru-red in its higher concentrations in the RuO₂ is dependent on the molecular distance. The activity analysis of the Ru-red adsorbed into RuO₂ matrix was carried out based on a random distribution of the adsorbed molecules [19,20]. We assume now that the Ru-red is adsorbed in the void space between the RuO₂ particles. In a void space adsorption model, the probability of the distance

distribution between the nearest-neighboring molecules is given by

$$P(r) = 4\pi r^2 N_A c \times 10^{-24} \times \exp[-4\pi(r^3 - s^3)] \times N_A c \times 10^{-24}/3 \quad (5)$$

where $P(r)$ (nm⁻¹), r (nm), N_A (mol⁻¹), c (mol dm⁻³), s (nm) are a probability density, the centre-to-centre distance between the nearest-neighboring molecules, Avogadro's constant, Ru-red concentration in the void space of RuO₂, and contact distance between the Ru-red molecules (the s value was calculated as 1.06 nm according to our previous report [4,5,7,9]), respectively. The c value was calculated by assuming the close-packed structure of the RuO₂ porous particles. The volume ratio of the void space in the RuO₂ particles is 25.9% for the close-packed structure. Considering the molecular weight of RuO₂ ($M = 133.07$ g mol⁻¹), density (6.97×10^{-3} g dm⁻³) [21] and the volume ratio of the void space, the void volume of RuO₂ was obtained as 4.9×10^{-3} dm³ mol⁻¹. According to Eq. (5), the relationship of $P(r)$ with the intermolecular distance between the nearest-neighboring molecules is depicted as Fig. 4.

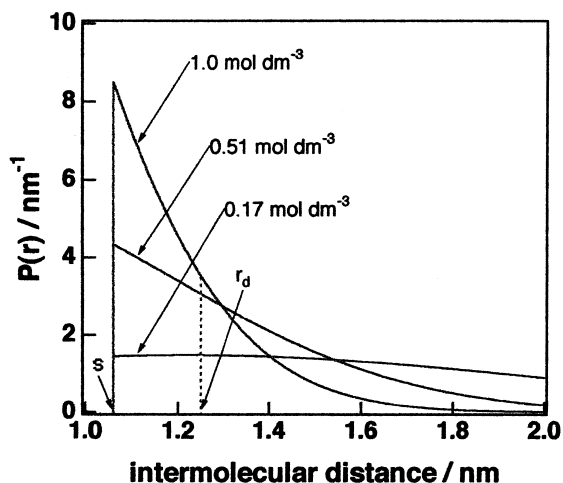


Fig. 4. Static distance distribution between the nearest-neighboring Ru-red in RuO₂ void space as a function of the Ru-red concentration in the RuO₂ void space.

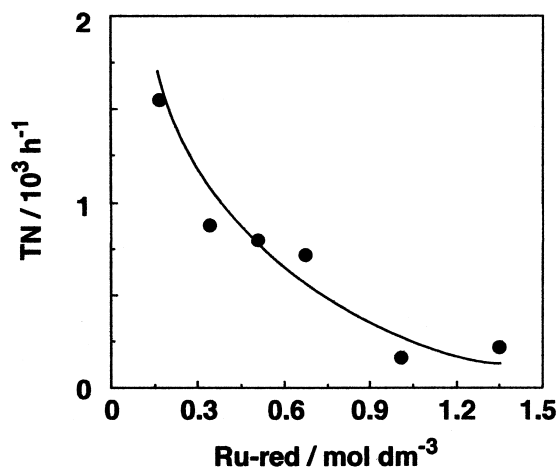


Fig. 5. Relationship between the turnover number (TN) of a Ru-red to oxidize water and the Ru-red concentration in RuO₂ void space. Solid line shows the best fitting curve based on Eq. (7).

It is assumed that the catalyst molecules located within the decomposition distance (r_d) undergo a bimolecular decomposition without oxidizing water. The fraction (R_{dec}) that the molecules are present within r_d is given by Eq. (6).

$$R_{dec} = \int_S^{r_d} P(r) dr = 1 - \exp[-4\pi(r_d^3 - s^3) \times N_A c \times 10^{-24}/3] \quad (6)$$

The fraction of $(1 - R_{dec})$ corresponds to the ratio of the effective catalyst. Since the turnover number (TN) of a Ru-red to evolve O₂ obtained from Fig. 3 should be proportional to the fraction of $(1 - R_{dec})$, Eq. (7) is derived,

$$TN = k_{int}(1 - R_{dec}) \quad (7)$$

where k_{int} represents an intrinsic activity of Ru-red on RuO₂. Fig. 5 obtained from Fig. 3 shows the TN of a Ru-red to oxidize water against the Ru-red concentration in the RuO₂ matrix. Eq. (7) was applied to the plots of Fig. 5 by using a non-linear least-squares method, and the best fitting values of k_{int} and r_d were obtained as $2.0 \times 10^3 \text{ h}^{-1}$ and 1.25 nm, respectively. The size of Ru-red is approximated as a cylinder with 0.75 nm diameter and 1.40 nm

length, indicating that almost contacted Ru-red molecules undergo bimolecular decomposition without working as a catalyst. The k_{int} ($2.0 \times 10^3 \text{ h}^{-1}$) is by one order of magnitude higher than the intrinsic rate constant in an aqueous solution ($1.8 \times 10^2 \text{ h}^{-1}$) [7]. The present analysis is not influenced by the effective area of the matrix. A similar result will be obtained even if the analysis is carried out with the surface adsorption model considering an effective area of the matrix. Validity of the analysis with the void space model have been shown in our earlier report [9].

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