

# Photocatalytic carbon dioxide photoreduction by $\text{Co}(\text{bpy})_3^{2+}$ sensitized by $\text{Ru}(\text{bpy})_3^{2+}$ fixed to cation exchange polymer

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## Abstract

Photocatalytic  $\text{CO}_2$  reduction was performed in a partially heterogeneous system using Ru and Co complexes:  $[\text{Ru}(\text{bpy})_3]^{2+}$  (bpy = 2,2'-bipyridine) as a photosensitizer was fixed to cation exchange polymers while  $[\text{Co}(\text{bpy})_3]^{2+}$  was used as a homogeneous catalyst. It was demonstrated that the metal complex system could be repeatedly used after replacement of the gaseous components by fresh  $\text{CO}_2$ . Reuse of the complexes in the homogeneous systems was also experimented. As a result, increased CO production (TN = 8.3) was achieved in the heterogeneous system due to the prolonged catalytic activity more than 400 h under atmospheric pressure. Apparent deactivation of the system was discussed in terms of the intermediates of the Co complex. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Photocatalytic reduction; Carbon dioxide; Cobalt complex; Ruthenium complex; Heterogeneous system

## 1. Introduction

About 20 years ago, Lehn et al. reported the pioneering work on a photocatalytic  $\text{CO}_2$  reduction system using Ru and Co polypyridine complexes in a homogeneous solution [1], which has collected increasing interest from not only academic but also energetic and environmental point of view [2–10]. The system is important because visible light ( $\lambda > 400$  nm), a major part of sunlight, can be used as an energy source. It is also interesting that two kinds of metal complexes play different roles [1]: the Ru and Co complexes work as a photosensitizer and a catalyst, respectively.

Although the mechanism is not completely elucidated [1b], the following is accepted; photo-excited Ru complex,  $^*\text{Ru}(\text{II})$ , transfers an electron to  $\text{Co}(\text{II})$  complex, which works as a reaction center of  $\text{CO}_2$ , and then the oxidized  $\text{Ru}(\text{III})$  complex is reduced by a tertiary amine known as the “sacrifice reagent”. Many research groups have worked on related systems for mechanistic study and/or for more efficient production of CO. Other combinations of metal complexes [3,5,6], other kinds of sensitizers and reducing agents [3,6,7] and dinuclear systems [8–10] have been investigated but little work has been done on heterogeneous systems.

Development of heterogeneous catalysts is usually advantageous for processing and also for recovery of the catalysts. When metal complexes are fixed to a solid matrix, dissociation of ligands from a metal ion could be suppressed due to restricted mobility, which

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should lead to a longer lifetime. Here we report a partially heterogeneous CO<sub>2</sub> photoreduction system, where [Ru(bpy)<sub>3</sub>]<sup>2+</sup> was fixed to an ion exchange polymer [11] and [Co(bpy)<sub>3</sub>]<sup>2+</sup> was dissolved in a mixture of dimethylformamide (DMF) as solvent and triethanol amine (TEOA) as a reducing agent and the amount of produced CO and its ratio to H<sub>2</sub> was discussed.

## 2. Experimental

### 2.1. Materials

All reagents and solvents were purchased from Wako Pure Chemical Industries Ltd., Sigma-Aldrich Corporation Inc. and Kanto Chemical Co. Ltd. of at least reagent grade quality, and were used as received except for DMF and TEOA, which were distilled from KOH.

All polymer supports, Amberlite IR-120 (Rohm & Hass), Nafion 112 (Du Pont), and Nafion NR-50 N (Du Pont), were used without further purification. Both complex fixed Nafions were cut into small pieces, approximately several square millimeter (Nafion 112) and cubic (Nafion NR-50) for photoreaction while Amberlite IR-120 was used in the original shape.

The Ru mononuclear complex, Ru(bpy)<sub>3</sub>Cl<sub>2</sub> [12], and the Ru-Co dinuclear complex (bpy)<sub>2</sub>Ru(phen-C<sub>2</sub>H<sub>4</sub>-phen)Co(bpy)<sub>2</sub> (phen = phenanthroline-4-yl) [10], were prepared according to the literature procedures. The Co mononuclear complex, Co(bpy)<sub>3</sub>Cl<sub>2</sub>, was prepared by the reaction of 1 eq. CoCl<sub>2</sub>·6H<sub>2</sub>O and 3 eq. of bpy in ethanol (80 °C, 2 h). After concentration of the reaction mixture, the precipitate was collected and used for the photochemical reaction without further purification: ES-MS; 264 [M-2Cl<sup>-</sup>]<sup>2+</sup>/2, 406 [M-bpy-Cl<sup>-</sup>]<sup>+</sup>, 186 [M-bpy-2Cl<sup>-</sup>]<sup>2+</sup>/2. Anal. Calcd for C<sub>30</sub>H<sub>24</sub>N<sub>6</sub>Cl<sub>2</sub>Co·1.5H<sub>2</sub>O: C, 57.56; H, 4.32; N, 13.43%. Found: C, 57.41; H, 4.23; N, 13.32%.

### 2.2. Spectroscopic study

The IR, UV, and emission spectrum were studied for Ru complexes fixed to Nafion 112 and compared with those of Ru(bpy)<sub>3</sub>Cl<sub>2</sub>. As shown in Fig. 1, almost the identical emission spectra with 20% lower

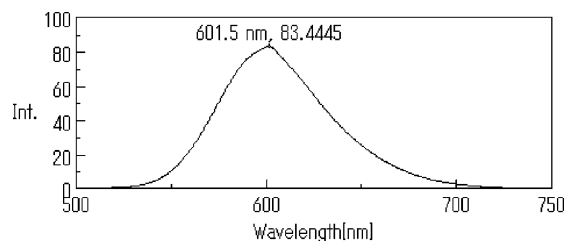


Fig. 1. Emission spectra of Ru(bpy)<sub>3</sub><sup>2+</sup> adsorbed to Nafion 112.

intensity was obtained for the solid membrane as that of the original complex (602 nm, intensity 107.2 a.u.). Obviously, however, it is impossible to quantitatively compare the data due to the differences in concentration and conditions between the Ru complexes. Some identical peaks were also observed in IR and UV measurement but the spectrum were not clear due to the membrane thickness (50 μm).

### 2.3. Photochemical reaction

All photoreactions were carried out by using a certain amount of the Ru and Co complexes or the dinuclear Ru–Co complex in the DMF/TEOA (4/1, v/v) or DMF/H<sub>2</sub>O/TEOA (3/1/1, v/v/v) (30 ml) mixed solvent. The reaction mixture was saturated with CO<sub>2</sub> by exposure to atmospheric pressure of CO<sub>2</sub> for at least 20 min and the solution was transferred to a gastight photolysis photoreaction vessel (Pyrex) [10]. Photoirradiation was carried out with a Xe lamp (Ushio UXL500D-O) with an IR-cut filter (HOYA, HA-50) and the irradiation was continued until the evolution of CO became negligible, less than approximately 2%, in more than 4 h for each experiment and the maximum experimental error was about 25%.

### 2.4. Measurements

Gas sampling (0.3 ml) was performed at various intervals with a gastight syringe through a septum. The amounts of CO and H<sub>2</sub> produced were detected by TCD-GC (Hitachi 263-50, 3 mm × 5 m activated charcoal column, at 70 °C using Ar as a carrier gas). Each gas was identified and quantified using the working curve, which had been previously obtained using standard CO and H<sub>2</sub> gas (GL Science).

### 3. Results and discussion

#### 3.1. Blend system

In order to prepare a heterogeneous photocatalyst system, we first blended metal complex(es) with a polymer. It was expected that  $\text{CO}_2$  dissolved in the solvent would diffuse into the polymer matrix and react with the metal complexes. A polymer-complex blend was prepared as follows: the polymer was dissolved in an appropriate solvent and the complex was added into the mixture. However, only a limited number of polymers were applicable, as the blends must be homogeneous in the solvent for photoreaction. For example, homogeneous polystyrene (PS)-based blend could not be prepared because the complexes did not dissolve in tetrahydrofuran, which is a good solvent for PS.

The Ru and/or Co complexes were blended into four polymers, polyvinyl chloride (PVC), poly(vinyl acetate) (PVAc), poly(vinyl alcohol) (PVA), and poly(vinyl cinnamate) (PVCm) and all of the mixtures formed membranes. Among them, PVC- and PVAc-based membranes were fed to the DMF- $\text{H}_2\text{O}$ -TEOA mixed solvent and were irradiated. On the other hand, PVA- and PVCm-based polymers were thermally and photochemically cross-linked, respectively [13]. The mixtures were applied to the photoreaction step. As a result, most of the blends maintained their membrane forms at least for one day, but the complexes soon came out of the polymer matrix due to polymer dilation in DMF- $\text{H}_2\text{O}$ -TEOA.

#### 3.2. Adsorption system

##### 3.2.1. Fixation of metal complexes

Three kinds of cation exchange polymers, PS-based Amberlite IR-120, perfluorinated Nafion 112 (membrane type), and Nafion NR-50 (grain type) were used for fixing the Ru and Co complexes. The first was expected to be compatible with organic solvents and the others should be stable for photoreduction. All polymers used seemed effective in fixing the Ru and Co complexes. Only small amounts of the complexes, probably physically adsorbed ones, came off during the first photo-irradiation but not any more as far as the solvent is the DMF-TEOA mixture. Most complexes, however, were completely taken off from the polymers under strongly acidic conditions at  $\text{pH} < 1$ .

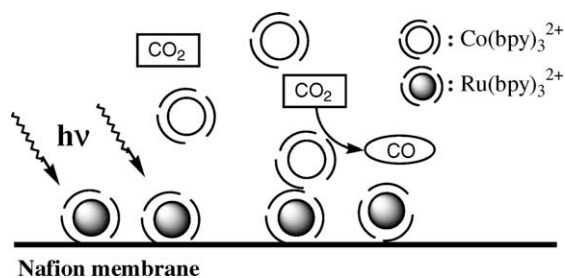


Fig. 2. Schematic of partially heterogeneous  $\text{CO}_2$  photoreduction.

This feature may be important for handling Ru-based compounds considering Ru is generally expensive.

##### 3.2.2. Photoreaction

The photosensitizer,  $\text{Ru}(\text{bpy})_3\text{Cl}_2$ , fixed to Nafion 112, photoactive in solid as mentioned in Section 2, was irradiated using a Xe lamp under atmospheric pressure of  $\text{CO}_2$  in the presence of  $\text{Co}(\text{bpy})_3\text{Cl}_2$  dissolved in DMF-TEOA. Only small amount of dilation of the polymer substrate was observed. The reaction system is schematically shown in Fig. 2. Production of CO was observed as seen Fig. 3; that is, photoreduction of  $\text{CO}_2$  in the partially heterogeneous Ru-Co system was achieved for the first time. Both CO ( $20.0 \mu\text{mol}$ ) and  $\text{H}_2$  ( $50 \mu\text{mol}$ ) were produced during the first irradiation for 2 days. For comparison, the homogeneous system was also examined under the identical conditions and about two times CO production ( $38 \mu\text{mol}$ ) was observed in 2 days as seen in Fig. 4. Low CO productivity in the heterogeneous system may be the result of decrease in the rate of electron transfer from the Ru complex on the polymer surface to the Co complex in solution.

The reddish-orange color of the polymer membrane and the homogeneous system was maintained after CO production apparently stopped. This observation suggested that the photosensitizer was still active. With this in mind, in order to examine the durability of the complexes, we tried to reuse the metal complexes for both heterogeneous and homogeneous systems. After CO production was stopped not only the gas phase but also the mixed solvent were resaturated by  $\text{CO}_2$  and the photoreaction was resumed. As a result, five cycles, totally more than 400 h of photoirradiations were repeated and it was demonstrated that the catalytic activity was maintained at more than 200 h in the present

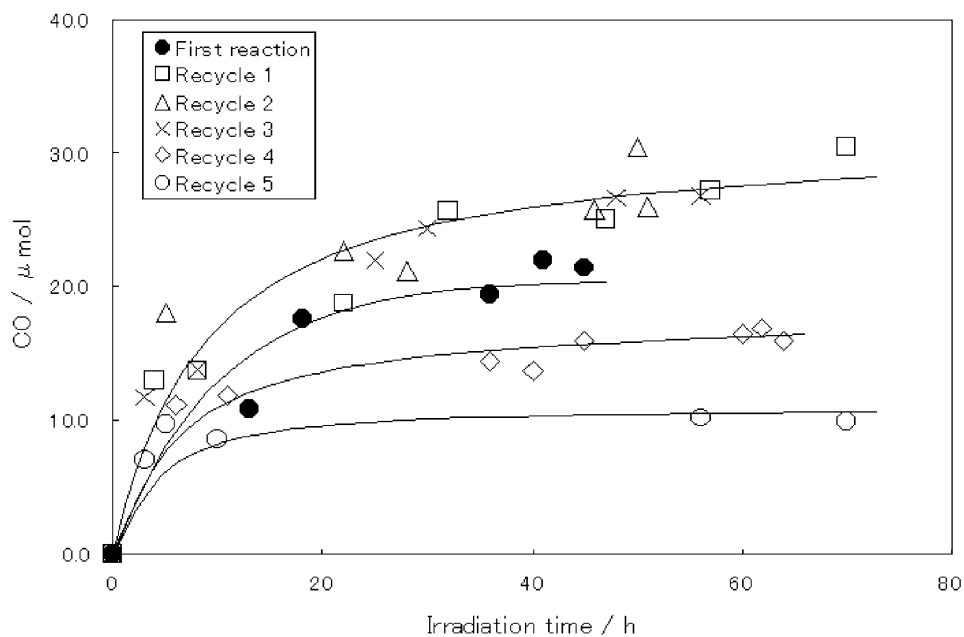


Fig. 3. Time dependence of  $\text{CO}_2$  photoreduction of the partially heterogeneous system (Run 1 in Table 1).

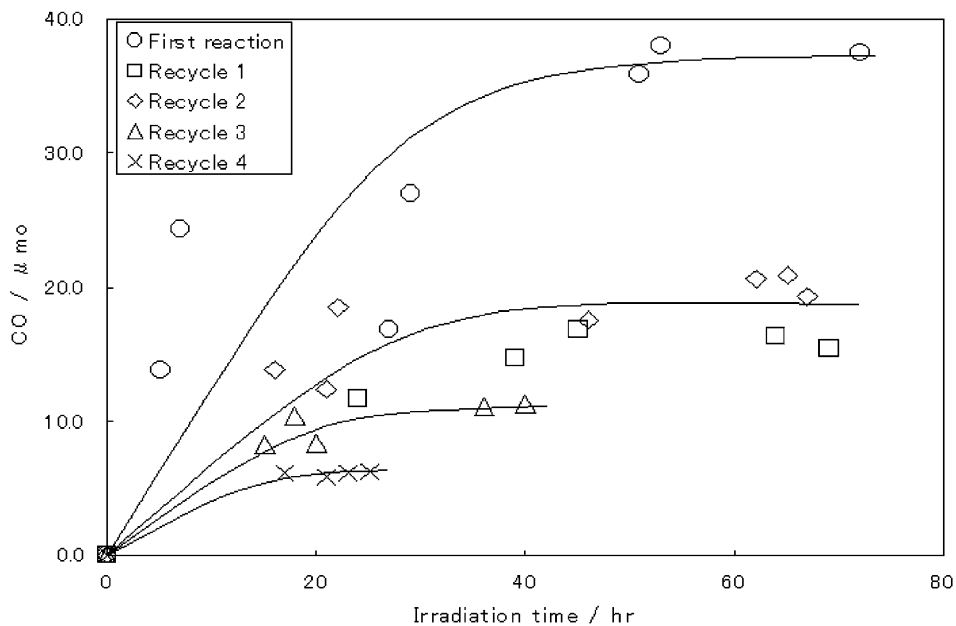


Fig. 4. Time dependence of the  $\text{CO}_2$  photoreduction by the homogeneous reaction system (Run 6 in Table 1).

Table 1  
Generation of CO and H<sub>2</sub> by photoreduction of CO<sub>2</sub><sup>a</sup>

Run	Cation exchange polymer	Amount (mg)	Fixed complex (μmol)	Reaction time <sup>b</sup> (h)	CO (μmol (TN))	H <sub>2</sub> (μmol (TN))	CO/H <sub>2</sub>
1 <sup>c</sup>	Nafion 112	50	Ru(bpy) <sub>3</sub> /15	404	125 (8.3)	276 (18.4)	0.45
2 <sup>d</sup>	Nafion 112	195	Co(bpy) <sub>3</sub> /114	22	–	–	–
3 <sup>c</sup>	Nafion NR-50	669	Ru(bpy) <sub>3</sub> /15	166	36 (2.4)	23 (1.5)	1.6
4 <sup>c</sup>	Amberlite IR-120	19	Ru(bpy) <sub>3</sub> /15	150	44 (2.9)	8 (0.5)	5.5
5 <sup>e</sup>	Nafion 112	100	Ru(bpy) <sub>3</sub> /15 and Co(bpy) <sub>3</sub> /15	46	25 (1.7)	21 (1.4)	1.2
6 <sup>f</sup>	Nafion 112	96	Ru-Co complex/15	21	–	–	–
7 <sup>g</sup>	None (homogeneous system)	–	Ru(bpy) <sub>3</sub> /15 and Co(bpy) <sub>3</sub> /15	213	93 (6.2)	236 (15.7)	0.39

<sup>a</sup> All reactions were performed in the mixed solvent of DMF/TEOA (4/1, v/v) (30 ml).

<sup>b</sup> Total irradiation time.

<sup>c</sup> Co complex (15 μmol) was dissolved in the mixed solvent.

<sup>d</sup> Ru complex (15 μmol) was dissolved in the mixed solvent.

<sup>e</sup> The mixed solvent was changed for each irradiation.

<sup>f</sup> Ru–Co complex is (bpy)<sub>2</sub>Ru(phen–C<sub>2</sub>H<sub>4</sub>–phen)Co(bpy)<sub>2</sub>.

<sup>g</sup> Control experiment. Both the Ru and Co complexes were dissolved in the mixed solvent.

heterogeneous system as shown in Table 1 (Run 1) and Fig. 3. As the lifetime of the metal complexes was extended greater than that in the homogeneous solution, the total amount of CO produced was comparable to the homogeneous system. In addition the CO/H<sub>2</sub> ratio was increased to 0.45. To our surprise, the complexes in the homogeneous system was also shown to be reusable (Table 1; Run 6), although the activity was largely decreased after the first reaction as shown in Fig. 4.

We thought the prolonged lifetime of the polymer-supported system was due to retardation of the decomposition of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> because the complex could not move from the ion exchange polymer surface so dissociation of the ligands was suppressed. Considering the negligible increase at each photoreaction after 2 days (~50 h), the photoreaction seemed to be inhibited in the course of time. At present, the deactivation of the Co complex seems highly probable as the color of the Ru complex did not change. The coordination of CO to the Co complex is speculated as one possible cause. However, this intermediate should not be so stable that the deactivation was temporary and resaturation or replacement of the reaction system by fresh CO<sub>2</sub> allowed iteration of the reaction.

When a granular type of Nafion, NR-50, was used, smaller amounts of gases with higher CO selectivity

(CO/H<sub>2</sub> = 1.2) were formed by photoirradiation and the lifetime of the system became shorter (Run 3). Another type of cation exchange polymer, Amberlite IR-120, was not so effective for CO formation but the selectivity was much higher (CO/H<sub>2</sub> = 5.5) (Run 4). When Co[(bpy)<sub>3</sub>]<sup>2+</sup> was fixed to Nafion, however, neither CO nor H<sub>2</sub> was produced (Run 2). Comparison of Runs 1, 2, 5, and 7 shows that fixation of Co[(bpy)<sub>3</sub>]<sup>2+</sup> was ineffective under the present experimental conditions. Because the interaction between the Ru and Co complexes should be almost the same for Runs 1 and 2, we suppose fixation of the Co complex drastically reduced the rate of interaction between [Co(bpy)<sub>3</sub>]<sup>+</sup> and CO<sub>2</sub>. Obviously that further spectroscopic and electrochemical analyses are necessary.

From the present results and the discussion by Ziesel et al. [1b], the following reaction feature was concluded: \*Ru(II) species was not quenched on cation exchange polymer for a certain period when electron transfer could effectively occur from the photosensitizer to Co[(bpy)<sub>3</sub>]<sup>2+</sup> in solution. It was also shown for the first time that a large amount of CO was produced by repeated use of the photosensitizer. On the other hand, fixation of the Co complex was not effective. Elucidation of the mechanistic feature and the state of the Ru complex on ion exchange polymer are currently being investigated.

#### 4. Conclusion

In the present study, it was found that the polymer-based photosensitizer was easily prepared from Ru polypyridine complex and Nafion membrane, cation exchange polymer, while  $[\text{Co}(\text{bpy})_3]^{2+}$  was necessarily dissolved in the reaction media for catalytic  $\text{CO}_2$  photoreduction. The present system allowed easy handling and recovery of the Ru complex including repeated cycles using  $\text{CO}_2$  refreshing. As a result, production of CO (TN = 8.3) was largely improved for the partially heterogeneous system. The prolonged lifetime would be owing to suppression of the decomposition of the Ru complex fixed on polymer surface.

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