Photosensitized Reduction of Carbon Dioxide in Solution Using Noble-Metal Clusters for Electron Transfer

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Dedicated to Prof. Hitoshi Ohtaki on the occasion of his 60th birthday

Carbon dioxide was reduced to methane by visible-light irradiation of a solution composed of tris(bipyridine)ruthenium(III) as photosensitizer, ethylenediaminetetraacetic acid disodium salt as sacrificial reagent, methyl viologen as electron relay, and a colloidal dispersion of polymer-protected noble-metal clusters, prepared by alcohol-reduction, as catalyst. Among the noble-metal clusters examined, Pt clusters showed the highest activity for the formation of methane as well as hydrogen. In order to improve the activity, oxidized clusters and bimetallic clusters were also applied. For example, the CH_4 yield in 3-h irradiation increased from 51×10^{-3} µmol with unoxidized Pt clusters to 72×10^{-3} µmol with partially oxidized ones. In the case of Pt/Ru bimetalic systems, the improvement of the catalytic activity by air treatment was much greater than in case of monometallic clusters.

Key words: Carbon dioxide, Photosensitized reduction, Electron transfer, Metal cluster, Colloidal catalyst.

Introduction

The reduction of carbon dioxide to produce organic compounds has been studied in various ways [1–4], using hydrogen [5], electricity [6], and so on. The report methods using solar photoenergy can be divided into two categories. One is using semiconductors [7–11] and the other using metal complexes [12–14] as a photosensitizer. The latter has the advantage of using visible light, while the former is more advantageous from viewpoint of energy transfer efficiency.

Semiconductor particles are effective photocatalysts, since their band gaps slow down the recombination of electron-hole pairs. Thus, the photoreduction of carbon dioxide to formate by ultraviolet-light irradiation of quantized semiconductor particles has often been reported [8–10].

As to systems with metal complexes as photosensitizer, the system using tris(bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$) as photosensitizer, (bipyridine)tri(carbonyl)chlororenium(I) ($Re(bpy)(CO)_3Cl$) as catalyst, and cobalt(II) chloride ($CoCl_2$) as electron relay was reported to reduce carbon dioxide [12], accompanied by the formation of hydrogen. Reduction of carbon dioxide to formate was reported in the system using $Ru(bpy)_3^{2+}$ as photosensitizer and triethanolamine as sacrificial reagent in a mixed solution of dimethylformamide and water [13].

Most of the reports deal with mono- and di-electron reduction of carbon dioxide to produce formate and carbon monoxide, while only little was reported on reduction which involves more than 4 electrons to produce methanol, methane, etc. The multi-electron reduction is favored thermodynamically but difficult in practice because the simultaneous multi-electron transfer is considered to require plural active cites which work cooperatively.

Recently, Willner reported the reduction of carbon dioxide to methane by visible-light irradiation of an electron transfer system involving Ru or Os colloid prepared by citrate reduction [15]. In this system, the conventional electron relay, methyl viologen, (MV^{2+}, $E(MV^{+\cdot}/MV^{2+}) = -0.45$ V vs. SHE) cannot be used, but a powerful electron relay, N,N′-bis(3-sulfonatopropyl)-3,3′-dimethyl-4,4′-bipyridinium, ($MPVS^0$, $E(MPVS^{\cdot-}/MPVS^0) = -0.79$ V vs. SHE) is successful, producing hydrogen and ethane as well as methane.

Here we report on the use of methyl viologen, a conventional electron relay, and colloidal dispersions of noble-metal clusters protected by polymers to produce methane from carbon dioxide. In general the colloidal dispersions of polymer-protected noble-metal clusters obtained by alcohol reduction and composed of ultrafine metal particles with an average

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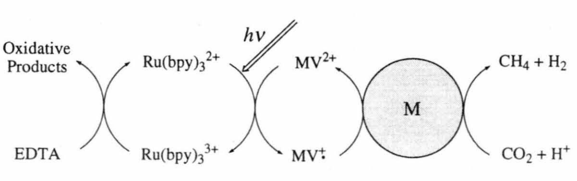
diameter of 1 to 5 nm are very stable. They are very active and selective catalysts for various reactions. For example, the colloidal dispersion of polymer-protected Pd clusters works as an active catalyst for selective partial hydrogenation of dienes [16, 17]. The colloidal dispersion of polymer-protected Pt clusters plays an important role for visible light-sensitized hydrogen production from water in the $Ru(bpy)_3^{2+}$/methyl viologen/EDTA system [18, 19]. The activity of the polymer-protected metal cluster can be improved by the partial oxidation of the metal [20, 21] and by the combination with another metal to form bimetallic clusters [22–27]. In this paper we have applied such clusters to the catalysis for visible light-sensitized reduction of carbon dioxide. The reaction process is shown in Scheme 1.



Scheme 1. Schematic presentation of photosensitized reduction of CO_2 using MV^{2+} as an electron relay.

Experimental

Preparation of Metal Clusters by Alcohol-Reduction

The colloidal dispersions of poly(N-vinyl-2-pyrrolidone) (PVP)-protected metal clusters were prepared by an alcohol-reduction method in the same way as previously reported [28]. Poly-(N-vinyl-2-pyrrolidone) (PVP-K30, MW = 40 000, Tokyo Kasei Ind., Ltd.) $5.0 \times 10^{-2} \sim 2.0$ mmol ($1 \sim 40$ times the mole of metal ions) and metal salts such as ruthenium(III) chloride $RuCl_3 \cdot 3H_2O$, hexachloroplatinic(IV) acid $H_2PtCl_6 \cdot 6H_2O$ and palladium(II) chloride $PdCl_2$ 5.0×10^{-2} mmol (concentration of metal ions: 1.0 mmol dm^{-3}) were mixed in ethanol/water (1/1, *v*/*v*) to form the 50 cm^3 solution. The mixed solutions were stirred and heated to refluxing under nitrogen at 95–100 °C for 2 h, giving brownish black colloidal dispersions.

Characterization of Metal Clusters

UV-vis spectra were measured for the solution of metal ions before and after reduction with a Hitachi model U-4000 photospectrometer. Transmission electron micrographs of the metal clusters were taken with a Hitachi model H-7000 electron microscope operated at 100 kV acceleration voltage at magnification of 100 000. A carbon-supported copper mesh, kindly provided by Dr. Adachi, was used as a support for the metal clusters. The diameter of the clusters was measured on the basis of 3 times enlarged TEM photographs (magnification 300 000). The histogram of the particle size distribution and the average diameter were obtained by measurements of three hundred particles in an arbitrarily chosen area.

Visible Light-Sensitized Reduction of Carbon Dioxide

Typical reactions were performed as follows: A 20-cm^3 Pyrex Schlenk tube was charged with an 8 cm^3 aqueous solution, containing 1.0×10^{-1} mol dm^{-3} of ethylenediaminetetraacetic acid disodium salt (Na_2EDTA, a sacrificial electron donor), 1.4×10^{-4} mol dm^{-3} of tris(bipyridine)ruthenium(II) dichloride ($[Ru(bpy)_3]Cl_2$, a photosensitizer), 1.4×10^{-3} mol dm^{-3} of 1,1′-dimethyl-4,4′-bipyridium dichloride (methyl viologen, $MVCl_2$, an electron relay), and 5.0×10^{-2} mol dm^{-3} of sodium hydrogencarbonate ($NaHCO_3$, a pH adjuster). Two cm^3 of the colloidal dispersion as prepared was added to the above solution. The mixtures were degassed three times by freeze-thaw cycles, and then the tubes were filled with 1 atm of carbon dioxide (Takachiho Chemicals, purity 99.95%). The photo-irradiation was carried out for 4 h with an Ushio 500 W super-high-pressure mercury lamp through a UV cut filter (UV-39, Toshiba Glass Co., $\lambda > 390$ nm) in a water bath maintained at 30 °C.

Analysis of the Products

The products in the gas phase were analyzed with an Ohkura Riken model GC-701 glpc (an MS 13X column, at 40 °C) and model GC-103 glpc (a Porapak Q column, at 60–120 °C) apparatus. The yields were calculated with a System Instruments model 5000 A intelligent integrator on the basis of the corresponding peak areas. The characterization of gaseous products was carried out with a Shimadzu model GC-14 A (an active carbon column, at 30–100 °C) and a GCMS-QP1100EX gas chromatograph mass-spectrometer.

Results and Discussions

Preparation and Characterization of Metal Clusters

The colloidal dispersion of noble-metal clusters was prepared and characterized at first.

The colloidal dispersion of polymer-protected noble-metal clusters can be obtained by reduction of the corresponding metal ions in the presence of poly-(N-vinyl-2-pyrrolidone) (PVP). Here, the colloidal dispersions of Pt, Ru, and Pd clusters were prepared by refluxing the water/ethanol (1/1, *v*/*v*) solution under nitrogen. The reaction formulae were:

$$2\,RuCl_3 + 3\,C_2H_5OH = 2\,Ru + 3\,CH_3CHO + 6\,HCl, \quad (1)$$

$$PdCl_2 + C_2H_5OH = Pd + CH_3CHO + 2\,HCl, \quad (2)$$

$$H_2PtCl_6 + 2\,C_2H_5OH = Pt + 2\,CH_3CHO + 6\,HCl. \quad (3)$$

The colloidal dispersions thus obtained had a dark brown or black color and did not show any coagulation for several weeks at room temperature under nitrogen. They remained homogeneous and transparent UV-Vis spectra of the colloidal dispersions of Pt, Ru, and Pd clusters are shown in Figure 1. They are quite different from those of the solutions of the corresponding ion salts (Fig. 2), indicating the complete reduction of the ions to produce colloidal dispersions of the metal clusters. In order to avoid any interaction with oxygen, the colloidal dispersions were kept under nitrogen until they were used for the reactions.

The particle size of the metal clusters was determined with an transmission electron microscope (TEM). The TEM photographs and the size distribution histograms of the Pt and Ru clusters are collected in Figs. 3 and 4. The micrographs show that fine particles are produced especially in the case of Ru.

In the case of Pt clusters, when the mole ratio of PVP to Pt is 40 (Pt/PVP = 1/40), the obtained Pt clusters are well-dispersed, as shown in Figure 3a. The average diameter is 2.8 nm (cf. Figure 4a). When the ratio Pt/PVP is 1/1 (Fig. 3b), the Pt clusters are still well-dispersed. However the size distribution becomes wide and the average diameter is 4.2 nm, as shown in the histogram (Figure 4b).

When a large amount of PVP is used for the preparation of the colloidal dispersion of metal clusters, then small particles are obtained, while when a small amount of PVP used, then large particles are obtained [16, 29]. In other words, the smaller the amount of PVP, the larger is the average diameter of the metal clusters obtained.

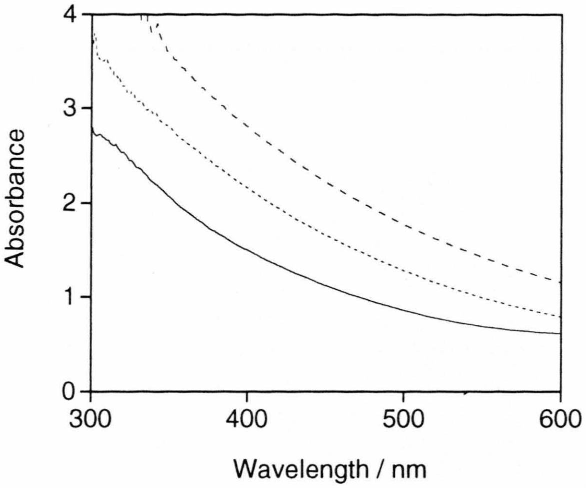


Fig. 1. UV-vis spectra of the colloidal dispersions of Pt (– – – –), Pd (· · · · ·), and Ru (———) clusters in ethanol/water (1/1, *v*/*v*). [Metal] = 1.0×10^{-3} mol dm^{-3}.

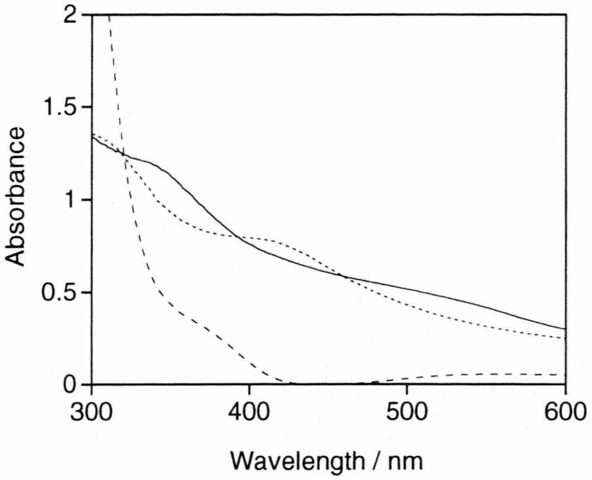
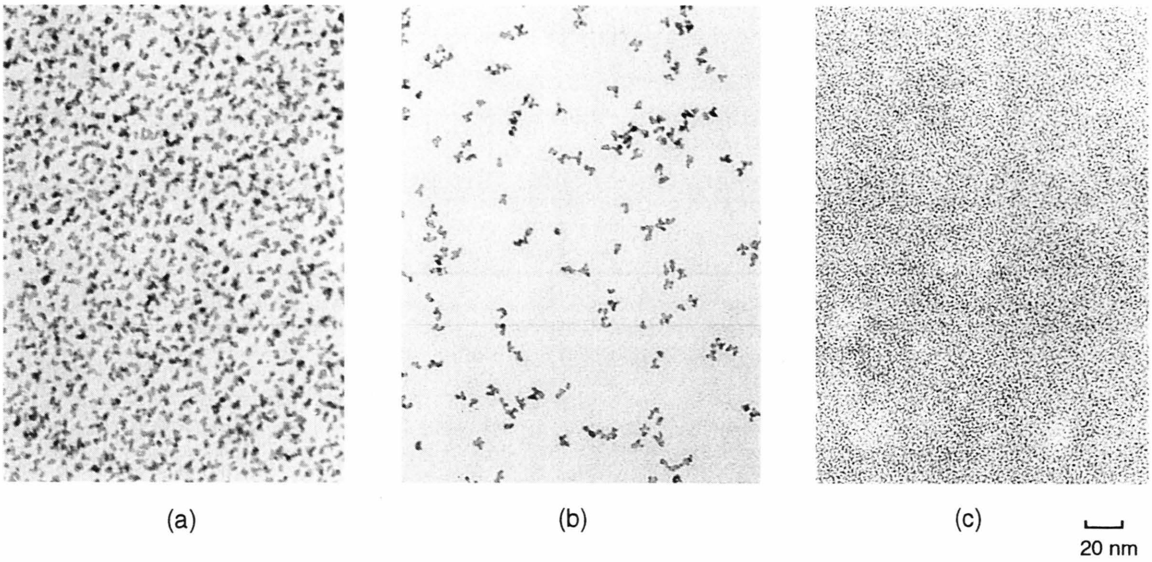


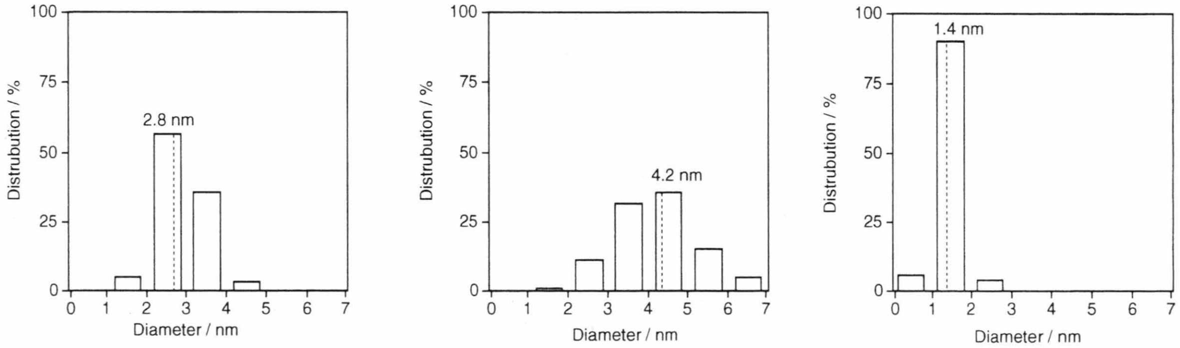
Fig. 2. UV-vis spectra of the solution of Pt (– – – –), Pd (· · · · ·), and Ru (———) ions in ethanol/water (1/1, *v*/*v*) before the refluxing. [Pt] = [Pd] = 1.0×10^{-3} mol dm^{-3}, [Ru] = 0.7×10^{-3} mol dm^{-3}.

In the case of the Ru clusters prepared with the ratio of Ru/PVP = 1/40, it is difficult to detect the particles by eye. Since the particles are so small, the accurate diameter cannot be determined. Its diameter can only be estimated to be smaller than 1.0 nm, which is the practical limitation of the TEM apparatus. When the same moles of PVP and Ru ions were used (Ru/PVP = 1/1), then the particles were larger



(a) (b) (c)

Fig. 3. Transmission electron micrographs of Pt (a, b) and Ru (c) clusters prepared by using various amounts of poly(N-vinyl-2-pyrrolidone) (PVP). (a) Pt/PVP = 1/40, (b) Pt/PVP = 1/1, (c) Ru/PVP = 1/1.



(a) (b) (c)

Fig. 4. Particle size distribution histograms of Pt (a, b) and Ru (c) clusters corresponding to Fig. 3, respectively. (a) Pt/PVP = 1/40, (b) Pt/PVP = 1/1, (c) Ru/PVP = 1/1.

than those in the former case. Thus, well-dispersed Ru clusters are obtained, as shown in Figure 3c. The average diameter is 1.4 nm from the histogram (Figure 4c).

Visible Light-Induced Reduction of Carbon Dioxide

Continuous irradiation experiments for the reduction of carbon dioxide were performed under carbon dioxide at 30 °C in a Schleck tube containing 10 cm^3 of the mixtures with the metal cluster catalyst thus prepared, a photosensitizer, an electron relay, a sacrificial reagent, and a pH adjuster. Ethylenediaminetetraacetic acid disodium salt ($Na_2 \cdot$ EDTA) or 2,2′,2″-nitrilotriethanol (triethanolamine, TEOA), $NaHCO_3$ or Na_2CO_3, $Ru(bpy)_3^{2+}$, and MV^{2+} were used as a sacrificial reagent, a pH adjuster, a photosensitizer and an electron relay, respectively.

In a typical experiment using Pt clusters (Pt/PVP = 1/40), about 50 × 10^{-3} μmol of methane as well as hydrogen were produced during 3-h visible-light irradiation. The production of methane was checked by the mass spectra. It is clear from the experiments that all the components except a pH adjuster are necessary for the methane evolution. Typical experimental results performed by using the colloidal dispersion of Pt as a catalyst under various reaction conditions are shown in Table 1.

Comparison of runs 1 and 2 in Table 1 shows that EDTA is a more effective reagent than TEOA as a sacrificial reagent in the reaction. Without the pH adjuster, the reaction mixtures are a little acidic (pH 5.3 as shown in run 4 of Table 1). When $NaHCO_3$ or Na_2CO_3 is added to the reaction mixtures as a pH adjuster, then the methane evolution is improved, as shown by runs 2 and 3 in Table 1. Thus, the alkaline solution is favorable to the methane evolution in the present system.

Effect of Metal Cluster Catalysts on the Methane Evolution

The methane evolution curves using the colloidal dispersions of Pt, Ru and Pd clusters are shown in Figure 5. Evidently the Pt clusters give the highest activity among the noble-metal clusters tested. However, the evolution rate decreases with the irradiation time and becomes constant at about 3 h. In the case of Ru clusters, in the initial stage the evolution rate is lower than with the Pt clusters, but it was maintained even after 4-h irradiation. In the case of Pd clusters, the activity is low not only in the initial stage but also after 4-h irradiation. Thus, the order of the catalytic activity of the metal clusters for methane evolution is Pt > Ru, Pd.

The initial rate of methane evolution and the yield of methane during 3-h irradiation increase with increasing concentration of Pt or Ru clusters, as shown in Table 2.

As mentioned in the previous section, the size of the metal clusters can be controlled by the quantity of the PVP added in the reduction of metal ions. When the metal clusters with different size are used as catalyst for the carbon dioxide reduction, then the rate of the methane evolution is altered as shown in Table 3. In the case of the Ru clusters, the large particles (Ru/PVP = 1/1, average diameter 1.4 nm) show higher activity than the small particles (Ru/PVP = 1/40, average diameter less than 1.0 nm). In the case of Pt clusters, whose size is generally larger than that of Ru clusters, on the contrary, the large Pt particles (Pt/PVP = 1/1, average diameter 4.2 nm) show lower activity than the small particles.

If the catalytic activity is caused by the number of active sites, then particles with smaller diameter should have higher activity, as has been reported so often [16]. However, it is not true in the case of the carbon dioxide reduction to methane by multi-elec-

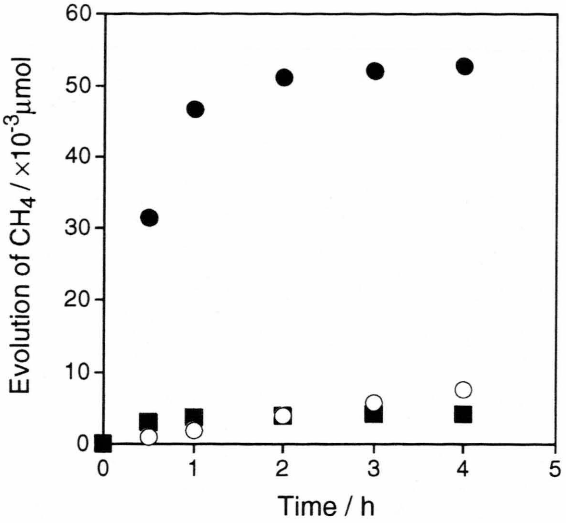


Fig. 5. Methane evolution using the colloidal dispersions of Pt (●), Pd (■), and Ru (○) clusters as catalysts. Reaction conditions: $[Ru(bpy)_3^{2+}] = 1.4 \times 10^{-4}$ mol dm^{-3}, $[MV^{2+}] = 1.4 \times 10^{-3}$ mol dm^{-3}, [EDTA] = 1.0 × 10^{-1} mol dm^{-3}, $[NaHCO_3]$ = 5.0 × 10^{-2} mol dm^{-3}, [Metal] = 2.0 × 10^{-4} mol dm^{-3}, Metal/PVP = 1/40. $p(CO_2) = 1$ atm, at 30 °C, $\lambda > 390$ nm.

Table 1. Photosensitized methane evolution catalyzed by the colloidal dispersion of platinum clusters under various reaction conditions[a].

Run	Components				Methane
	Metal catalyst	Sacrificial reagent	pH adjuster	pH	Yield at 3 h/ × 10^{-3} μmol
1	Pt	TEOA	$NaHCO_3$	7.6	37
2	Pt	EDTA	$NaHCO_3$	6.1	51
3	Pt	EDTA	Na_2CO_3	6.7	54
4	Pt	EDTA	None	5.3	33

[a] [Pt] = 2.0 × 10^{-4} mol dm^{-3}, [Pt/PVP] = 1/40, [Sacrificial reagent] = 1.0 × 10^{-1} mol dm^{-3}, [pH adjuster] = 5.0 × 10^{-2} mol dm^{-3}, $[Ru(bpy)_3^{2+}] = 1.4 \times 10^{-4}$ mol dm^{-3}, $[MV^{2+}]$ = 1.4 × 10^{-3} mol dm^{-3}, $p(CO_2) = 1.0$ atm, at 30 °C, $\lambda >$ 390 nm.

Table 2. Effect of the concentration of clusters for methane evolution[a].

Run	Catalyst				Methane	
	Metal	M/PVP ratio	Diameter/ nm	Conc./ mmol dm^{-3}	Initial rate/ $\times 10^{-3}$ µmol h^{-1}	Yield at 3 h/ $\times 10^{-3}$ µmol
1	Ru	1/1	1.4	0.20	2.9	8.0
2	Ru	1/1	1.4	0.80	8.7	25
3	Pt	1/40	2.8	0.20	42	51
4	Pt	1/40	2.8	0.80	210	250

[a] Reaction conditions: $[Ru(bpy)_3^{2+}] = 1.4 \times 10^{-4}$ mol dm^{-3}, $[MV^{2+}] = 1.4 \times 10^{-3}$ mol dm^{-3}, $[EDTA] = 1.0 \times 10^{-1}$ mol dm^{-3}, $[NaHCO_3] = 5.0 \times 10^{-2}$ mol dm^{-3}, $p(CO_2) = 1.0$ atm, at 30 °C, $\lambda > 390$ nm.

Table 3. Effect of particle size of metal clusters for the methane evolution[a].

Run	Catalyst			Methane[a]
	Metal[b]	Metal/PVP ratio	Diameter/ nm	Yield at 3 h/ $\times 10^{-3}$ µmol
1	Ru	1/40	<1.0	5.7
2	Ru	1/1	1.4	8.0
3	Pt	1/40	2.8	250
4	Pt	1/1	4.2	110

[a] Reaction conditions: $[Ru(bpy)_3^{2+}] = 1.4 \times 10^{-4}$ mol dm^{-3}, $[MV^{2+}] = 1.4 \times 10^{-3}$ mol dm^{-3}, $[EDTA] = 1.0 \times 10^{-1}$ mol dm^{-3}, $[NaHCO_3] = 5.0 \times 10^{-2}$ mol dm^{-3}, $p(CO_2) = 1.0$ atm, at 30 °C, $\lambda > 390$ nm.

[b] $[Ru] = 2.0 \times 10^{-4}$ mol dm^{-3}, $[Pt] = 8.0 \times 10^{-4}$ mol dm^{-3}.

Table 4. Improvement of the catalytic activity of metal clusters by air treatment[a].

Run	Catalyst		Product yield at 3 h	
	Metal	Oxidizing treatment	CH_4/ $\times 10^{-3}$ µmol	H_2/ µmol
1	Ru	None	5.7	21
2	Ru	By air[b]	8.0	27
3	Pt	None	51	37
4	Pt	By air[b]	72	36

[a] Reaction conditions: $[Ru(bpy)_3^{2+}] = 1.4 \times 10^{-4}$ mol dm^{-3}, $[MV^{2+}] = 1.4 \times 10^{-3}$ mol dm^{-3}, $[EDTA] = 1.0 \times 10^{-1}$ mol dm^{-3}, $[NaHCO_3] = 5.0 \times 10^{-2}$ mol dm^{-3}, $[Metal] = 2.0 \times 10^{-4}$ mol dm^{-3}, Metal/PVP = 1/40, $p(CO_2) = 1.0$ atm, at 30 °C, $\lambda > 390$ nm.

[b] Stirred under air for 2 h.

tron transfer. Thus, small particles are less favorable to the present 8-electron transfer reaction. On the basis of the results of both Ru and Pt clusters, it could probably be concluded that the most effective particle size is around 2–3 nm for the present system. A similar result has been concluded in the case of visible light-induced hydrogen evolution from water [18].

Until now all the colloidal dispersions were prepared under nitrogen and used as prepared. However, it is known that the activity of noble-metal catalysts can be improved by partial oxidation. For example, the activity of a colloidal dispersion of clusters as catalyst for hydrogenation of olefins can be improved by air treatment [21]. In the case of Pd/Pt bimetallic clusters, it has been concluded on the basis of EXAFS measurements that the improvement of the catalytic activity by air treatment is due to the partial oxidation of palladium in the bimetallic cluster [20]. Thus, colloidal dispersions of Pt and Ru clusters prepared under nitrogen were stirred under air for 2 h and examined as catalysts. The results are shown in Table 4. In both cases the yield of methane is improved by the air treatment, although the improvement is not so big for hydrogen. The mechanism of the improvement is not clear yet, but it might be considered that the surface of the metal clusters becomes rough by the oxidation which increases the activity [20].

Pt/Ru Bimetallic System

In general the bimetallic clusters are often more active as catalysts than the corresponding monometallic clusters. For example, Pd/Pt bimetallic clusters are more active than Pd clusters for selective partial hydrogenation of dienes [22, 25], and Pd/Au bimetallic clusters are also more active than the Pd clusters for the same reaction [24]. In the present electron transfer system, the colloidal dispersion of Pt clusters has a high initial activity, while that of Ru clusters has a rather long-term activity. Thus, it was considered that if the bimetallic clusters could be prepared, they should have both merits as catalysts.

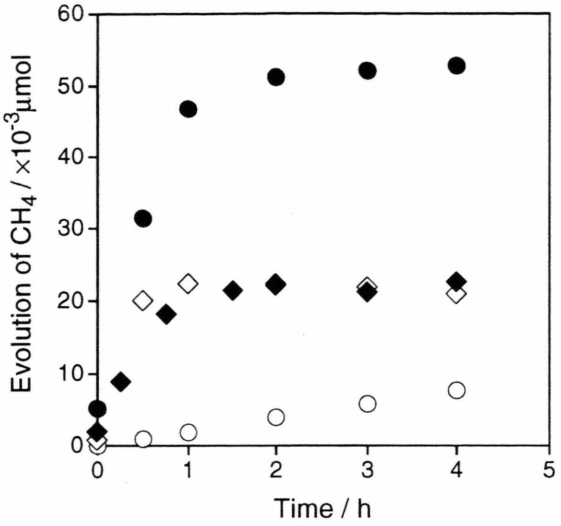
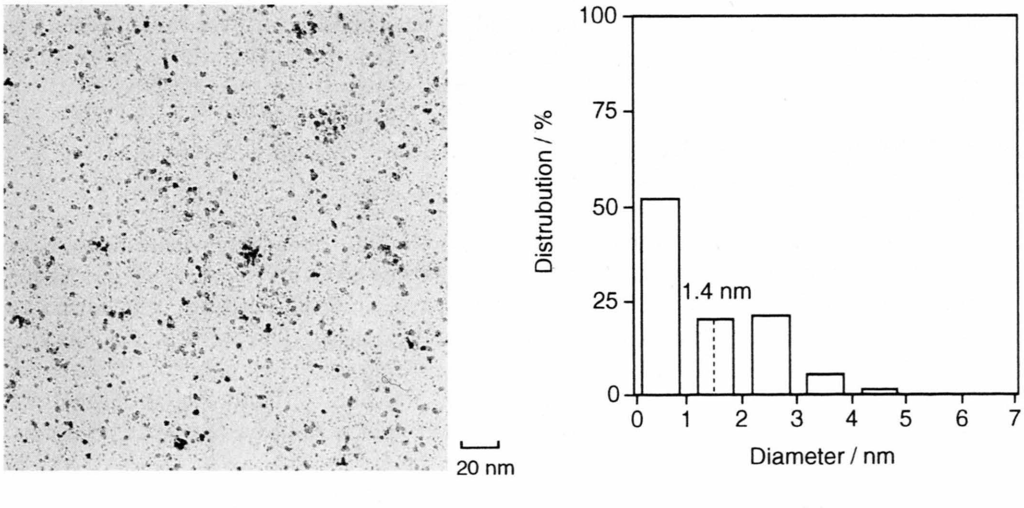


Fig. 6. Visible light-sensitized methane evolution using Pt/Ru (1/1) bimetallic system prepared by simultaneous reduction (◆), 1/1 mixture of Pt and Ru monometallic clusters (◇), Pt monometallic cluster (●), and Ru monometallic clusters (○). Reaction conditions are the same as those of Figure 5.

Therefore, equal moles of Pt and Ru ions were put into a clean flask and simultaneously reduced by refluxing alcohol.

The visible light-sensitized methane evolution in the present electron transfer system by the Pt/Ru bimetallic catalyst is shown in Figure 6. The methane evolution by the Pt/Ru bimetallic catalyst is almost the same as that of the mixture of Pt and Ru monometallic clusters, located nearly in the middle of those of Pt and Ru clusters. The TEM photograph of the Pt/Ru bimetallic catalyst prepared by simultaneous reduction (Fig. 7) may suggest that the bimetallic catalyst could be a mixture of Pt and Ru monometallic clusters.

As mentioned in the previous section, the oxidation of the Pt clusters by air treatment promotes the methane evolution. Thus, it was speculated that a similar treatment by air could improve the catalytic activity of the Pt/Ru bimetallic catalyst. The results are as expected. When a colloidal dispersion of Pt/Ru bimetallic system is used as the catalyst after the treatment by air, about 7 times the amount of methane as that before the air treatment is evolved, as shown in Figure 8. In the case of the 1:1 physical mixture of Pt and Ru clusters, on the other hand, the increase in the methane evolution by air treatment is smaller than twice. The difference in the results between the Pt/Ru bimetallic system and the physical mixture is quite clear: The Pt/Ru bimetallic system, prepared by simultaneous reduction of Pt and Ru ions by refluxing alcohol, is not the same as the physical mixture of monometallic Pt and Ru clusters prepared separately by alcohol-reduction of the corresponding ions. Thus, something in the Pt/Ru bimetallic system has changed by the air treatment, and the resulting structure works efficiently as catalyst.



(a) (b)

Fig. 7. Transmission electron micrograph (a) and particle size distribution histogram (b) of the Pt/Ru (1/1) bimetallic system prepared by simultaneous reduction of the corresponding ions.

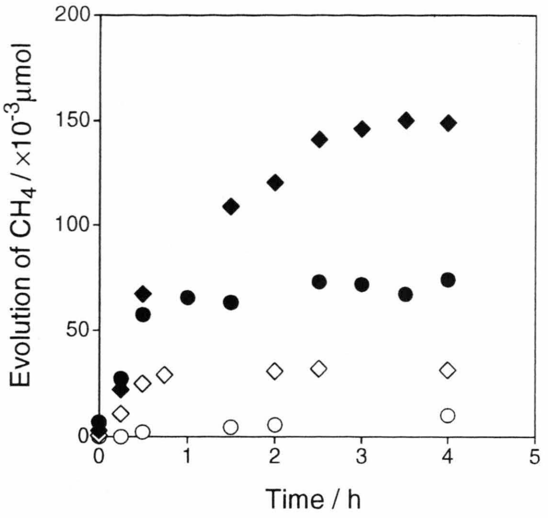


Fig. 8. Visible light-sensitized methane evolution using Pt/Ru (1/1) bimetallic system prepared by simultaneous reduction (◆), 1/1 mixture of Pt and Ru monometallic clusters (◇), Pt monometallic clusters (●), and Ru monometallic clusters (○) after air treatment as catalysts. Reaction conditions are the same as those of Figure 5.

In order to make the structural change complete, repeated oxidation, i.e., three cycles of oxidation by air and reduction by hydrogen, and then an additional oxidation by air was examined for the Pt/Ru bimetallic system. However, no difference was observed from the bimetallic system once oxidized by the air treatment.

Conclusion

Visible-light irradiation of the electron transfer system of EDTA/Ru(bpy)$_3^{2+}$/MV^{2+}/metal cluster/carbon dioxide can produce methane and hydrogen. This is the first example of the reduction of carbon dioxide by visible light-sensitized electron transfer using methyl viologen, a conventional electron relay, although the quantum yield of methane formation is much lower (a few % of the reported value) than the reported value in the system using N,N′-bis(3-suflonatopropyl)-3,3′-dimethyl-4,4′-bipyridinium MPVS^0 as an electron relay ($\phi = 5.7 \times 10^{-4}$) [15]. All reaction components of the solution except a pH adjuster are indispensable for the photoreduction of carbon dioxide. In the present system, the colloical dispersion of metal clusters works as a multi-electron transfer catalyst and plays an important role in the methane evolution. The catalytic activity of the metal clusters for the methane evolution varied in the order Pt > Ru, Pd.

The methane evolution also depends on the particle size of the metal clusters. In the case of Ru clusters, the catalytic activity for the methane evolution of the particles with an average diameter of 1.4 nm was higher than that with an average diameter of less than 1.0 nm. In the case of Pt clusters, on the contrary, the particles with an average diameter of 2.8 nm had higher activity than those of an average diameter of 4.2 nm. Thus, the most effective particle size is considered around 2–3 nm.

The colloidal dispersion of the Pt/Ru bimetallic system, prepared by simultaneous reduction of Pt and Ru ions by refluxing alcohol/water in the presence of PVP under nitrogen, shows a similar catalytic activity for methane evolution to the physical mixture of monometallic Pt and Ru clusters prepared separately by the same method.

The treatment of the dispersion with air can improve the catalytic activity of Pt and Ru monometallic cluster. Surprisingly, the improvement of the catalytic activity was much larger for the Pt/Ru bimetallic catalyst (about 7 times) than for Pt or Ru monometallic clusters. The mechanism of the improvement is not clear yet, but it might be considered that the surface of the metal cluster particles becomes rough by the oxidation to leave oxygen-metal bonding or to distribute electrons partially in the metal particles, which increases the activity.

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