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LETTER

Photoreduction of CO_2 to CH_4 in Water Using Dititanodecatungstophosphate as Multielectron Transfer Catalyst

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CO_2 has been recognized as a serious pollutant released from fossil fuel power stations, internal combustion engines and many industrial operations. From a need for the conversion of this pollutant into harmless, or even useful products, of particular interest is the photochemical fixation of CO_2 in connection with biological photosynthesis by green plants, as well as from the viewpoint of carbon resource utilization [1]. The reduction of CO_2 via multielectron transfer reactions might produce formic acid (HCO_2H), carbon monoxide (CO), formaldehyde (HCHO), methanol (CH_3OH) or methane (CH_4), as denoted by eqns. (1)–(5); the reduction potentials (E°) are thermodynamic values, calculated from the half-cell reactions at pH 7.0 in aqueous solutions versus NHE [2].

$$CO_2 + 2H^+ + 2e^- \longrightarrow HCO_2H \qquad E^\circ = -0.61\ \mathrm{V} \qquad (1)$$

$$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O \qquad E^\circ = -0.52\ \mathrm{V} \qquad (2)$$

$$CO_2 + 4H^+ + 4e^- \longrightarrow HCHO + H_2O \qquad E^\circ = -0.48\ \mathrm{V} \qquad (3)$$

$$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O \qquad E^\circ = -0.38\ \mathrm{V} \qquad (4)$$

$$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O \qquad E^\circ = -0.24\ \mathrm{V} \qquad (5)$$

These reactions require much less free energy per electron transferred than does the direct monoelectronic reduction of CO_2, producing the $CO_2^{\cdot -}$ radical anion, which has been estimated at approximately −2 V versus NHE [3]. Hence it is advantageous to find catalysts capable of facilitating the two- to eight-electron-transfer processes (reactions (1)–(5)) at potentials close to the thermodynamic values. In this paper, we exemplify the application of polyoxotungstates as photocatalysts for the photoreduction of CO_2 to CH_4, in the course of our studies on the photochemistry of polyoxometalates [4]. The results show that dititanodecatungstophosphate $[PTi_2W_{10}O_{40}]^{7-}$ functions as a multielectron transfer catalyst for the photochemical reduction of CO_2 to CH_4 in aqueous solutions containing organic electron donors such as alcohols. The photoredox reaction of $[PTi_2W_{10}O_{40}]^{7-}$ with CH_3OH has been recently reported by us [5]: photoexcitation of the O → W LMCT band in α-Keggin structural $[PTi_2W_{10}O_{40}]^{7-}$ leads to the formation of $[PTi_2W_{10}O_{40}]^{8-}$, HCHO and H_2. The d^1 electron injected in the polyoxoanion lattice is delocalized over ten WO_6 octahedra and the protonation of $[PTi_2W_{10}O_{40}]^{8-}$ is followed by intramolecular electron transfer to the TiO_6 octahedron, with resultant localization of the d^1 electron at the TiO_6 site.

Experimental

$K_7[PTi_2W_{10}O_{40}]\cdot 6H_2O$ and $K_5[BW_{12}O_{40}]\cdot 15H_2O$ were synthesized according to refs. 6–8. All other chemicals were of analytical grade and were used without further purification. Solutions of $[W_7O_{24}]^{6-}$ were prepared by adjusting pH levels of the solution of Na_2WO_4 to 5–7. Solution pH levels were adjusted by $HClO_4$ or KOH.

All experiments were performed according to the previously reported method [8]. A 500 W super-high-pressure mercury lamp was used as a light source. Sample solutions (20 mm^3) for long-term photolyses in quartz tubes were deaerated by solvent-saturated CO_2 or argon (Ar) gas. Analysis for W^V and Ti^{III} in the photolyte was carried out at room temperature by iodometry under an atmosphere of nitrogen. HCHO in the photolyte was determined by the acetylacetone procedure. H_2 and CH_4 analyses were performed by gas chromatography (Carbosieve S column), the latter being done by comparison to an authentic sample as well as by mass spectrometry. Electronic spectra were recorded on a Hitachi 330 spectrometer. X-band ESR spectra were recorded on a Varian E12 spectrometer at 77 K. Polarograms and cyclic voltammograms were measured on EG & G PAR 174A and 303 instruments and a standard cell with an Ag/AgCl reference electrode.

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Results and Discussion

An aqueous solution containing 1–10 mM $[PTi_2W_{10}O_{40}]^{7-}$ and 2.5 M CH_3OH at pH 5.4 under an atmosphere of CO_2 showed an intense absorption band at 255 nm ($\epsilon = 3.9 \times 10^4$ M^{-1} cm^{-1}) due to the $O \rightarrow W$ LMCT band. The $O \rightarrow Ti$ LMCT band, which is expected to lie in the long-wavelength ultraviolet regions, is covered by the intense $O \rightarrow W$ LMCT band, due to its small extinction coefficient. Exposure of the solution to light ($\lambda > 270$ nm) results in the appearance of a mixed-valence blue complex ($\lambda_{sh} = 460$ and ~ 1050 nm, $\lambda_{max} = 640$ and ~ 800 nm) with accompanying formations of HCHO, CH_4 and H_2. No other volatile products such as C_2H_6, C_2H_4 and CO were detected.

The amounts of products for the long-term photolyses of the solutions are shown in Fig. 1(a), where the result for the photolyses under Ar atmosphere at pH 5.4 is also represented. In addition, the results for the substitutions of $[BW_{12}O_{40}]^{5-}$ and $[W_7O_{24}]^{6-}$ for $[PTi_2W_{10}O_{40}]^{7-}$ are shown in Fig. 1(b) to account for the functions of $[PTi_2W_{10}O_{40}]^{7-}$ in the system that lead to the reduction of CO_2. In the absence of CO_2, an approximately stoichiometric relationship among the yields of HCHO, CH_4, H_2 and $W^V + Ti^{III}$ was maintained during the photolyses, if CH_4 is regarded as a two-electron reduction product of CH_3OH ($CH_3OH + H_2O + 2e^- \rightarrow CH_4 + 2OH^-$; $E^\circ = -0.66$ V versus NHE at pH 7.0 [9]). Removal of $[PTi_2W_{10}O_{40}]^{7-}$ resulted in little formation of HCHO, H_2 and CH_4. As shown in Fig. 1(a), the photolysis of $[PTi_2W_{10}O_{40}]^{7-}$ under CO_2 atmosphere increased the yield of CH_4 about 3 times but decreased the amounts of $W^V + Ti^{III}$ to about 1/3, compared with the case under Ar atmosphere. On the other hand, there was a minor change in the yield of HCHO between the two atmospheres, when other parameters were kept constant. Since there was no observable formation of other products, therefore, the difference in the yields of the photoproducts between the two atmospheres suggests that the photoredox reaction of $[PTi_2W_{10}O_{40}]^{7-}$ with CH_3OH in the presence of CO_2 leads to the eight-electron reduction of CO_2 to CH_4 (eqn. (5)) with an approximately stoichiometric relationship among the photoproducts of HCHO, $W^V + Ti^{III}$, H_2 and CH_4. Quantum yield (ϕ_{CH_4}) of the CO_2 reduction to CH_4 for the 313-nm light irradiation was 6×10^{-4} and ϕ_{HCHO} 4×10^{-3}.

The effect of the photocatalyst structure on the relative yields of the photoproducts under the CO_2 atmosphere is shown in Fig. 1(b). The results for the long-term photolyses of $[BW_{12}O_{40}]^{5-}$ and $[W_7O_{24}]^{6-}$ in the presence of CH_3OH under CO_2 atmosphere show little occurrence of the reduction of CO_2: α-Keggin structural $[BW_{12}O_{40}]^{5-}$ eliminated the release of CH_4 almost perfectly so that the stoichiometric relationship with HCHO as the two-electron oxidation product, H_2 as the two-electron reduction product and W^V was observed. Similarly, the $[W_7O_{24}]^{6-}$ system provided a good stoichiometric relationship between HCHO and W^V, without formations of CH_4 and H_2. $[BW_{12}O_{40}]^{5-}$ was photochemically reduced to both $[BW_{12}O_{40}]^{6-}$ and $[BW_{12}O_{40}]^{7-}$ at pH 5.4 and their oxidation potentials (of $E^\circ = -0.28$ and -0.52 V versus NHE at pH 5.4 respectively [8]) were more negative than $E^\circ_{CO_2/CH_4} = -0.15$ V versus NHE at pH 5.4. From the kinetic difficulty of CO_2 reduction in the $[BW_{12}O_{40}]^{5-}$ system, thus, it is emphasized that CH_4 release in the $[PTi_2W_{10}O_{40}]^{7-}$ system can be associated with electron transfer on the TiO_6 octahedron site in the Keggin-structural lattice.

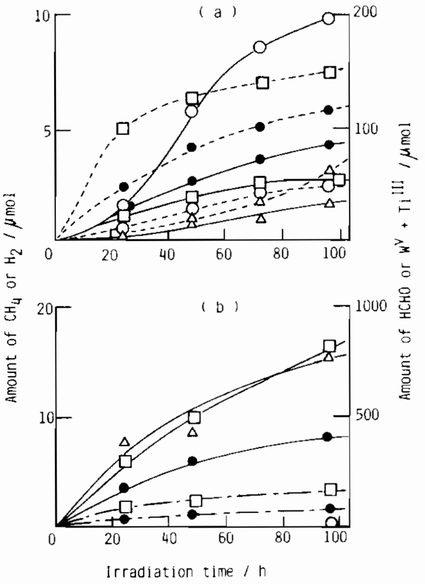

Fig. 1. Plots of amounts of photoproducts, CH_4 (○), H_2 (△), HCHO (●) and $W^V + Ti^{III}$ (□) against irradiation time ($\lambda >$ 270 nm) for solutions (20 mm^3) containing 10 mM photocatalyst and 2.5 M CH_3OH in water at pH 5.4. (a) $[PTi_2W_{10}O_{40}]^{7-}$ photocatalyst under CO_2 (——) and Ar (- - - -) atmospheres; (b) $[BW_{12}O_{40}]^{5-}$ (——) or $[W_7O_{24}]^{6-}$ (– – –) photocatalyst under CO_2 atmosphere.

It should be recalled that the d^1 electron injected into the $[PTi_2W_{10}O_{40}]^{7-}$ lattice by the photoredox reaction with CH_3OH is delocalized over ten WO_6 octahedra in the lattice and transferred to the TiO_6 octahedron during the protonation of the lattice with resultant localization on the TiO_6 site [5]. The intramolecular electron transfer from the W^VO_6 sites to the TiO_6 site on the protonation of the lattice is also supported by a perfect transformation of the ESR signal at $\langle g \rangle = 1.77$ into the one at $g_\parallel = 1.999$ and $g_\perp = 1.920$ on acidification (for example pH = 2.0) of the photolyte at pH 7.0: UV photolysis

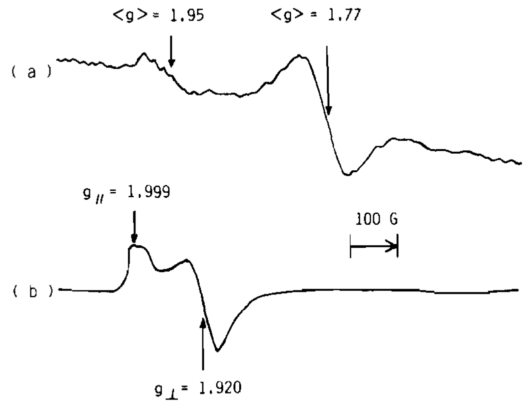

Fig. 2. ESR spectra of the photolytes at 77 K: (a) long-term photolysis (24 h) of the solution containing 10 mM $[PTi_2W_{10}O_{40}]^{7-}$ and 2.5 M CH_3OH at pH 7.0 under an Ar atmosphere; (b) acidification of the photolyte at pH 7.0 to pH 2.0 in the dark.

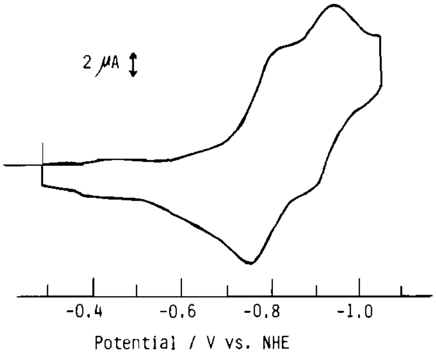

Fig. 3. Cyclic voltammogram at a hanging mercury electrode for a solution containing 1.3 mM $K_7[PTi_2W_{10}O_{40}]\cdot 6H_2O$ and 0.2 M KCl at pH 5.4. Scan rate was 200 mV s^{-1}.

of the solution containing 10 mM $[PTi_2W_{10}O_{40}]^{7-}$ and 2.5 M CH_3OH under Ar atmosphere at pH 7.0 gave the ESR signal at $\langle g \rangle = 1.77$ ($\Delta H_{ms} \approx 100$ G) due to the delocalized d^1 electron over the WO_6 sites and the acidification of the photolyte to pH = 2.0 in the dark resulted in change of the ESR signal to $\langle g \rangle = 1.95$ due to the localized d^1 electron at the TiO_6 site, as shown in Fig. 2. The $[PTi_2W_{10}O_{40}]^{7-}$ system showed no change in the pH level of the photolyte during the photolysis. This is different from the $[BW_{12}O_{40}]^{5-}$ system, in which the photolysis resulted in a decrease in solution pH [8]. Thus, it is reasonable to assume that in the $[PTi_2W_{10}O_{40}]^{7-}$ system at pH 5.4 most of the protons liberated by the oxidation of CH_3OH to HCHO are bound to the polyoxoanion lattice. Such protonations on the lattice during photolysis elucidate the delayed appearance of the Ti^{III} signal for the photolyte. The W^V signal intensity at $\langle g \rangle = 1.77$ increased continuously as photolysis at pH 5.4 proceeded and then decreased with further photolysis which was reflected by the observation of an additional Ti^{III} signal at $\langle g \rangle = 1.95$, as reported previously [5]. The decrease in the signal at $\langle g \rangle = 1.77$ on further photolysis can be ascribed to the formation of the two- to four-electron blue species, $[PTi_2W^V{}_2W_8O_{40}H_2]^{7-}$, $[PTiTi^{III}W^V{}_2W_8O_{40}H_3]^{7-}$ and $[PTi^{III}{}_2W^V{}_2W_8O_{40}H_4]^{7-}$, exhibiting the super-exchange between the two W^V electrons over the ten WO_6 octahedra in the lattice. Cyclic voltammetry of a solution containing 1.3 mM $[PTi_2W_{10}O_{40}]^{7-}$ and 0.2 M KCl at pH 5.4 revealed two successive quasi-reversible one-electron redox waves exhibiting reduction peaks at −0.82 and −0.93 V versus NHE on a hanging mercury electrode, as shown in Fig. 3. The approximate reversibility of the one-electron reduction–oxidation steps was confirmed by a d.c. polarogram obtained with a dropping mercury electrode: a linear plot of the electrode potential (E) versus $\log[(i_d - i)/i]$* for the wave at half-wave potential ($E_{1/2}$) of −0.75 V versus NHE showed a slope of 60 mV. Controlled-potential reduction of the electrolyte at −0.85 V versus NHE led to the development of the ESR signal due to W^V at 77 K which was the same $\langle g \rangle$ value as the photolyte. Therefore, it is reasonable to assume that the photoreduced one-electron species is identical to the electrochemical one-electron reduction species. As discussed previously [8], the UV-induced formation of H_2 was attributed to the coupling of the one- and two-electron reduction species with H^+, since oxidation potentials for $[PTi_2W^VW_9O_{40}H]^{7-}$, $[PTi_2W^V{}_2W_8O_{40}H_2]^{7-}$ and $[PTiTi^{III}W^VW_9O_{40}H_2]^{7-}$ are highly negative compared with the reduction potential of −0.31 V versus NHE for H^+/H_2 at pH 5.4. The reduction potential of CO_2 to CH_4 should be thermodynamically more feasible than that required to reduce protons to H_2. Nevertheless, despite the thermodynamic feasibility of reducing CO_2, the $[BW_{12}O_{40}]^{5-}$ system (Fig. 1(b)) showed kinetic difficulty in accomplishing the process due to the need to pursue a multielectron reduction process. This implies that a kinetic factor may be the formation of the four-electron reduction species during photolysis. The $[BW_{12}O_{40}]^{5-}$ system exhibited no photochemical formation of the more than three-electron reduction species at pH 5.4 [8]. The localization of the d^1 electron at the TiO_6 site as a result of the intramolecular transfer from the WO_6 sites in the lattice during photolysis of the $[Ti_2W_{10}O_{40}]^{7-}$ system [5] leads to an increase in the density of the d^1 electrons at the particular site where CO_2 reduction proceeds In connection with the fact that $[PTi_2W_{10}O_{40}]^{7-}$

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*Where i and i_d denote current and diffusion-limited current, respectively.

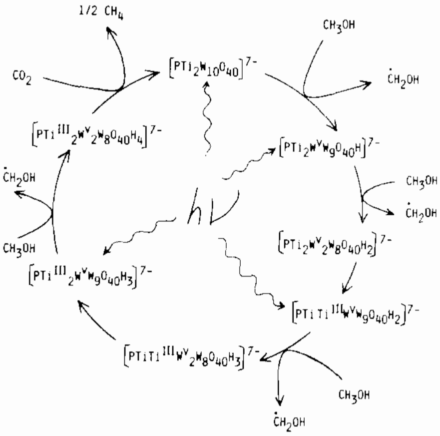

Fig. 4. Postulated schematic representation of the reduction of CO_2 to CH_4.

is of C_2 symmetry [5, 6], therefore, the occurrence of the CO_2 reduction in the $[PTi_2W_{10}O_{40}]^{7-}$ system may be explained in terms of the distribution of four d^1 electrons in the four-electron reduction species of $[PTi^{III}_2W^V_2W_8O_{40}H_4]^{7-}$ as the kinetic factor which gives the configuration $(\underline{Ti^{III}{-}O{-}W^V{-}O{-}Ti^{III}{-}O{-}W^V{-}O}$ of the Ti^{III} and W^V atoms at the $Ti^{III}_2W^V_2O_4$ ring in the anion lattice. Based on the photoredox properties of $[BW_{12}O_{40}]^{5-}$ [8], thus, a plausible scheme for CO_2 reduction to CH_4 for the $[PTi_2W_{10}O_{40}]^{7-}$ system is shown in Fig. 4 where $[PTi_2W_{10}O_{40}]^{7-}$ indicates a multi-electron transfer catalyst. In Fig. 4, the photoredox reaction of $[PTi_2W^VW_9O_{40}H]^{7-}$ with CH_3OH to yield $[PTi_2W^V_2W_8O_{40}H_2]^{7-}$ and $\dot{C}H_2O(\dot{C}H_2OH)$ is proposed, as was established for the $[BW_{12}O_{40}]^{5-}$ system [8].

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