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Journal of Photochemistry and Photobiology A: Chemistry 115 (1998) 223–226

Journal of Photochemistry and Photobiology A:Chemistry

Photocatalytic reduction of high pressure carbon dioxide using TiO_2 powders with a positive hole scavenger

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Received 22 December 1997; received in revised form 20 March 1998; accepted 7 April 1998

Abstract

The photocatalytic reduction of high pressure CO_2 using TiO_2 powders with a positive hole scavenger has been reported. The TiO_2 powders suspended in iso-propyl alcohol solution were irradiated with a Xe lamp. The main reduction product from CO_2 by photocatalytic reduction was methane. Iso-propyl alcohol acted as the positive hole scavenger. Under the optimum experimental conditions, 1.3 $\mu mol \cdot (g\text{-}Ti)^{-1}$ of methane was obtained by the photochemical reduction of high pressure CO_2, corresponding to 0.43 $\mu mol \cdot (g\text{-}Ti)^{-1}\, h^{-1}$ of the formation rate. The CO_2-reduction system developed may become of practical interest for the efficient CO_2-conversion and fixation system, storage of solar energy and the production of raw materials for the photochemical industry.

Keywords: Photocatalytic reduction; High pressure carbon dioxide; Titanium dioxide; Positive hole scavenger; Methane

1. Introduction

The identification of photoinduced CO_2 reduction pathways leading to gaseous hydrocarbon species would be of importance in the development of alternative fuel sources [1]. The photocatalytic reduction of CO_2 using photosensitive semiconductor powders in aqueous solutions has been widely studied [2–21]. Thus far, the studies have been performed exclusively at room temperature and atmospheric pressure. In these conditions, however, the concentration of CO_2 in water is extremely small because of its low solubility [22,23]. Furthermore, the photoreduction of CO_2 is in competition with hydrogen formation due to water decomposition. Therefore, selective reduction of CO_2 is one of the major problems for the photocatalytic reduction of CO_2 in aqueous solutions.

Increase in CO_2 pressure is one of the methods for increasing the concentration of CO_2 and improving the CO_2 reduction selectivity. Actually, in the electrochemical and photoelectrochemical reduction of CO_2, some investigations under high pressure have been reported [24–26]. A similar effect could be expected for the photocatalytic reduction of CO_2 in aqueous solutions. In a previous work [27,28], we have investigated the photocatalytic reduction of CO_2 using TiO_2 powders at high pressure. It has been found that hydrocarbons such as methane and ethylene, which were not produced at ambient CO_2 pressure, were obtained under high CO_2 pressure. However, it needed more than 24 h of irradiation for the formation of the hydrocarbons because electron donors are absent during the irradiation.

In this work, we select iso-propyl alcohol as a positive hole scavenger and present the photocatalytic reduction of high pressure CO_2 using TiO_2 suspensions in iso-propyl–alcohol solution.

2. Experimental

2.1. Procedures

The instruments and the stainless steel vessel used here for the photocatalytic reduction of high pressure CO_2 were reported in a previous paper [29]. For the irradiation, the laboratory-made stainless steel vessel (inner volume, 43.0 ml) equipped with a window was employed. A commercially available pressure glass device of 21 mm diameter aperture (KLINPORT KPT-C1Q, Nihon Klingage) was fitted in the window. The window glass transmitted almost all the light rays of wavelength above 340 nm and energy of 3.6 eV, which is higher than the band gap energy of TiO_2 (3.0 eV). In order to prevent contamination from the stainless steel and its catalytic effect on CO_2 reduction, the inner surface was com-

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PII S1010-6030(98)00274-3

pletely covered by Teflon. The vessel was placed in a water bath at 293 K.

The photocatalyst substrate used was TiO_2 (Degussa P-25, specific surface of 50 $m^2 g^{-1}$, diameter 24 nm). The TiO_2 powders (100 mg) were suspended in 20 ml of 1.0 mol l^{-1} iso-propyl alcohol solution and transferred to the stainless steel vessel. After the deoxygenation by flowing highly purity CO_2 (99.9999%) through the vessel for 30 min, the vessel was closed tightly and then the CO_2 pressure was increased to the given values below 2.8 MPa. Before use, trace contaminants (hydrocarbon, carbon monoxide etc.) in the carbon dioxide was checked. The TiO_2 powders were continuously dispersed in iso-propyl alcohol solution by a magnetic stirrer during the irradiation with a Xe lamp (4.2 kW, Ushio Electronics) through the window. The light intensity was 0.62 kW m^{-2}. Gaseous reduction products were sampled through a sampling valve and analyzed by FID and TCD gas chromatography. The liquid sample was analyzed by high performance liquid chromatography with a UV detector and FID gas chromatography.

3. Results and discussion

In many studies for the photocatalytic reduction of CO_2, TiO_2 has been widely used, which is one of the effective catalysts for the reduction by irradiation with light [6–21]. Therefore, TiO_2 was selected as the photocatalyst for the reduction of CO_2 in this study.

3.1. Effect of positive hole scavenger

Choi and Hoffmann [30] investigated the effect of electron donors such as 2-propanol, methanol and tert-butanol on the photoreductive decomposition of CCl_4 on TiO_2 powders. It was found that the addition of 2-propanol was effective for the photoreductive decomposition of CCl_4. Therefore, iso-propyl alcohol was used as the positive hole scavengers in this reduction system. The effect of iso-propyl alcohol on the photocatalytic reduction of high pressure CO_2 on TiO_2 powders was investigated for 5 h irradiations. The results are shown in Table 1. When the irradiations were performed without iso-propyl alcohol, CO_2 was not reduced. However, methane was exclusively produced by the photocatalytic reduction of high pressure CO_2 in iso-propyl alcohol solution. The production of acetone, also, was observed because of oxidation of iso-propyl alcohol. These results may indicate that iso-propyl alcohol acted as the positive hole scavenger in the high pressure CO_2 photoreduction and the addition of it accelerated the formation of methane. Consequently, 1.0 mol l^{-1} of iso-propyl alcohol was used for all subsequent irradiations.

3.2. Effect of CO_2 pressure

Inoue et al. [6] described that formic acid, formaldehyde and methyl alcohol were produced through the photocatalytic reduction of CO_2 in aqueous solution at ordinary pressure, while no gaseous products were definitely obtained. However, it was reported in our previous study [28] that methane and ethylene were produced by CO_2 photocatalytic reduction under high pressure on TiO_2 in an aqueous solution. Therefore, the effect of CO_2 pressure on the photocatalytic reduction of CO_2 using TiO_2 suspensions in iso-propyl alcohol solution was investigated. The results are shown in Table 2. The formation of methane increased as CO_2 pressure increased up to 2.8 MPa. A similar tendency was observed for the high pressure CO_2 photocatalytic reduction on TiO_2 in the aqueous solution [28]. Therefore, it was found that high CO_2 pressure was effective for the formation of methane in the photocatalytic CO_2 reduction using TiO_2 powders. This may be attributable that the adsorption spices on the surface sites of TiO_2 changed from hydrogen to carbon with increasing the pressure and the reaction between the carbon and hydrogen species proceeded to form the lower hydrocarbon such as methane. In the aqueous solution, a small amount of ethylene was produced at only 2.5 MPa [28]. In the iso-propyl alcohol solution, however, ethylene was not produced even at relatively high pressure. Since no dimerization take place because of accelerated formation of methane, it seems that ethylene is not produced. At only the CO_2 pressure of 0.75 MPa, the production of formic acid was extraordinary in the high pressure CO_2 photocatalytic reduction on TiO_2 powders suspended in iso-propyl alcohol solution. Even after the remeasurements, the results were same and the reason could not be made clear. In the photocatalytic high pressure

Table 1
Effect of iso-propyl alcohol on the photocatalytic reduction of high pressure CO_2 on TiO_2

Concentration of 2-propanol, mol l^{-1}	Yield of CH_4, 10^{-6} mol · (g-Ti)$^{-1}$
0	0
1.0	1.2
3.0	0.62

TiO_2, 100 mg; irradiation time, 5 h; pressure 2.8 MPa, temperature, 293 K.

Table 2
Effect of CO_2 pressure on the photocatalytic reduction of high pressure CO_2 on TiO_2 suspensions in iso-propyl alcohol solution

CO_2 pressure MPa	Products, 10^{-6} mol · (g-Ti)$^{-1}$		Energy conversion efficiency, % [b]
	CH_4	HCOOH	
0.20	0.10	– [a]	0.00055
0.75	0.42	2.3	0.0059
1.6	0.70	– [a]	0.0038
2.3	0.62	– [a]	0.0034
2.8	1.2	– [a]	0.0065

TiO_2, 100 mg; irradiation time, 5 h; temperature, 293 K; Medium, 1.0 mol l^{-1} iso-propyl alcohol.

[a] Less than detectable level (< 0.1).

[b] 100 (Heat of combustion of products)/(Incident light energy).

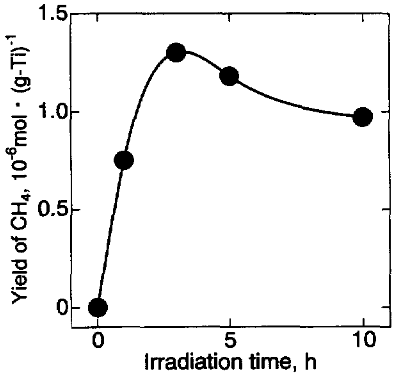


Fig. 1. Effect of irradiation time on the yield of methane. TiO_2, 100 mg; temperature, 293 K; pressure, 2.8 MPa; Medium, 1.0 mol l^{-1} iso-propyl alcohol.

CO_2 reduction on TiO_2 in the aqueous solution [28], it was characteristic that methanol formation exhibited the large peak at about 1.0 MPa. Therefore, the photocatalytic reduction characteristics of CO_2 on TiO_2 at approximately 1.0 MPa seem to be specific.

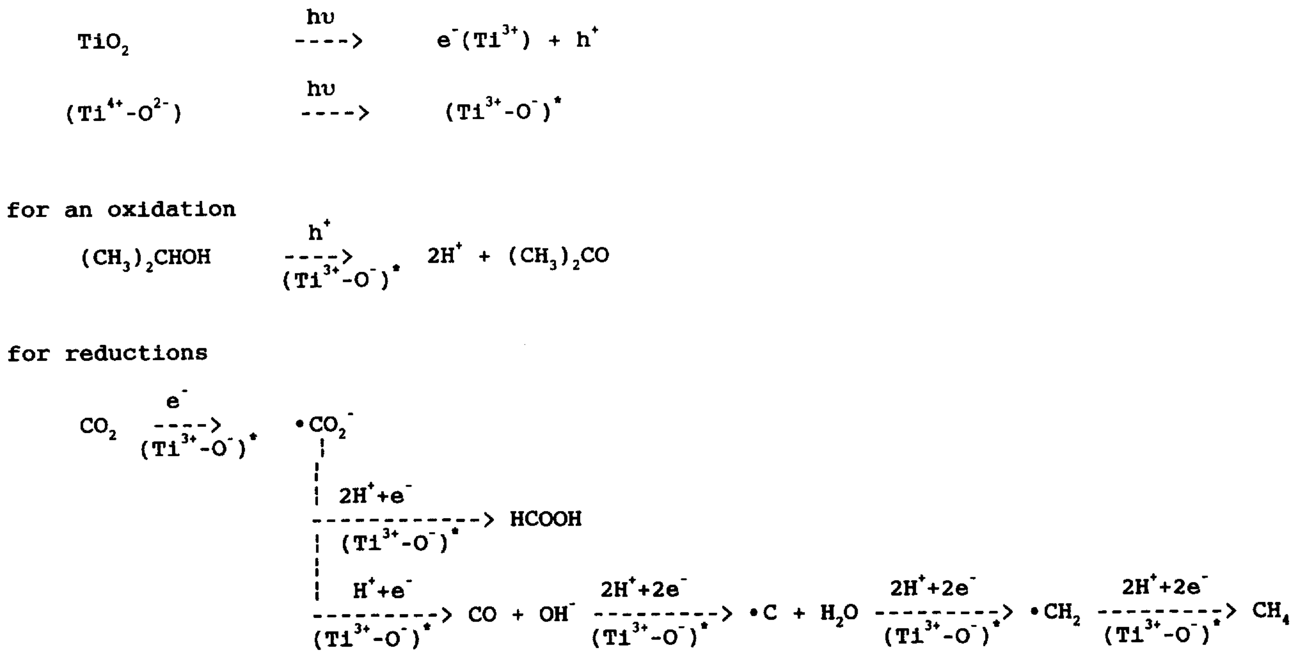
Solar to chemical energy conversion efficiencies were calculated from the sum of the heats of combustion of the products, divided by the total incident light energy (Table 2). The maximum energy conversion efficiency was 0.0065%. The value was better than those in the photoassisted reduction of aqueous carbon dioxide on TiO_2 (0.0035%) [10].

3.3. Effect of irradiation time

In order to select optimal irradiation time for methane formation, the effect of irradiation time was investigated. The results are illustrated in Fig. 1. The yield of methane increased sharply with irradiation time until 3 h. After 3 h irradiation, the formation yield decreased gradually until 10 h. These phenomena may be due to deterioration of photocatalytic activity and the decomposition of methane at the interface between gas and liquid phase. The maximum quantity of methane was 1.3 μmol · (g-Ti)$^{-1}$ for 3 h of irradiation time, corresponding to 0.43 μmol · (g-Ti)$^{-1}$ h^{-1} of the methane formation rate. When UV irradiation of TiO_2 in the presence of CO_2 and gaseous H_2O was carried out at 275 K [18], 0.044 μ · (g-Ti)$^{-1}$ of methane was produced for 6 h. Ishitani et al. [15] reported that the yield of methane was 0.078 μmol · (g-Ti)$^{-1}$ in the photocatalytic reduction of CO_2 on TiO_2 at 650 Torr for 5 h irradiation. The maximum value of methane in this system was approximately the same as the yield obtained by the photocatalytic high pressure CO_2 reduction in the water [28] and better than those obtained at various conditions [15,18]. The formation rate of methane was more than 8 times higher than those obtained in the aqueous solution [28]. Consequently, it was found that the addition of iso-propyl alcohol as the positive hole scavenger was effective for the increase in methane production rate in the photocatalytic reduction of high pressure CO_2 on TiO_2.

3.4. Mechanism

There are many reports dealing with the mechanism of the photocatalytic reduction of CO_2. In CO_2-saturated aqueous solution containing powdered suspensions of TiO_2 and copper [16], the formation process of methyl alcohol, formaldehyde, methane and carbon monoxide occurred on TiO_2 and O_2 formed on Cu was proposed by Hirano et al. Anpo and Chiba [17] described that UV irradiation of TiO_2 catalyst in the presence of CO_2 and H_2O led to the formation of ·C radicals, H atoms and Ti^{3+} ions as intermediates which



$$TiO_2 \xrightarrow{h\nu} e^-(Ti^{3+}) + h^+$$

$$(Ti^{4+}\text{-}O^{2-}) \xrightarrow{h\nu} (Ti^{3+}\text{-}O^-)^*$$

for an oxidation

$$(CH_3)_2CHOH \xrightarrow[(Ti^{3+}\text{-}O^-)^*]{h^+} 2H^+ + (CH_3)_2CO$$

for reductions

$$CO_2 \xrightarrow[(Ti^{3+}\text{-}O^-)^*]{e^-} \cdot CO_2^-$$

$$\cdot CO_2^- \xrightarrow[(Ti^{3+}\text{-}O^-)^*]{2H^+ + e^-} HCOOH$$

$$\cdot CO_2^- \xrightarrow[(Ti^{3+}\text{-}O^-)^*]{H^+ + e^-} CO + OH^- \xrightarrow[(Ti^{3+}\text{-}O^-)^*]{2H^+ + 2e^-} \cdot C + H_2O \xrightarrow[(Ti^{3+}\text{-}O^-)^*]{2H^+ + 2e^-} \cdot CH_2 \xrightarrow[(Ti^{3+}\text{-}O^-)^*]{2H^+ + 2e^-} CH_4$$

Scheme 1. Reaction mechanism of the photocatalytic reduction of high pressure CO_2 using TiO_2 powders suspended in iso-propyl alcohol solution.

detected through electron spin resonance (ESR) measurements.

From the results in the present study and the literature [17–21,27–29,31–37], the formation process of methane and formic acid by the photocatalytic reduction of high pressure CO_2 using TiO_2 powders suspended in iso-propyl alcohol solution can be estimated to be as Scheme 1. An increase in CO_2 pressure probably seems to accelerate the formation of $\cdot C$ radicals during the irradiation. Hence, high pressure CO_2 may be more efficient in the formation of methane, compared to ordinary pressure.

In conclusion, the photocatalytic reduction of high pressure CO_2 using TiO_2 suspensions in iso-propyl alcohol solution was performed. The main reduction product from CO_2 was methane. It seems that iso-propyl alcohol acted as the positive hole scavenger. In this reduction system using the positive hole scavenger, ethylene was not produced, but methane was obtained for short irradiation time. Therefore, it was found that the addition of iso-propyl alcohol enhanced the formation rate for methane in the photocatalytic high pressure CO_2 reduction using TiO_2 powders. Since the TiO_2 catalysts are inexpensive, the CO_2-photoreduction system developed may be economically feasible in large scale methane productions. In other words, the system may become one of the promising method for the fixation and removal of CO_2 because of the simplicity, the easy control and low cost of the system. However, higher energy conversion efficiency is expected for the practical application of the system. Further investigation is in progress.

Acknowledgements

This work was supported financially by the Ministry of Education of Japan, as well as by the Chubu Electric Power Research Foundation.

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