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Effect of CO_2 pressure on photocatalytic reduction of CO_2 using TiO_2 in aqueous solutions

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Abstract

The photocatalytical reduction of CO_2 at high pressure was investigated using TiO_2 suspensions in water and caustic solution. An increase in CO_2 pressure significantly accelerated the CO_2 reduction in both water and the caustic solution. The major reduction products are liquid phase products such as acetic acid and alcohols, and gaseous products such as methane, ethane and ethylene were also observed as a minor portions.

Keywords: Pressure; Photocatalytic reduction; Carbon dioxide; Titanium dioxide

1. Introduction

Photocatalytic reduction of CO_2 using semiconductor suspensions has been widely studied in aqueous solutions [1–5]. The studies have so far been performed exclusively at ordinary temperature and pressure. In these conditions, however, the concentration of CO_2 in water is very small because of its low solubility and, furthermore, photocatalytical CO_2 reduction is competitive with H_2 formation via water reduction. Hence 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 measures for increasing the concentration of CO_2 and improving the CO_2 reduction selectivity [6,7]. Actually, in electrochemical reduction on metal electrodes, it has been reported that the reduction rate and the yield of reduction products were improved with increasing CO_2 pressure and, furthermore, the selectivity of the reduction products was also changed. A similar effect could be expected for photocatalytic reduction of CO_2 in aqueous solutions. The present authors have investigated the photocatalytic reduction of CO_2 at high pressure (2.8 MPa) using copper-loaded TiO_2 suspensions in water. It has been found that hydrocarbons such as methane, ethane and ethylene, which were not produced at ambient CO_2 pressure, were formed under high CO_2 pressure [8].

In this paper we report the effects of CO_2 pressure on photocatalytic reduction of CO_2 using TiO_2 suspensions in purified water and caustic solutions. Moreover, the selectivity of CO_2 reduction compared with water reduction was examined.

2. Experimental details

The photocatalytic reduction was carried out in stainless steel autoclave (inner volume, 100 ml) with a window through which CO_2 medium was irradiated, as shown in Fig. 1. A commercially available pressure glass device with 21 mm diameter aperture (KLINPORT KPT-C1Q, Nihon Klingage Co. Ltd.) was fitted in the window, because 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). The inner surface was completely covered by Teflon to prevent contamination from stainless steel and its catalytic effect on CO_2 reduction. The autoclave was placed in a water bath at 293 K.

TiO_2 (Wako Junyaku, anatase, specific surface of 8.7 m^2 g^{-1}) was pretreated by boiling in HNO_3 and then thoroughly rinsed with distilled water prior to use. The TiO_2 powders (50 mg) were sonically suspended in 30 ml of purified water and 0.2 N NaOH solution and transferred to the autoclave. After deoxygenation by bubbling CO_2 for 30 min, the autoclave was closed tightly and then the CO_2 pressure was increased to the given values ranging from 98 kPa to 2.5 MPa. The solution in the autoclave was continuously stirred by a magnetic stirrer during irradiation with a 4.5 kW xenon lamp

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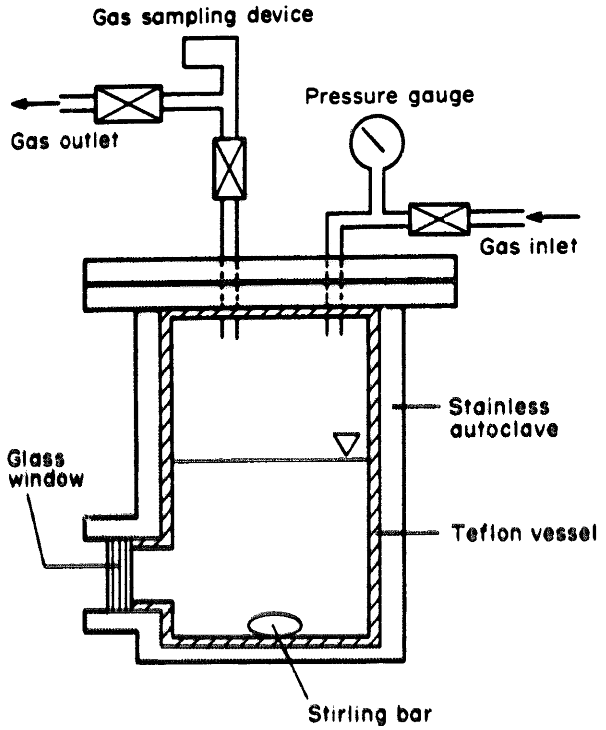

Fig. 1. Schematic diagram of photolysis cell for CO_2 reduction under high CO_2 pressure.

through the window. After the end of irradiation, gaseous reduction products were sampled through a sampling valve and analysed by FID gas chromatography for hydrocarbons and TCD for CO and H_2. The liquid sample was taken after pressure reduction to the ordinary state and analysed by high performance liquid chromatography.

3. Results and discussion

3.1. *Effect of CO_2 pressure*

Under ambient CO_2 pressure in purified water, no products produced by CO_2 reduction were definitely observed in the gas phase as reported previously [1]. However, as the CO_2 pressure increased to 0.5 MPa, methane was observed as the reduction product in the gas phase and its yield increased with increasing CO_2 pressure as shown in Fig. 2. Furthermore, at 2.5 MPa CO_2 pressure ethylene and ethane were also observed, although these yields were much smaller than that of methane. It has been reported by Anpo and coworkers that these gaseous reduction products were produced by photocatalytic reduction of gaseous CO_2 and H_2 mixtures [9-11], although in the case of aqueous solution saturated by 1 atm CO_2 the gaseous products have not identified as mentioned above. These facts indicate that as the CO_2 pressure increases the absorption on the TiO_2 surfaces shift from hydrogen species to carbon species, resulting in progress of the reaction between the hydrogen and carbon species and then formation of the lower hydrocarbons as gaseous products.

Fig. 3 shows that the reduction products in the liquid phase were formic acid and methanol, as reported by other workers at ambient pressure except for formaldehyde [1,12]. Although at ambient pressure a small amount of formic acid was produced, its yield increased linearly but slightly with the pressure. Methanol was also observed at ambient pressure, and its yield increased sharply with increase in CO_2 pressure to 1.0 MPa, and then decreased sharply with its further increase. It was characteristic that only methanol exhibited the large peak at 1 MPa in its yield, but the reason for that is not clarified yet. Comparing Fig. 2 with Fig. 3, it

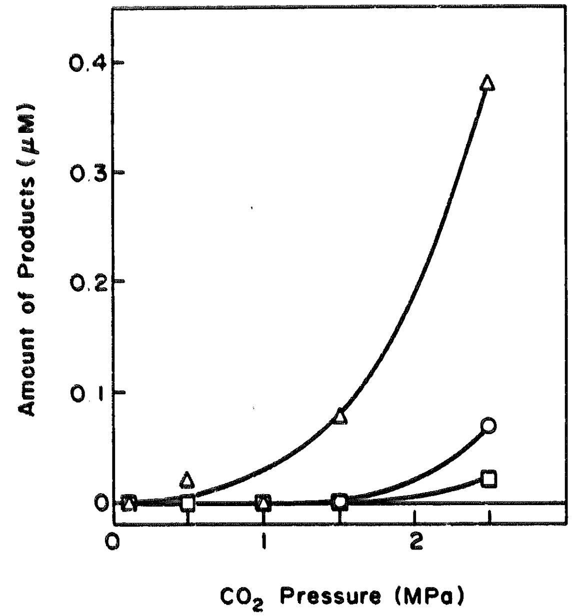

Fig. 2. Effect of CO_2 pressure on its photoreduction (medium, purified water; irradiation time, 24 h; catalyst, TiO_2): △, CH_4; ○, C_2H_4; □, C_2H_6.

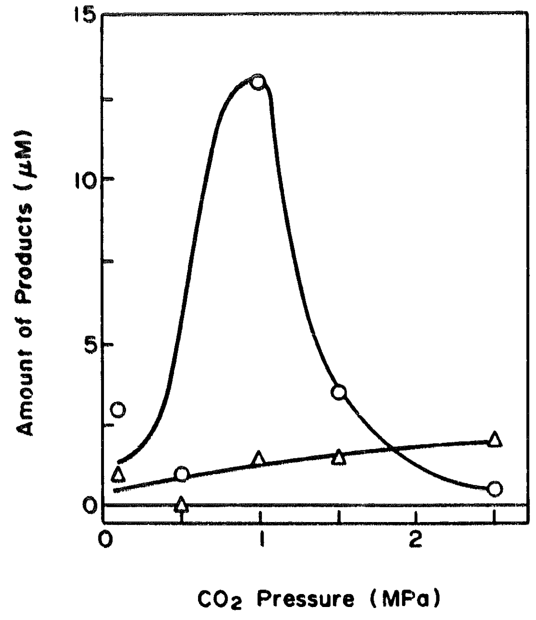

Fig. 3. Effect of CO_2 pressure on its photoreduction (medium, purified water; irradiation time, 24 h; catalyst, TiO_2): ○, CH_3OH; △, HCOOH.

should be noted that the yield of the liquid reduction products was roughly one order of magnitude larger than that of the gaseous products, on average. Thus it was demonstrated that increase in CO_2 pressure accelerated significantly the photocatalytic reduction of CO_2 and preferentially produced liquid products, although an optimal CO_2 pressure might exist for formation of methanol.

From these results, it is suggested that increasing CO_2 pressure increases the CO_2 availability on the TiO_2 surfaces so that the selectivity of photocatalytic reduction of CO_2 in water is accelerated and furthermore the reduction similar to that in the gaseous phase mixture of CO_2 and H_2O proceeds simultaneously.

3.2. Effect of electrolytes

Previous work by others has shown that addition of electrolytes such as Na_2CO_3 and NaOH increased photocatalytic decomposition of water and reduction of CO_2 [13,14]. We tried to examine the effect of electrolyte addition under pressurized CO_2 conditions using 0.2 N NaOH solution as the initial composition of the aqueous solution before pressurizing with CO_2. Fig. 4 shows that the gaseous product was methane only and any higher hydrocarbons such as ethane and ethylene were not observed. Methane was produced exclusively under pressurized CO_2 conditions, and its dependence on the CO_2 pressure was similar to that in water as mentioned above. The total yield of gaseous products at 2.5 MPa was about 2 times larger in the NaOH solution than in water.

As shown in Fig. 5, for the liquid products, contrary to the gaseous products it was characteristic that two carbon compounds such as ethanol and acetaldehyde were observed at 2.5 MPa and their amount was several times larger in the NaOH solution than the total amount of all liquid reduction products in purified water. The results demonstrated that the addition of NaOH as an electrolyte significantly enhanced the CO_2 reductions to produce both a gaseous product and liquid products. It might be a factor in this enhancement that the NaOH solution dissolved a larger amount of CO_2 than water although many of them dissociated. On the contrary, a similar enhancement caused by the electrolyte addition was reported in the photocatalytical decomposition of water to H_2 and O_2 by Sayama and Arakawa [13,14]. This implies that the photocatalytic reaction itself could be accelerated with the addition of electrolytes, even though the role of the carbonate ions has not been clarified yet.

3.3. Reduction rate of CO_2 under high pressure

Fig. 6 shows the time course of formation of reduction products in the 0.2 N NaOH solution at 2.5 MPa CO_2. This indicated that the amount of H_2 as a reduction product of water sharply decreased with irradiation time. On the contrary, CO_2 reduction products such as methane, ethylene, ethane, methanol and ethanol all increased with the time. This suggests that photochemical reduction of water has proceeded in the early stage of irradiation, and then the reduction was replaced by CO_2 reduction reactions, which proceeded over 48 h. The decrease in initially produced H_2 indicates its photochemical consumption, that is it might be oxidized by positive holes on the TiO_2 or react with any transient intermediates of CO_2 reduction to produce hydrocarbons or

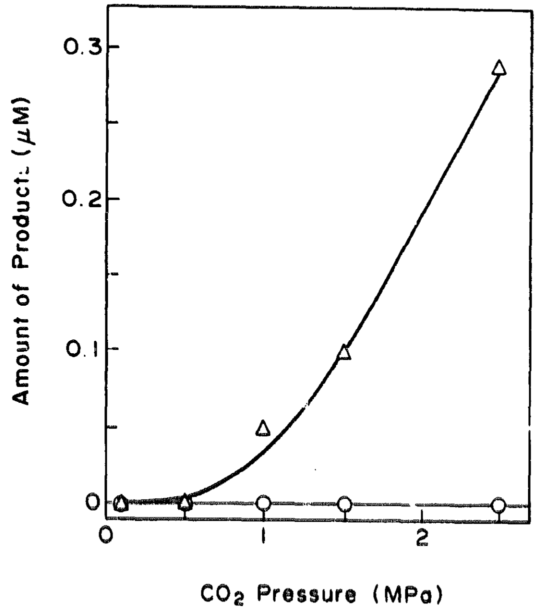

Fig. 4. Effect of CO_2 pressure on its photoreduction (medium, 0.2 N NaOH; irradiation time, 24 h; catalyst, TiO_2): Δ, CH_4; O, C_2H_4.

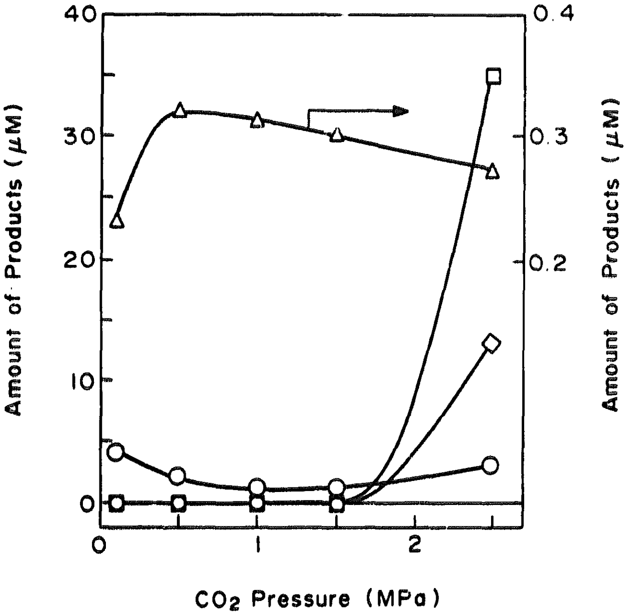

Fig. 5. Effect of CO_2 pressure on its photoreduction (medium, 0.2 N NaOH; irradiation time, 24 h; catalyst, TiO_2): O, CH_3OH; Δ, HCOOH; □, CH_3CHO; ◇, C_2H_5OH.

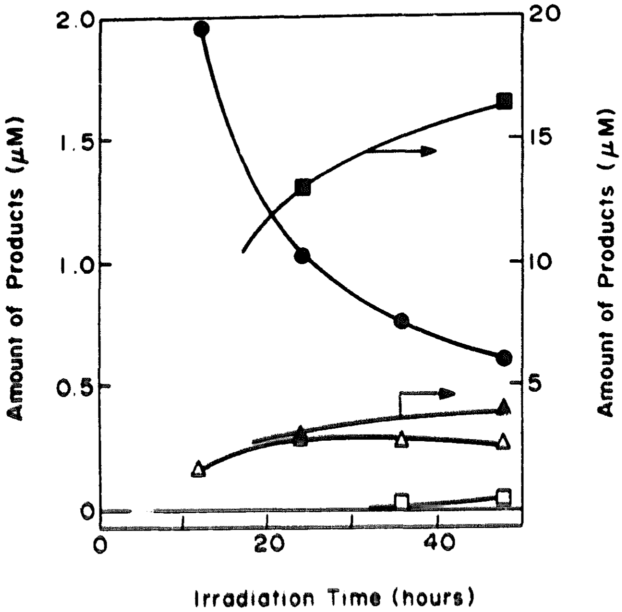

Fig. 6. Effect of irradiation time on amount of reduction products (medium, 0.2 NaOH; CO_2, 2.5 MPa; catalyst, TiO_2): ●, H_2; △, CH_4; □, C_2H_4; ▲, CH_3OH; ■, C_2H_5OH.

alcohols, although its quantity is only a minor proportion of that of the CO_2 reduction products because the amount of H_2 was considerably smaller than that of the CO_2 reduction products.

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