Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Photochemistry and Photobiology A: Chemistry 160 (2003) 11–17

Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Sonophotocatalysis of water in a CO_2–Ar atmosphere

Hisashi Harada*, Chigusa Hosoki, Makoto Ishikane

Faculty of Physical Sciences and Engineering, Meisei University, Hino-shi, Tokyo 191-8506, Japan
Advanced Materials Research and Development Center, Meisei University, Hino-shi, Tokyo 191-8506, Japan

Received 24 December 2002; received in revised form 29 March 2003; accepted 10 April 2003

Abstract

A system combining photocatalysis and sonolysis, named a sonophotocatalysis system, was carried out. Sonophotocatalysis means simultaneous irradiation of ultrasound and light with a photocatalyst (TiO_2 powder). As one of possibilities for this system, the resemblance between the reaction of this combined system and photosynthesis was discussed. The overall process of photosynthesis can be divided into two parts: reduction of CO_2 and generation of oxygen from water. In this study, sonophotocatalysis was performed in a CO_2–Ar atmosphere, resulting in reduction of CO_2 to CO and continuous generation of O_2 from water. Thus, photosynthesis-like reactions can be achieved using this combined system, though incident light energy does not accumulate. Further development of this system in the future is discussed in this paper.

Keywords: Sonophotocatalysis; CO_2 reduction; O_2 production; TiO_2; Photosynthesis

1. Introduction

Much interest has recently been shown in artificial photosynthesis. Photosynthesis is a system for conversion or accumulation of energy. It is also interesting that some reactions occur simultaneously and continuously. Fujishima et al. [1] pointed out that a photocatalytic system resembles the process of photosynthesis in green plants. They described that there are three important parts of the overall process of photosynthesis: (1) oxygen generation by the photolysis of water, (2) photophosphorylation, which accumulates energy, and (3) the Calvin cycle, which takes in and reduces carbon dioxide. We report here that two reactions, reduction of CO_2 and generation of O_2 from water, occur simultaneously and continuously by a sonophotocatalytic reaction.

Generation of O_2 from water is thought to be important. By the combined effects of sonolysis and photocatalysis, water has been decomposed into O_2 and H_2 stoichiometrically and continuously [2]. Namely, overall water splitting, evolution of O_2 and H_2, was achieved using a sonophotocatalytic technique in the presence of a TiO_2 photocatalyst under white light illumination of a xenon lamp. Effects of ultrasonic irradiation on heterogeneous photocatalytic reaction systems have been reported by Mason [3], Sawada and Hirano [4], Kado et al. [5], Suzuki et al. [6] and Ragaini et al. [7].

On the other hand, it has been reported that reduction of CO_2 was achieved by the use of sonolysis [8,9]. It was pointed out that in those reports the dissolved gas in the solution was important and that the rate of CO_2 reduction depended on the concentration of CO_2 in the matrix.

Thus, generation of O_2 and reduction of CO_2 are supposed to occur by a combination of photocatalysis and sonolysis. In order to achieve photosynthesis-like reactions, sonophotocatalysis of water was carried out in a CO_2–Ar atmosphere in the present study.

Before using the combined system, photocatalysis and sonolysis in a CO_2 atmosphere were carried out separately. The photocatalysis was performed under a solid–solid (solvent-free) condition in order to eliminate the influence of the solvent, since it has been reported that the addition of a solvent to a solid–solid system causes changes in product selectivity and reactivity [10,11]. A solvent, however, is necessary for sonochemical effects. Thus, the effects of additional water on the reactivity and product selectivity were important. On the other hand, sonolysis in a CO_2 atmosphere is difficult [8]. A suitable matrix gas is needed.

2. Experimental

2.1. Photocatalysis

Commercial TiO_2 powders (P-25; anatase-rich, fine particles and specific surface area of 48.7 m^2/g, Nippon Aerosil;

---

* Corresponding author. Tel.: +81-42-591-7462; fax: +81-42-591-8181.
E-mail address: harada@chem.meisei-u.ac.jp (H. Harada).

1010-6030/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S1010-6030(03)00214-4

rutile-rich and specific surface area of 1.9 m^2/g, Soekawa Chemicals) were used as photocatalysts. A platinum-loaded titanium oxide (Pt/TiO_2) was prepared by mixing 5% Pt black (N E Chemcat) in an agate mortar. In the case of a suspension system, a Pyrex glass bulb (250–350 cm^3) containing the powdered photocatalyst suspended in a reactant solution (90–120 cm^3) was used as a reactor. In the case of a solid–solid photocatalytic reaction system, on the other hand, the powdered photocatalyst was mixed with powdered reactants in an agate mortar. The Pyrex reactor containing the reactant mixture or solution was irradiated from the bottom with an ultra high pressure Hg lamp (Toshiba, SHL100-UV-Q2, 100 W). Before irradiation, the reactor was filled with gases of atmospheric pressure.

2.2. Sonolysis

A Pyrex glass bulb (250–350 cm^3) containing CO_2 dissolved in distilled water (40–100 cm^3) was used as a reactor. Distilled water (Wako for HPLC) was purged with argon gas in order to expel air before the addition of CO_2. After the desired amount of CO_2 had been introduced into the reactor through a needle, ultrasonic irradiation was performed from the bottom of the reactor using a 200 W ultrasonic generator (Kaijo TA-4021-4611, 200 kHz). During sonication, the reactor was placed in a temperature-controlled bath (EYELA NTT-1200 and ECS-0).

2.3. Sonophotocatalysis

Simultaneous irradiation was performed from one side of the reactor using a 500 W xenon lamp (Ushio UXL500D-O) and from the bottom of the reactor using a 200 W ultrasonic generator in a CO_2–Ar atmosphere at 25 °C. The Pyrex reactor (300–1250 cm^3) was placed in a Pyrex bath with a temperature controller during the reaction. Atmospheric gases were introduced using the above described technique.

2.4. Analysis

The amount of evolved gases and remaining CO_2 were determined by gas chromatography (Shimadzu GC8AIT equipped with Molecular Sieve 5A and Porapak Q columns). Hydrogen peroxide in the reaction solution was analyzed by colorimetry (JASCO V-530, 407 nm) using a titanium sulfate solution (Nacalai Tesque).

3. Results and discussion

3.1. Photocatalytic reactions in a CO_2 atmosphere using a Pt/TiO_2 photocatalyst

Before using the combined system, photocatalysis in a CO_2 atmosphere was carried out. The selection of atmospheric gas is important for photocatalysis. There have been many reports on photocatalytic reactions but few reports on photocatalytic reactions in a CO_2 atmosphere [12–15]. The influence of CO_2 in the atmosphere on the photocatalytic reaction was examined in this section. Photocatalysis of water in a pure CO_2 atmosphere was carried out, but no appreciable products could be obtained.

Table 1
Solid–solid photocatalytic reaction products from malonic acid (2 h irradiation)

Atmosphere	Product (μmol)		
	CH_4	CO_2	H_2
CO_2	44	–	4
Ar	24	127	2
O_2	1	364	–
Air	–	195	–

Table 1 shows the effects for the influence of atmospheric gas on photocatalytic reaction products obtained from the reaction mixture. Methane (CH_4) was produced from malonic acid ($CH_2(COOH)_2$) in a CO_2 atmosphere by a solid–solid photocatalytic reaction:

$$CH_2(COOH)_2 \rightarrow CH_4 + 2CO_2 \qquad (1)$$

$$CH_2(COOH)_2 \rightarrow CH_3COOH + CO_2 \qquad (1a)$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad (1b)$$

It has been reported that CH_4 is the characteristic product obtained from malonic acid by a solid–solid photocatalytic reaction in an Ar atmosphere [10,11]. As shown in the above equations, it is presumed that mono-decarboxylation occurs in the first stage and that this is followed by decarboxylation of the product, acetic acid. The observation of an induction period before the production of CH_4 production supports this sequential reaction mechanism. The ratio of CH_4 to CO_2 after 24 h of irradiation was almost 0.5, which is consistent with the reaction stoichiometry [16]. Although the mechanism remains unclear, the yield of CH_4 in a CO_2 atmosphere was greater than that in an Ar atmosphere. It was thought that CO_2 is adsorbed on the surfaces of TiO_2 particles, resulting in modification of their surface properties.

The rate of CH_4 production decreased suddenly when a small amount of water was added to the system. Only a very small amount of CH_4 was detected in a solid–liquid system (suspension).

CO_2 was obtained together with CH_4 in an Ar atmosphere, while it was difficult to determine the amount of evolved CO_2 in a CO_2 atmosphere. In an O_2 atmosphere, only CO_2 was obtained as a major product; production of CH_4 was not observed. As shown in the equation below, oxidation of malonic acid occurred to produce only CO_2. Similar behavior was observed in air.

$$CH_2(COOH)_2 + 2O_2 \rightarrow 3CO_2 + 2H_2O \qquad (2)$$

Production of H_2 by photocatalysis in a CO_2 or Ar atmosphere using oxalic acid and 2-propanol as reactants and

Table 2

H_2 production from oxalic acid and 2-propanol by photocatalysis (2 h irradiation)

Reactant	Atmosphere	Product (μmol)	
		H_2	CO_2
$(COOH)_2$	CO_2	154	–
	Ar	129	362
$(CH_3)_2CHOH$	CO_2	576	–
	Ar	511	–

Pt/TiO_2 as a photocatalyst was also examined. As shown in Table 2, H_2 was produced by the photocatalytic reaction in not only an Ar atmosphere but also in a CO_2 atmosphere. The photocatalytic reactions proceeded smoothly in a CO_2 atmosphere. No gaseous products other than H_2 and CO_2 were detected. Thus, CO_2 did not react with H_2

$$(COOH)_2 \rightarrow H_2 + 2CO_2 \quad (3)$$

$$(CH_3)_2CHOH \rightarrow H_2 + (CH_3)_2CO \quad (4)$$

3.2. Reduction of CO_2 by sonication

It has been reported that the sonochemical reduction of CO_2 in water was accelerated at an optimal concentration of CO_2 in an Ar matrix [8,9], but in a CO_2 atmosphere, unfortunately, no sonochemical products were detected. This is attributed to restrained cavitation by dissolved CO_2. Cavitation is the process in which micro-bubbles are formed in a liquid during the rarefaction cycle of an acoustic wave and then undergo violent collapse during the compression cycle of the wave [17]. Henglein [18] reported that chemical effects caused by the collapse of bubbles were generally confirmed only in the presence of a mono- or diatomic gas.

In order to perform the sonolysis of CO_2, this gas was mixed with a matrix gas (Ar). Then sonolysis was carried out in a CO_2–Ar atmosphere. Fig. 1 shows sonolytical products obtained from water in a 5% CO_2–Ar atmosphere. Hydrogen peroxide (111 μmol) and CO (114 μmol) were the major products, and the amount of these two products were similar. Small amounts of hydrogen (11 μmol) and O_2 (16 μmol) were also detected as minor products. In this experiment, 240 μmol of CO_2, which was almost twice larger than the molar amount of CO produced, disappeared from the gas phase. This difference might be caused by the difference in solubility of CO and that of CO_2 in water; CO_2 is much more soluble than CO. Fig. 2 shows time dependencies of CO_2 reduction. It is clear that CO increased with decrease in CO_2. Thus, reduction of CO_2 proceeded sonochemically to produce CO along with H_2O_2 liberation.

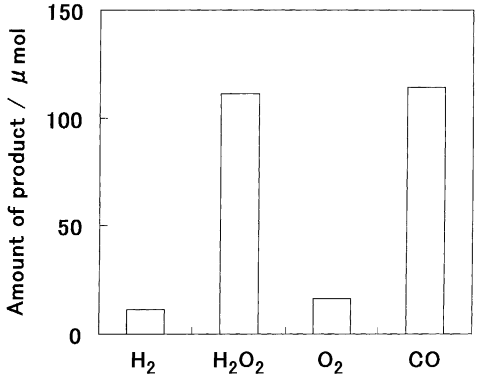

Fig. 1. Sonolytical products from water in a CO_2–Ar atmosphere; ultrasound, 200 kHz, 200 W; temperature, 25 °C; CO_2 concentration, 5% (440 μmol); H_2O, 100 cm^3; reaction time, 2 h.

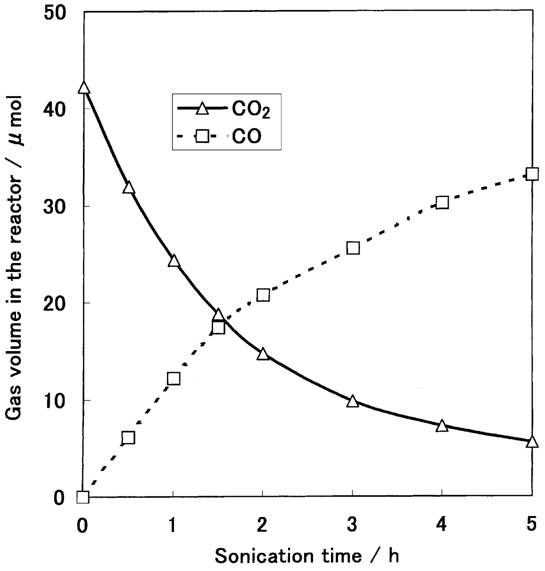

Fig. 2. Consumption of CO_2 and production of CO in a CO_2–Ar atmosphere under sonication; ultrasound, 200 kHz, 200 W; temperature, 25 °C; CO_2 concentration, 0.4% (44 μmol); H_2O, 40 cm^3.

Hydrogen peroxide and H_2 were also obtained from water in an Ar atmosphere by sonication, as shown in the following reaction equations [2,19]. As shown in Fig. 3, the amounts of these two products were similar in the absence of CO_2.

$$2H_2O \rightarrow H_2 + H_2O_2 \quad (5)$$

$$H_2O \rightarrow H^\bullet + OH^\bullet \quad (5a)$$

$$2H^\bullet \rightarrow H_2 \quad (5b)$$

$$2OH^\bullet \rightarrow H_2O_2 \quad (5c)$$

In the presence of CO_2, as described above, the H_2 yield was reduced and CO was liberated, while the H_2O_2 yield did not decrease. Reduction of CO_2 by H_2 and/or $H^\bullet$ radicals might occur during the sonolysis, as shown below:

$$CO_2 + H_2 \rightarrow CO + H_2O \quad (6)$$

$$CO_2 + H^\bullet \rightarrow CO + OH^\bullet \quad (7)$$

$$2OH^\bullet \rightarrow H_2O_2 \quad (7a)$$

$$H^\bullet + OH^\bullet \rightarrow H_2O \quad (7b)$$

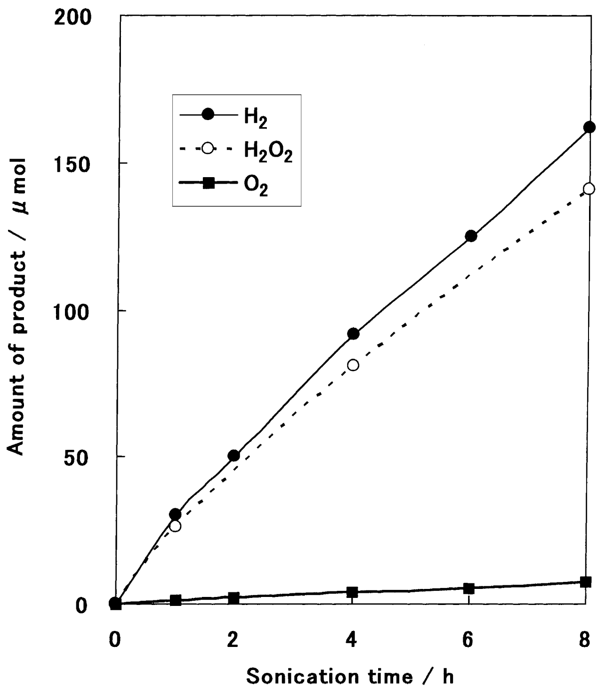

Fig. 3. Sonolytical products from water in an Ar atmosphere; ultrasound, 200 kHz, 200 W; temperature, 25 °C; H_2O, 100 cm^3.

To determine whether H_2 participates in the CO_2 reduction (Eq. (6)), sonolysis of CO_2 in the presence of H_2 from the beginning was carried out. Fig. 4 shows the results. A decrease in CO_2 with an increase in CO was observed as observed in the absence of H_2 in the beginning, but negligible H_2 was consumed. Although the solubility of H_2 is low, an appreciable amount of H_2 is dissolved in water from the beginning of the reaction and there seems to be no enhancement of CO production. Therefore, $H^\bullet$ produced from water by sonication would be used in the process of CO_2 reduction. The effect of H_2 will be discussed again in the following section.

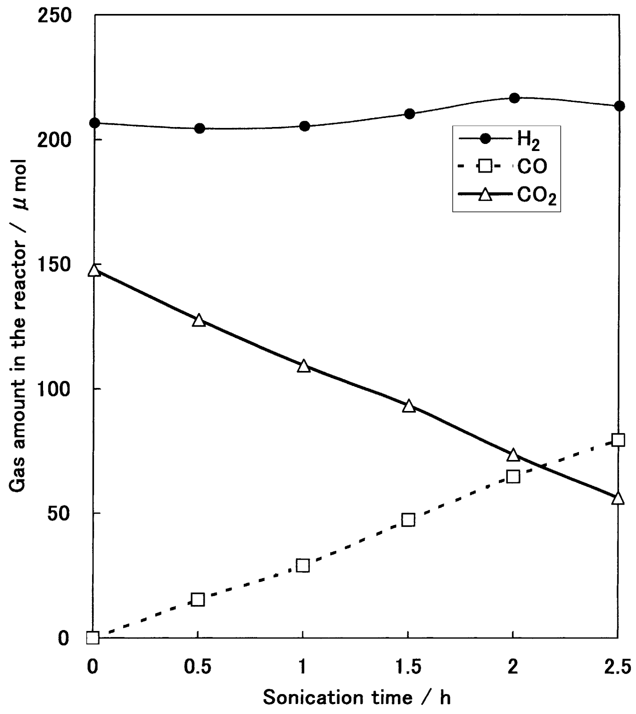

Fig. 4. Effect of H_2 in the reactor on the sonolytical reaction of CO_2; ultrasound, 200 kHz, 200 W; temperature, 25 °C; H_2O, 40 cm^3; atmosphere, H_2–CO_2–Ar, CO_2 concentration, 2% (220 μmol) and H_2 concentration, 2% (220 μmol).

As another possible reaction pathway of CO_2 reduction during sonication, Henglein [9] suggested direct deoxygenation of CO_2 into CO via following the reaction and also suggested that reaction (8b) is the main process

$$CO_2 \rightarrow CO + O \tag{8}$$

$$2O \rightarrow O_2 \tag{8a}$$

or

$$2H^\bullet + O \rightarrow H_2O \tag{8b}$$

($H^\bullet$ liberated from H_2O by sonication). In both reaction pathways (Eqs. (7) and (8)), CO_2 is deoxygenated into CO and the production of H_2 is suppressed. Since, as Fig. 1 shows, only a small amount of O_2 was produced along with the CO_2 reduction, the O_2 evolution reaction, Eq. (8a), seems to be a minor pathway even if reaction (8) proceeds.

The effect of concentration of CO_2 in the atmosphere on the rate of sonolysis is shown in Fig. 5. As mentioned above, sonolysis did not proceed in a pure CO_2 atmosphere but did proceed in a CO_2–Ar atmosphere. It was found that the rate of CO liberation was almost proportional to the CO_2 concentration up to 3%. The yield of H_2 decreased with increase in CO_2 concentration, as reasonably interpreted by the consumption of its precursor, $H^\bullet$, by CO_2. The maximum rate

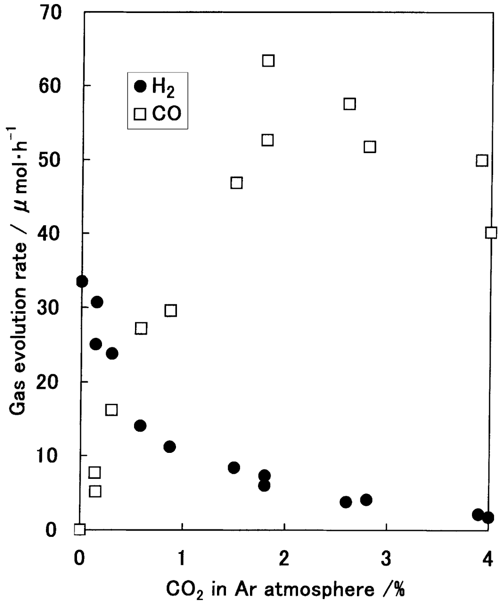

Fig. 5. Effects of CO_2 concentration on the production rates of CO and H_2 in a CO_2–Ar atmosphere under sonication; ultrasound, 200 kHz, 200 W; temperature, 25 °C; H_2O, 40 cm^3.

of CO evolution was obtained in an atmosphere containing 2–3% CO_2 in Ar as was found in our previous study [8].

3.3. Combined system for CO_2 reduction and H_2O oxidation

Sonophotocatalysis was carried out to obtain O_2 from water. The combined reaction system was used since overall water splitting could not be achieved by only photocatalysis or sonolysis. This combined system consisted of sonochemical and photocatalytic reactions. In the case of water splitting, sonolysis and photocatalysis proceed simultaneously as shown by the following reaction equations [2]:

$$\text{Sonochemical reaction}: \quad 4H_2O \rightarrow 2H_2 + 2H_2O_2 \tag{9}$$

$$\text{Photocatalytic reaction}: \quad 2H_2O_2 \rightarrow O_2 + 2H_2O \tag{10}$$

Totally, water is decomposed into H_2 and O_2 stoichiometrically and continuously. In other words, overall water splitting was achieved using sonophotocatalysis [2].

According to the conclusion given in Section 3.2, hydrogen is consumed through the CO_2 reduction process when CO_2 is present in the reaction solution. Thus, it is expected that O_2 would remain liberated and that CO_2 would be deoxygenated in the reactor in a CO_2–Ar atmosphere in the combined sonophotocatalytic reaction system. As mentioned above, 2–3% CO_2 in the atmosphere was found to be the optimal concentration of CO_2 for its reduction. Since an appreciable amount of CO_2 is dissolved in water before and during irradiation, the amount of CO_2 in the gas phase was less than the amount of introduced CO_2. It was confirmed by gas chromatography that the introduction of 3.5% CO_2 gave that there was 2.8% CO_2 in the gas phase of the reactor used in the following experiments.

Fig. 6 shows the products obtained from water in a 3.5% CO_2–Ar atmosphere under the condition of simultaneous irradiation of sonic waves and light in the presence of a TiO_2 photocatalyst. Carbon monoxide and O_2 were the major products. The reaction of this sonophotocatalysis of water in a CO_2–Ar atmosphere is formally shown below:

$$\text{Sonolysis of } H_2O: \quad 4H_2O \rightarrow 2H_2 + 2H_2O_2 \tag{9}$$

$$\text{Photocatalysis of } H_2O_2: \quad 2H_2O_2 \rightarrow O_2 + 2H_2O \tag{10}$$

$$\text{Sonolysis of } CO_2: \quad 2CO_2 + 2H_2 \rightarrow 2CO + 2H_2O \tag{11}$$

$$\text{Total reaction}: \quad 2CO_2 \rightarrow 2CO + O_2 \tag{12}$$

Coincidence of the amounts of liberated CO and consumed CO_2 (ca. 1500 μmol) is consistent with reaction (12). Stoichiometry of reaction (12) also predicts that the amount of O_2 produced is half that of CO. Taking into account the fact that H_2 was detected and that a half molar amount of O_2 is attributed to this side reaction ($2H_2O \rightarrow 2H_2 + O_2$) ca. 800 μmol of O_2 was expected. However, the actual amount of O_2 detected was ca. 700 μmol, and the reason for this shortage is not known at present.

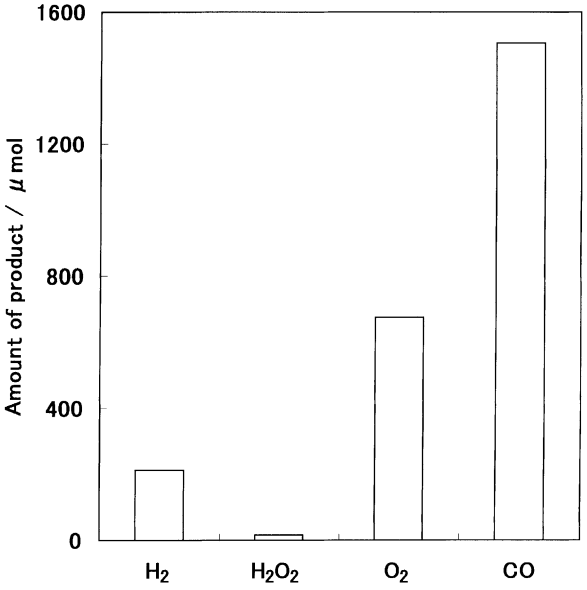

Fig. 6. Sonophotocatalytic products from water in a CO_2–Ar atmosphere; ultrasound, 200 kHz, 200 W; light illumination, 500 W Xe; photocatalyst, TiO_2 (Soekawa), 200 mg; 500 W Xe; temperature, 25 °C; CO_2 concentration, 3.5% (1780 μmol); H_2O, 40 cm^3; reaction time, 20 h.

Table 3 shows the products obtained from sonophotocatalytic reactions at various concentrations of CO_2 in an Ar matrix. In all cases except for 20% of CO_2, CO_2 was reduced into CO selectively, while, again, the O_2 yields were a little smaller than those expected from reaction (12). The negligible reaction products in 20% CO_2 atmosphere are attributed to the absence of cavitation as described in the previous section. At a low concentration (0.5%) of CO_2 in an Ar matrix, almost all of the CO_2 in the reactor was deoxygenated to CO within 3 h. The ratio of evolved H_2 to O_2, about 2.0, suggested preferential overall water splitting because of the low CO_2 concentration.

As shown in Fig. 5, ca. 1 and 5% of CO_2 are the middle points of the increasing and decreasing slopes of the CO evolution curve, respectively. Satisfactory results were obtained in those conditions. In the case of 0.9% CO_2, a better result was obtained for H_2 evolution since, as shown in Table 3, the lower CO_2 concentration gave a higher yield of H_2. The evolution of H_2 would be important for the next step of the system.

Table 3
Sonophotocatalytic reaction products from water under various concentration of CO_2

Atmosphere (% of CO_2 in Ar matrix)	Reaction time (h)	Product (μmol)				Reduced CO_2 (μmol)
		H_2	H_2O_2	O_2	CO	
20	21	Trace	3	–	–	–
5	17	160	74	216	392	417
0.9	20	623	16	430	437	446
0.5	3	88	10	43	39	44

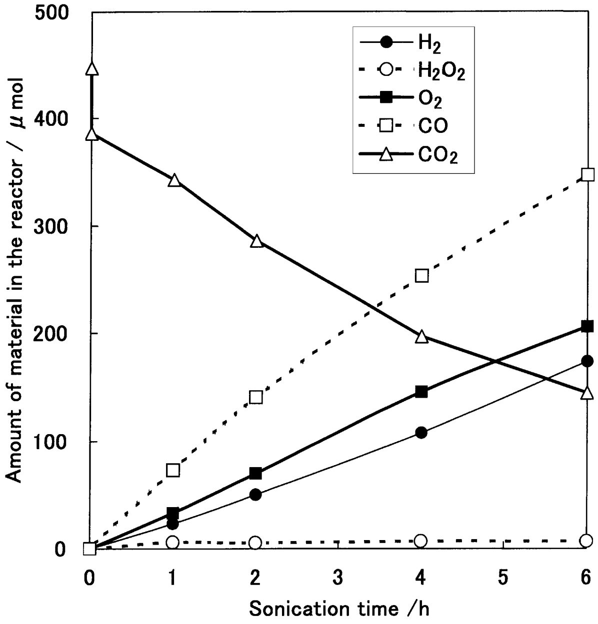

Fig. 7. Sonophotocatalysis of water in a CO_2–Ar atmosphere; ultrasound, 200 kHz, 200 W; light illumination, 500 W Xe; photocatalyst, TiO_2 (Soekawa), 200 mg; temperature, 25 °C; CO_2 concentration, 0.9% (440 μmol); H_2O, 100 cm^3.

The time dependence of the composition of the reactant and products in the reactor during simultaneous irradiation was examined. Fig. 7 shows the results for a 0.9% CO_2–Ar atmosphere. CO_2 decreased with an almost linear increase in CO, and O_2 and H_2 were observed with the decrease in CO_2. A small amount of H_2O_2 was also detected. These facts suggest that the rates of photocatalytic reactions are faster than that of sonolysis, since in the present sonophotocatalytic reaction, photocatalytic reactions proceed with the products, $H^\bullet$ and H_2O_2, of sonolysis.

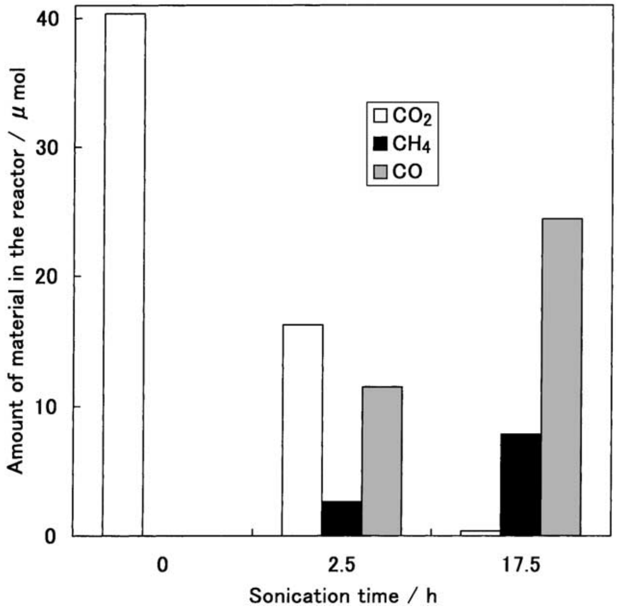

Fig. 8. CH_4 production in a CO_2–H_2 atmosphere under sonication; ultrasound, 200 kHz, 200 W; temperature, 25 °C; CO_2 concentration, 0.3% (44 μmol); H_2O, 40 cm^3.

As a further extension, production of methane (CH_4) as well as CO from CO_2 was investigated. As shown in Fig. 8, in an H_2 matrix, CH_4 was produced during the sonolysis of CO_2, and the yield increased with sonication time. As shown in Fig. 4, CH_4 was negligibly liberated when the concentration of H_2 was lower (2%). A combination of this CH_4 production from CO_2 with photocatalysis to yield O_2, which resembles photosynthesis, is now being investigated.

4. Conclusions

A solid–solid photocatalytic reaction of malonic acid to give CH_4 was found to be accelerated in a CO_2 atmosphere. Although photocatalysis alone could not split water into H_2 and O_2, a combined system of photocatalysis and sonolysis could drive water splitting. Similarly, CO_2 was negligibly reduced by photocatalysis, while it was reduced by sonolysis. By a combination of photocatalysis and sonolysis, we could perform the overall CO_2 deoxygenation into CO and O_2.

Acknowledgements

The authors greatly thank Prof. B. Ohtani (Hokkaido University, Sapporo, Japan) for his kind suggestions and comments. The authors are grateful to Nippon Aerosil Co. Ltd. for supplying P-25.

References

[1] A. Fujishima, K. Hashimoto, T. Watanabe, TiO_2 Photocatalysis—Fundamentals and Applications, BKC Inc., 1999, p. 146.
[2] H. Harada, Ultrason. Sonochem. 8 (2001) 55;
H. Harada, Int. J. Hydrogen Energy 26 (2001) 303.
[3] T.J. Mason, in: G.J. Price (Ed.), Current Trends and Future Prospects in Current Trends in Sonochemistry, The Royal Society of Chemistry, Cambridge, 1992, p. 171.
[4] K. Sawada, K. Hirano, Mizushori-Gijutsu 39 (1998) 9 (in Japanese).
[5] Y. Kado, M. Atobe, T. Nonaka, Denki Kagaku (Electrochemistry) 66 (1998) 760;
Y. Kado, M. Atobe, T. Nonaka, Ultrason. Sonochem. 8 (2001) 69.
[6] Y. Suzuki, Warsito, H. Arakawa, A. Maezawa, S. Uchida, Int. J. Photoenergy 1 (1999) 1;
Y. Suzuki, A. Maezawa, S. Uchida, Jpn. J. Appl. Phys. 39 (5B) (1998) 2958.
[7] V. Ragaini, E. Selli, C.L. Bianchi, C. Pirola, Ultrason. Sonochem. 8 (2001) 247.
[8] H. Harada, Ultrason. Sonochem. 5 (1998) 73.
[9] A. Henglein, Z. Naturgorsch. B 40 (1985) 100.
[10] O. Ishitani, T. Inoue, K. Suzuki, T. Ibusuki, J. Photochem. Photobiol. A 72 (1993) 269.
[11] Z. Goren, I. Willner, A.J. Nelson, A.J. Frank, J. Phys. Chem. 94 (1990) 3784.

[12] B. Aurian-Blajeni, M. Halmann, J. Manassen, Solar Energy 25 (1980) 165.
[13] I. Inoue, A. Fujishima, S. Konishi, K. Honda, Nature 277 (1979) 673.
[14] H. Harada, T. Naoi, Nippon Kagaku Kaishi (J. Chem. Soc. Jpn., Chem.) 1996 (1996) 1064 (in Japanese).
[15] H. Harada, K. Suda, Denki Kagaku (Electrochemistry) 70 (2002) 435.
[16] H. Harada, Res. Bull. Meisei Univ. 30 (1994) 21 (in Japanese).
[17] J. Lindley, Sonochemistry, in: T.J. Mason (Ed.), The Royal Society of Chemistry, Cambridge, 1991, Chapter 8, p. 102.
[18] A. Henglein, Ultrasonics 25 (1987) 6.
[19] E.L. Mead, R.G. Sutherland, R.E. Verall, Can. J. Chem. 54 (1976) 1114.