Hydrogen formation by the photodecomposition of water over Pt/TiO_2 suspended in a water in oil emulsion

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Received 4 November 1999; accepted 19 April 2000

Hydrogen formation by the photodecomposition of water has been successfully achieved in a water in oil emulsion (w/o emulsion) system containing Pt/TiO_2. The hydrogen formation rate was affected by the amount of water added to the emulsion. It was concluded that water in the w/o emulsion containing Pt/TiO_2 was more active than free water for the photodecomposition to form hydrogen.

Keywords: w/o emulsion, photolysis, water decomposition, Pt/TiO_2

1. Introduction

In the last few decades, the photocatalytic decomposition of water and the formation of hydrogen/oxygen have been studied extensively over various semiconductors. Among these, TiO_2 is the most commonly used catalyst due to its high activity for the decomposition of water and high stability against photocorrosion under UV irradiation in liquid water. The presence of group VIII transition metals is required to bring about hydrogen evolution and Pt is usually selected for this purpose. However, when Pt/TiO_2 catalyst was simply suspended in pure liquid water, the rate of water decomposition was very slow [1]. To improve the efficiency of water decomposition over metal/TiO_2 catalysts, various efforts have been made. Yamaguchi and Sato reported that the stoichiometric decomposition of water vapor into H_2 and O_2 occurred over NaOH-coated Rh/TiO_2 and Pd/TiO_2 catalysts [2]. But, when the water-vapor pressure exceeded about 21 Torr (saturated vapor pressure at the reaction temperature), photolysis became very slow because of the formation of a liquid water layer on the catalyst surface. Sayama and Arakawa reported that addition of carbonate salts to Pt-loaded TiO_2 led to highly efficient stoichiometric photocatalytic decomposition of liquid water [3]. They concluded that the backward reaction of water decomposition was suppressed by covering both Pt and TiO_2 surfaces with carbonate species. In both cases, separation of the catalyst surface from bulk-liquid water or rapid desorption of oxygen from the catalyst surface was considered to be important.

In this letter, we propose a new system for the photodecomposition of water over Pt/TiO_2 catalysts by using a w/o emulsion. When Pt/TiO_2 powder is suspended in a w/o emulsion composed of a small amount of water, oil and surfactant, the Pt/TiO_2 particles will be encapsulated into the colloidal particles because of their hydrophilic property, and will consequently be separated from the bulk water if the amount of water added is little enough. If too much water is added, the suspension may show poor dispersion stability of Pt/TiO_2 [4]. The photocatalytic reactions in such w/o emulsions have been reported already. Zang and Shen have investigated successful photoreduction of methyl yellow in a w/o microemulsion system composed of AOT/isooctane [5]. Shiojiri et al. investigated photocatalytic oxidation of cyclohexane on TiO_2 ultra-fine particles formed in AOT/cyclohexane reverse micelles [6]. Meyer et al. reported hydrogen formation from the photoreduction of water on Pt/CdS particles in AOT/isooctane reversed micelles with sacrificial agent [7]. But the effects of the micelle formation and the surfactant properties for the photodecomposition of water have not been clarified yet. In this letter, the water decomposition rates in various w/o emulsion systems containing Pt/TiO_2 were quantitatively compared with that in the pure water system. In addition, the effects of the amount of water addition as well as the decomposition of surfactants upon the rate of hydrogen formation were discussed in depth.

2. Experimental

The TiO_2 powder employed in this study was obtained from Japan Aerosil (anatase, P-25). 0.5 wt% Pt/TiO_2 was prepared with a conventional impregnation method by using a H_2PtCl_6 aqueous solution. The catalyst powder was pre-reduced by 200 Torr of H_2 at 573 K for 6 h before being dispersed into a w/o emulsion. The w/o emulsion was composed of sodium bis-ethylhexylsulfosuccinate (supplied by Nikko Chemicals, OTP-100S) as an anionic surfactant or polyoxyethylene nonylphenyl ether (supplied by Lion, NP-6) as a nonionic surfactant and cyclohexane as a solvent. The surfactant, OTP-100S, is the same anionic surfactant known as AOT, but is a special high purity grade, containing less than 1% of water and no methanol which

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may act as a sacrificial reagent for photoreaction. The OTP-100S was further dried in a desiccator before use. The cyclohexane was also dried with molecular sieve 5A before the reaction measurement.

The photolysis was carried out in a Pyrex glass reactor connected to a vacuum line and an on-line TCD gas chromatograph. Water was added to the emulsion before mixing with the Pt/TiO_2 powder (method 1), or after mixing with the powder and irradiating for a few hours (method 2). 0.2 g of the catalyst powder was suspended in 140 ml of AOT/cyclohexane solution with a concentration of 100 mmol/l. The ratio of water to the surfactant (R_w value) was controlled by changing the amount of added water. Before irradiation, the suspension was deaerated by freezing with liquid nitrogen. The light source was a 450 W high-pressure Hg lamp (Ushio, UM-452), which was filtered through a water jacket to cool the reactor during irradiation. The gas products were analyzed by TCD gas chromatography with a MS-13X column. The SO_4^{2-} ion contained in the emulsion was supersonically extracted into pure water and separated before quantitative measurement by ion chromatography.

3. Results and discussion

The dispersion stability of Pt/TiO_2 was strongly affected by the amount of added surfactant. If no surfactant was added to the suspension, the Pt/TiO_2 particles settled immediately at the bottom of the reactor. When a certain amount of surfactant was added to the suspension, the dispersion was stable for more than 24 h. The quantitative measurement of the dispersion stability was difficult because of low concentration of solid. From eye measurements, the sample showed enough dispersion with the concentration of surfactant above 100 mmol/l.

Figure 1 shows the time courses of the formation of hydrogen under irradiation from the emulsion of Pt/TiO_2 in the OTP-100S/cyclohexane system. The gaseous products detected by TCD were hydrogen and a small amount of CO. Oxygen evolution was not observed in all the cases in this study. Shiojiri et al. reported that, cyclohexanol and cyclohexanone were formed by the photooxidation of cyclohexane on TiO_2 dispersed in AOT/cyclohexane when oxygen was present in the gas phase [6]. In the absence of oxygen, H_2 and CO were formed slowly by the reduction of water and the decarbonylation of organic compounds, respectively. In our study, ^{1}H-NMR measurement of the emulsion after the photodecomposition of water revealed the formation of a small amount of cyclohexanol. Accordingly, it is reasonable to suppose that the oxidation of cyclohexane may take place simultaneously with the reduction of water in our study. As shown in figure 1, even without addition of water to the emulsion in the first 3 h period, hydrogen was evolved by the irradiation of the emulsion with the initial rate of 43 μmol/h, but the rate dropped to almost zero after 3 h of irradiation. At that time, 2.3 g of

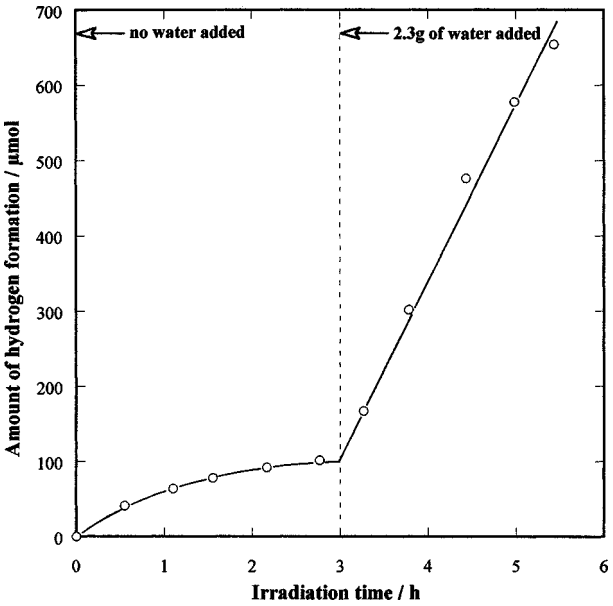

Figure 1. Effect of water addition on hydrogen formation.

pure water were added. Then the rate of hydrogen formation increased drastically up to 261 μmol/h, which remained almost constant during additional 3 h. Under the dark reaction, no hydrogen was formed during the prolonged reaction period. These results indicate that, in our w/o emulsion system, the hydrogen formation can occur from the photodecomposition of water. It is also reasonable to suppose that the formation of hydrogen before water addition may be due to the water originally remaining in the reagents, and not from the decomposition of surfactant or solvent. When D_2O was added to the solution of OTP-100S and cyclohexane instead of H_2O, the products were dominated by D_2. Since the amount of H_2 formed was very small compared to D_2, most of the hydrogen evolved came from water decomposition.

Figure 2 shows the dependence of the rate of the formation of hydrogen upon the ratio of water to surfactant (R_w). The R_w was adjusted by two different procedures as described in section 2. When water was added to the emulsion before mixing with Pt/TiO_2 (method 1), the formation rate of hydrogen was increased to a maximum at around $R_w = 3$–5 and then slightly decreased with increasing R_w value. The highest value of the hydrogen formation rate was 117 μmol/h at $R_w = 5.7$. It is thought that the slow formation rate in the region of R_w less than 2 may be caused by a capture of water in the micelles which does not contain any Pt/TiO_2 particles, and the adsorption of water to the Pt/TiO_2 surface would be suppressed. The decreasing of the formation rate in the range of R_w larger than 8 may be resulted from a change in the structure of water. Jain et al. reported that in the water/AOT/isooctane system, one surfactant molecule could be hydrated with a maximum extent of five molecules of water [8]. From the result of FT-IR measurements, they proposed the existence of three different types of water in the microemulsion: bound water, trapped water and free water. The trapped wa-

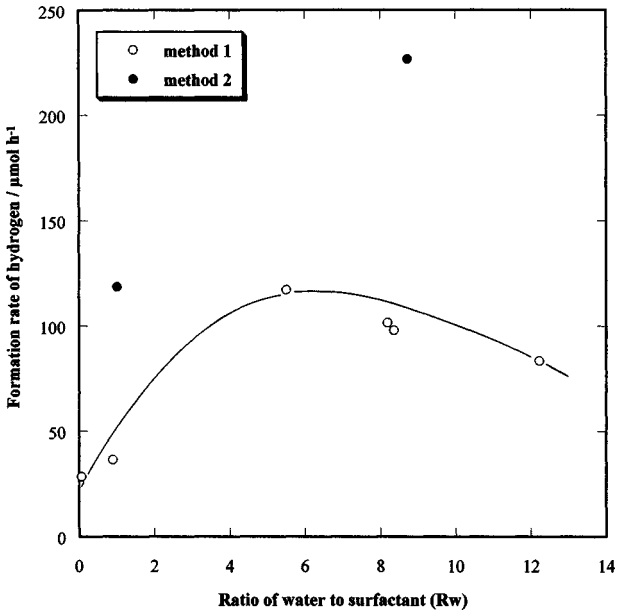

Figure 2. Effect of the ratio of water to surfactant on the hydrogen formation rate.

Table 1
The rate of H_2 and CO formation from various dispersion systems.

Surfactant	Solvent	Formation rate (μmol/h)	
		H_2	CO
–	Water	22	–
–	Cyclohexane	64	–
OTP-100S	Cyclohexane	90	11
NP-6	Cyclohexane	545	51

ter and bound water were thought to be the water hydrated to AOT molecules. Accordingly it is reasonable to suppose that free water was also formed in our study when the R_w was increased more than 5, and the decrease in the rate of hydrogen formation at around $R_w = 5$ might have been caused by the formation of free water. It is worth noticing that the hydrogen formation rate by the irradiation of Pt/TiO_2 suspension in the pure water was 22 μmol/h, as shown in table 1, which is about five times smaller than that from Pt/TiO_2 in w/o emulsion. From these experimental results, it is concluded that water hydrated to the surfactant is more reactive than free water for hydrogen formation. In table 1, the hydrogen formation rate from a w/o emulsion composed of nonionic surfactant (NP-6) was also shown, which was about six times higher than that from the emulsion composed of OTP-100S as a surfactant. In the literature has been reported that a surface of TiO_2 is charged cationically under UV irradiation. Accordingly it is reasonable to suppose that stronger interaction between surfactant and cationic surface of TiO_2 may suppress the decomposition of water in the case of anionic OTP-100S surfactant.

When water was added to the emulsion, which was already mixed with the Pt/TiO_2 and irradiated for few hours (method 2), the rate of hydrogen formation was higher than

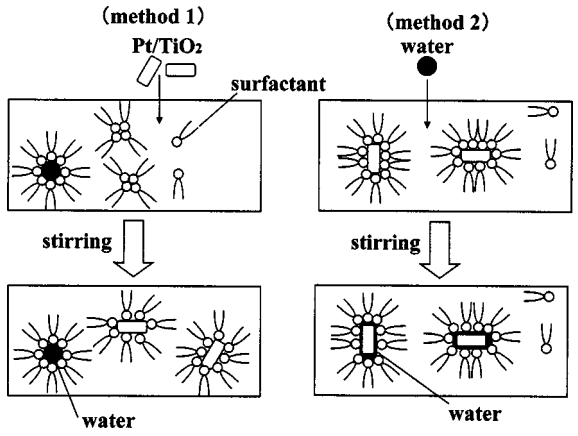

Figure 3. Schematic diagram of water adsorption onto Pt/TiO_2 in w/o emulsion.

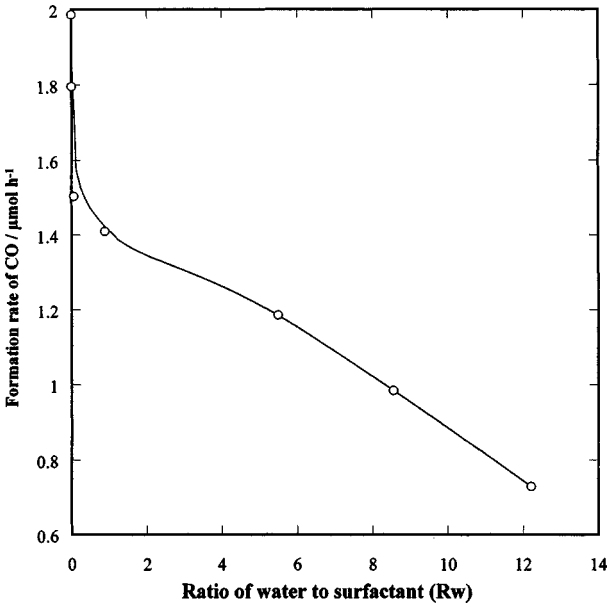

Figure 4. Change in CO formation with the ratio of water to surfactant.

the rate of method 1, as plotted by closed circles in figure 2. The schematic diagrams of adsorption of water and surfactant on the catalyst surface in methods 1 and 2 are shown in figure 3. When the emulsion is mixed with the Pt/TiO_2 powder before addition of water, the surfactants are fully adsorbed to the Pt/TiO_2 surface, and the amount of water contributing to hydrogen formation may increase. The hydrogen formation rate during the experiment by method 2 was 227 μmol/h at $R_w = 8$.

Figure 4 demonstrates the effect of R_w value on the formation rate of CO during irradiation, which decreased considerably with the increase in value of R_w. It is considered that at low R_w values, the surfactant molecules were adsorbed easily onto the surface of the Pt/TiO_2 and decomposed by the irradiation of UV light. Hidaka et al. investigated the photodegradation of various surfactants in aqueous suspensions of TiO_2 [9], and reported the decomposition of dodecylbenzenesulphonate (DBS) into CO_2 under UV irradiation with air. DBS is an anionic surfactant

Table 2
Amounts of CO and SO_4^{2-} formed during water decomposition.[a]

Sample	SO_4^{2-}[b] (μmol)	CO (μmol)	H_2 (μmol)	DLS[c] (nm)
a.r.[d]	68	21	370	400
b.r.[e]	n.d.	–	–	430

[a] Amounts formed during reaction for 10 h.
[b] Determined by ion chromatography.
[c] DLS – dynamic light scattering.
[d] a.r. – after reaction.
[e] b.r. – before reaction, after 24 h mixing under dark condition.

and has a sulfonic acid group as a hydrophobic group similarly to OTP-100S. In our study, the formation of SO_4^{2-} ion was also observed in the suspension used for the reaction by the analysis of ion chromatography as shown in table 2. These results indicate that the decomposition of the surfactant molecules adsorbed onto the catalysts takes place during irradiation with UV. The formation of CO instead of CO_2 was due to the reductive circumstance of our study, differing from the experiments of Hidaka et al. The degree of dispersion of Pt/TiO_2 particles was not so strongly affected by the irradiation during the reaction in spite of the decomposition of the surfactants. From the result of dynamic light-scattering measurements (DLS) as shown in table 2, the sizes of Pt/TiO_2 aggregates suspended in the emulsion were about 430 and 400 nm before and after the reaction, respectively. The amount of SO_4^{2-} formed during irradiation for 10 h was 68 μmol which corresponds to only 0.5% of total surfactant molecules in the suspension. From these results, it is concluded that the decomposition of surfactant is negligible to use the w/o emulsion as a new system of photo-assisted hydrogen production.

4. Conclusions

(1) Hydrogen formation from the photodecomposition of water was successfully achieved in the w/o emulsion system of Pt/TiO_2 in OTP-100S/cyclohexane.

(2) The water in the w/o emulsion was more active than free water for the photodecomposition to form hydrogen.

(3) The hydrogen formation was accelerated much more by the addition of water to the emulsion of surfactant and solvent after mixing with Pt/TiO_2 than before mixing with the catalyst powder.

(4) In the absence of water, the decomposition of OTP-100S took place slowly and small amounts of CO and SO_4^{2-} were formed. The decomposition of the surfactant was suppressed by an addition of water.

Acknowledgement

This work was financially supported by the Ministry of Education, Science, Sports and Culture of Japan through a Grant-in-Aid for Encouragement of Young Scientists (No. 11750678). The authors acknowledge Professor M. Igawa and Dr. H. Okochi for the measurements with the ion chromatograph and also thank Nikko Chemicals for the supply of the OTP-100S.

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