# Stoichiometric photocatalytic decomposition of pure water in $Pt/TiO_2$ aqueous suspension system

S. Tabata [1], H. Nishida, Y. Masaki and K. Tabata

*Research Institute of Innovative Technology for the Earth (RITE),*
*Kizugawadai 9-2, Kizu-cho, Kyoto 619-02, Japan*

Received 2 February 1995; accepted 8 June 1995

The influence of the direction of ultraviolet irradiation upon the yields of the photocatalytic decomposition of pure water has been investigated in $Pt/TiO_2$ aqueous suspension system. The yields of the photocatalytic decomposition irradiated from the top of the reaction cell are about $10^3$ times higher than those irradiated from the bottom. The difference seems due to the reverse reaction of the formed $H_2$ and $O_2$ in the suspension.

**Keywords:** photocatalysis; water decomposition; $Pt/TiO_2$; $Pt/TiO_2$ suspension

## 1. Introduction

$TiO_2$ has been most widely used for the study of photocatalytic decomposition of pure water, because of its high stability against photocorrosion and its favorable band-gap energy. There have been many studies on photocatalytic decomposition of water over Pt-loaded $TiO_2$ catalysts. Sato et al. reported that in a very thin layer of water, which is not in aqueous suspension system, $Pt/TiO_2$ could decompose water stoichiometrically [1–3].

Most of the studies concluded, however, that in aqueous suspension system $Pt/TiO_2$ could not decompose water stoichiometrically [4–7]. Attempts of photocatalytic decomposition of water often resulted in $H_2$ evolution without $O_2$. Furthermore, the rate of $H_2$ evolution decreased rapidly with irradiation time. The only exception is Sayama et al.'s report on photocatalytic water decomposition over $Pt/TiO_2$ in $Na_2CO_3$ aqueous solution [8]. This work attracted considerable attention, and the $Pt/TiO_2$ suspension system has become a candidate for water decomposition catalyst. Till Sayama et al.'s report [8], $Pt/TiO_2$ aqueous suspension system had been believed to be inactive for stoichiometric water decomposition because of reverse reaction caused by hydrogen spillover [3] or its inability to evolve

---

[1] To whom correspondence should be addressed.

oxygen due to the formation of peroxospecies [6]. This hypothesis was also supported by results on $NiO_x/TiO_2$ and $CeO_2/TiO_2$ catalysts that could catalyze water decomposition in NaOH aqueous suspension system [9,10].

We have observed reproducible and stoichiometric decomposition of water over the $Pt/TiO_2$ photocatalyst when the suspension of the photocatalyst was irradiated from the top of the reaction cell with the light of a Hg lamp. In this letter, we will show that the reaction proceeds over a long period in an aqueous suspension of $Pt/TiO_2$ without any electrolyte. We will also show the experimental details for the stoichiometric decomposition of water over the $Pt/TiO_2$ photocatalyst.

## 2. Experimental

$TiO_2$ powder obtained from Degussa (P25, anatase 78%) was used as the support without any pretreatment. Platinum was loaded on the $TiO_2$ powder using the photochemical deposition method. The $TiO_2$ powder (1.0 g) was suspended in 200 cm$^3$ of aqueous solution of methanol (2%) and $H_2PtCl_6$ (0.1 wt% per $TiO_2$). After it had been sufficiently deaerated, the suspension was irradiated with the light of a high-pressure Hg lamp (about 5 mW at 366 nm) for 8 h. Then the suspension was centrifuged (5000 rpm) and washed with pure water. After the centrifugation and pure-water washing had been repeated five times, the sediment was dried and used as the $Pt/TiO_2$ catalyst.

The photocatalytic decomposition of water was carried out in a cylindrical closed reaction cell (60 mm diameter, 50 mm height, 148 cm$^3$ volume) of pyrex. The reactor has neither O-ring seal nor ground-glass joint except a glass greaseless vacuum valve (YOUNG POR6RA, Teflon sealing, glass piston) in order to reduce air leakage and grease contamination (fig. 1). The greaseless valve served as the only port for the introduction of the reactant and carrier gas and the sampling of the product and degassed components. The outer nozzle of the valve was connected

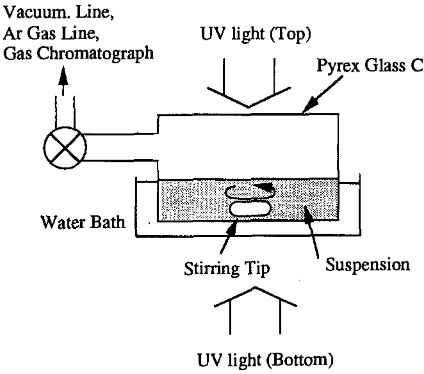

Fig. 1. The closed reaction cell for photocatalytic decomposition of water: 60 mm in diameter, 50 mm in height.

to a pressure gauge, a vacuum line and an Ar line. It was kept vacuum during the reaction to prevent air leaking through the Teflon sealing of the valve into the reaction cell. To reduce the gas evolution from and absorption into the materials in the reaction cell, we used a small stirring tip (5 mm diameter, 15 mm length) for magnetic stirring; the stirring tip was well degassed in vacuum (1 h) and purged by Ar gas (1 h) in advance. With the above precautions, the rate of background $O_2$ evolution was 11 nmol $h^{-1}$ at the start of photoreaction and 1.2 nmol $h^{-1}$ 24 h later.

Pure water, which was treated by $KMnO_4$, deionized, and distilled was used as the reactant. No electrolyte was added to the reactant. After 300 mg of photocatalyst (Pt/TiO$_2$) and 16 cm$^3$ of reactant (pure water) had been introduced to the reaction cell, the aggregated catalyst was dispersed by ultrasound (1 min) and suspended by magnetic stirring (500 rpm). Under this condition, the absorption coefficient of the suspension at ultraviolet rays (350 nm) was 40 $\mu m^{-1}$.

The suspension underwent repeated cycles of Ar introduction to 140 kPa and evacuation to 10 kPa for 1 h for deaeration. Care was taken to prevent the suspension from bubbling and splashing the window for the incident light where the catalyst might react with $H_2O$ vapor. After the reaction cell was filled with 20 kPa of Ar gas, the irradiation was started. The temperature of the reaction cell was controlled to 295 K with a water bath.

The light source was a 250 W high-pressure Hg lamp (USIO, SPOT CURE); the light of the Hg lamp was collected by a mirror and illuminated the suspension from the top or the bottom of the reaction cell. The light was focused into a spot of about 40 mm in diameter to avoid reaction on the side wall of the cell. The photon flux from the Hg lamp was measured by a chemical actinometer in which photodecomposition of $K_3Fe(C_2O_4)_3$ was used. The photon flux was about $1.8 \times 10^{18}$ photons $s^{-1}$ when both Toshiba UV-D35 filter (300–400 nm) and pyrex glass filter were used.

The evolved gases were sampled (9 cm$^3$ at a time) at appropriate intervals and analyzed with a gas chromatograph (Ar carrier, MS5A column, TCD).

## 3. Results and discussion

Fig. 2a shows the evolution of $H_2$ and $O_2$ of four runs of photoreaction as a function of time when the suspension was irradiated with the light of the Hg lamp from the top of the reaction cell. Each run lasted 4–6 h during which gas sampling was carried out. Gas evacuation for 3 min and introduction of Ar gas to 20 kPa were done at intervals, which is indicated by arrows in fig. 2. Even at the first run, both $H_2$ and $O_2$ evolve into the gas phase, though the $O_2$ evolution is smaller than half the $H_2$ evolution ($H_2/O_2 = 2.6$ at 4 h). $CO_2$ was also detected only at the first run (0.06 μmol at 4 h). The shortage of $O_2$ at the first run could be attributed to residual organic compounds which act as sacrificial electron donor. After the second

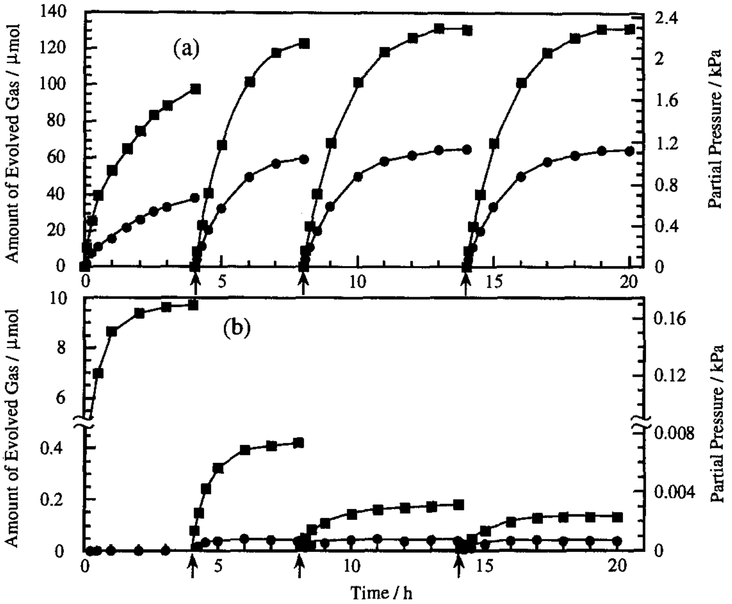

Fig. 2. Evolution of $H_2$ and $O_2$ of four runs of photoreaction as a function of time: (a) the suspension is irradiated from the top of the pyrex cell; (b) the suspension is irradiated from the bottom of the cell. (■) $H_2$, (●) $O_2$. Arrows indicate the gas evacuation and introduction of Ar gas. Light source, 250 W high pressure Hg lamp; catalyst, 0.3 g; pure water, 16 $cm^3$.

run, $H_2$ and $O_2$ evolve stoichiometrically ($H_2/O_2 = 2.1$–$2.0$). Furthermore, photocatalytic activities do not deteriorate after 14 h of reaction. The partial pressures of $H_2$ and $O_2$ increase as a function of time, then saturate. This means that the reverse reaction of $H_2$ and $O_2$ into $H_2O$ over the catalyst also becomes faster, with the time course, then equilibrates with the forward reaction at 5–6 h after the start of the gas accumulation, at which the partial pressures of $H_2$ and $O_2$ are 2.2 kPa and 1.1 kPa, respectively. The average rate of $H_2$ evolution for the initial 5 min of the fourth run is 106 $\mu mol\ h^{-1}$ without filter and 76 $\mu mol\ h^{-1}$ with the filter (TOSHIBA, UVD-35), which means 1.4% of quantum efficiency.

The photocatalytic activity reproduces within about ±10% for four different $Pt/TiO_2$ catalysts supported on P25 of the same lot and another one supported on P25 of a different lot. For all of the five catalysts we observed the stoichiometric evolution of $H_2$ and $O_2$ with the $H_2O_2$ ratio within the range from 2.0 to 2.1 when the suspension was irradiated from the top of the reaction cell.

Fig. 2b shows the evolution of $H_2$ and $O_2$ of four runs of photoreaction as a function of time when the suspension was irradiated with the light of the Hg lamp from the bottom of the reaction cell. With the proceeding of the reaction, the rate of $H_2$ evolution decreases rapidly. This decrease of the $H_2$ evolution rate could be attributed to the consumption of residual organic compounds which act as sacrificial electron donor. The average rate of $H_2$ evolution for the initial 5 min of the fourth run in fig. 2b is 0.12 μmol h$^{-1}$; this is about $10^{-3}$ times smaller than that of top irradiation. Though the evolution of $O_2$ is observed from the second run, the rate does not reach the stoichiometric value ($H_2/O_2 = 3.5$ at the end of the fourth run).

We believe that the difference of photocatalytic activity between the two directions of light irradiation is based on the reverse reaction of $H_2$ and $O_2$. When the suspension is irradiated from the top of the reaction cell, $H_2$ and $O_2$ form near the surface of the suspension. Therefore, the $H_2$ and $O_2$ evolve easily from the surface of the suspension to the gas phase. When the suspension is irradiated from the bottom of the reaction cell, on the contrary, $H_2$ and $O_2$ form far from the surface of the suspension. Therefore, most of the $H_2$ and $O_2$ recombine in the suspension before evolving from the surface of the suspension to the gas phase.

## 4. Conclusion

The results show that the Pt/TiO$_2$ photocatalyst can decompose water stoichiometrically in an aqueous suspension system when the suspension is irradiated with the light of the Hg lamp from the top of the reaction cell.

## Acknowledgement

This research was supported by the NEDO Environmental Catalyst Research Program.

## References

[1] S. Sato and J.M. White, Chem. Phys. Lett. 72 (1980) 83.
[2] T. Kawai and T. Sakata, Chem. Phys. Lett. 72 (1980) 87.
[3] S. Sato, New J. Chem. 12 (1988) 859.
[4] R.S. Magliozzo and A.I. Krasna, Photochem. Photobiol. 38 (1983) 15.
[5] A. Mills and G. Porter, J. Chem. Soc. Faraday Trans. I 78 (1982) 3659.
[6] G. Munuera, A.R. Gonzalez-Elipe, A. Fernandez, P. Malet and J.P. Espinos, J. Chem. Soc. Faraday Trans. I 85 (1989) 1279.
[7] D. Duonghong, E. Borgarello and M. Gratzel, J. Am. Chem. Soc. 103 (1981) 4685.
[8] K. Sayama and H. Arakawa, J. Photochem. Photobiol. A 77 (1994) 243.
[9] A. Kudo, K. Domen, K. Maruya and T. Onishi, Chem. Phys. Lett. 133 (1987) 517.
[10] Y. Sakata, Y. Hirata, K. Miyahara, H. Imamura and S. Tsuchiya, Chem. Lett. (1993) 2381.