

Significant Effect of Carbonate Addition on Stoichiometric Photodecomposition of Liquid Water into Hydrogen and Oxygen from Platinum–Titanium(IV) Oxide Suspension

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The addition of carbonate into a Pt-loaded TiO₂ suspension leads to the highly efficient photocatalytic decomposition of liquid water into H₂ and O₂ stoichiometrically.

The photocatalytic decomposition of water using promoted semiconductor powders such as Pt–TiO₂ has been investigated extensively from the point of photon energy conversion to chemical energy.^{1,2} Although the evolution of H₂ by irradiation is always detected, in most cases O₂ evolution is not

observed. Hydrogen evolution which is not accompanied by O₂ evolution has been interpreted in terms of the formation of peroxy species on the catalyst during irradiation^{3–6} or the presence of Ti³⁺ in the fresh catalyst.^{7,8} It should be noted that Pt–TiO₂ coated with NaOH, as has been reported by Sato *et*

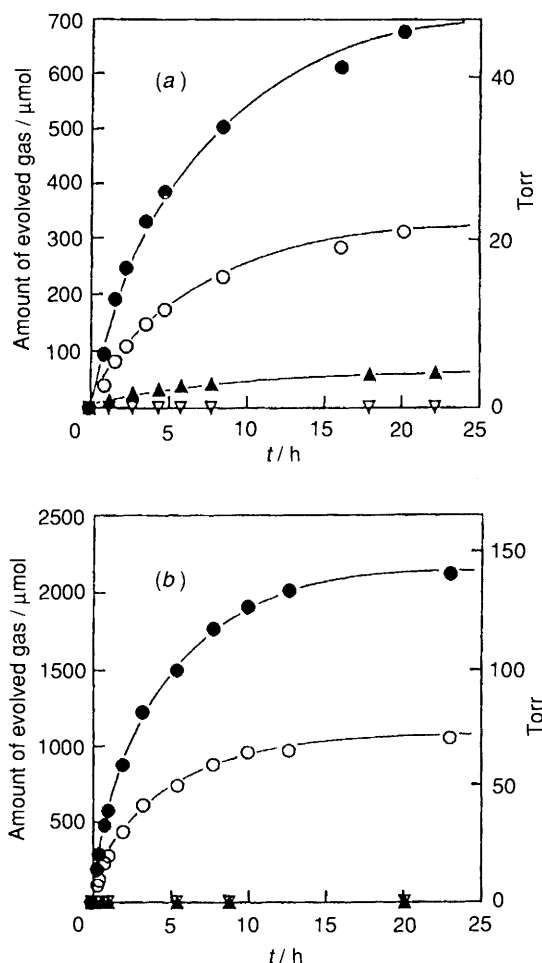


Fig. 1 Time course of H₂ and O₂ evolution at both the first run (a) and the 9th run (b) over Pt(0.3 wt%)-TiO₂ suspended in water with and without Na₂CO₃; with Na₂CO₃ (H₂ evolved: ●, O₂ evolved: ○) and without Na₂CO₃ (H₂ evolved: ▲, O₂ evolved: ▽). Catalyst: 0.3 g, water: 350 ml, Na₂CO₃: 0.76 mol, an inner irradiation type quartz cell, high pressure Hg lamp (400 W).

al.,⁹ can decompose water vapour, but the backward reaction was very fast and liquid water could be scarcely used in this system.

This report deals with the effect of the addition of several electrolytes on the photocatalytic evolution of H₂ and O₂ from Pt-TiO₂ suspended in liquid water. We have found a significant effect of the addition of a carbonate salt, especially Na₂CO₃, on the overall photocatalytic decomposition of water.

The photocatalytic reaction was performed using a closed gas-circulating system with an inner irradiation quartz reactor equipped with 400 W high pressure Hg lamp (Riko Kagaku). A reaction mixture was prepared by introduction of TiO₂ (anatase, Nihon Aerosil P-25, 0.3 g), H₂PtCl₆ (Wako Chemical, Pt:0.3 wt% to TiO₂) and a certain amount of additive such as carbonate into distilled water (350 ml) in a quartz reactor. Then the reaction mixture was mixed well and deaerated. After the introduction of argon into this circulating system (4.6 kPa), the first run was started by the irradiation. The catalyst was prepared by *in situ* photochemical deposition of Pt on TiO₂ under the irradiation. The next run was started after pumping away the evolved gases following the introduction of argon. The evolution of H₂ and O₂ was detected by on line gas chromatography (thermal conductivity detector, molecular sieve 5Å, Ar carrier) and pressure sensor.

Table 1 The rate of H₂ and O₂ evolution from several electrolyte solutions over Pt(0.3wt%)-loaded TiO₂^a

Electrolyte	Amount/mol	Rate of gas evolution/ μmol h ^{-1b}			pH
		H ₂	O ₂	H ₂ /O ₂	
None	—	1	0	—	7.9
Na ₂ CO ₃	0.10	3	1	3.0	10.9
	0.38 ^c	316	158	2.0	11.0
	0.76	568	287	2.0	11.0
	1.14	39	13	3.0	11.0
K ₂ CO ₃	0.38 ^c	5	1	5.0	11.5
	1.45	20	10	2.0	11.8
NaHCO ₃	0.10	4	2	2.0	8.4
NaOH	0.76 ^c	5	0	—	13.3
NaCl	0.76 ^c	5	0	—	6.8
Na ₂ SO ₄	0.38 ^c	4	0	—	5.5
Na ₃ PO ₄	0.25 ^c	5	0	—	12.0
Na ₂ HPO ₄	0.38 ^c	2	0	—	8.6

^a Catalyst: 0.3 g, water: 350 ml, an inner irradiation type quartz cell, high pressure Hg lamp (450 W). ^b Initial activity after several runs. ^c They contain 0.76 mol Na or K.

Fig. 1 shows the time courses of H₂ and O₂ evolution from the reaction mixture containing Na₂CO₃ additive at both the first run (a) and the ninth run (b). The time course of an experiment without additive is also shown. The effect of Na₂CO₃ addition on H₂ and O₂ evolution is clearly shown during irradiation. In the case of addition of Na₂CO₃, the evolved H₂:O₂ ratio became nearly two after 3 hours from initiation. The evolution rate decreased gradually with irradiation time, however, the activity of the catalyst itself did not become worse because the evolution rate was recovered by pumping away the evolved gases. The increase of pressure due to evolved gas in the system seems to suppress the further evolution of H₂ and O₂. Moreover, the initial activity of the catalyst in each run was getting better with longer irradiation time and became constant. After 70 hours from the start of irradiation, that is the ninth run (b), the initial rates of H₂ and O₂ evolution reached up to 568 μmol h⁻¹ (0.3 g catalyst) [12.7 ml standard temperature and pressure (STP) h⁻¹] and 287 μmol h⁻¹ (0.3 g catalyst) (6.3 ml STP h⁻¹), respectively. From the ninth run to at least the 20th run, the initial rate in each run became constant. As far as we know, these rates are the best results so far. The total amounts of evolved gases for 95 hours irradiation were 7.6 mmol (170 ml STP) of H₂ and 3.7 mmol (83 ml STP) of O₂. In the case of no Na₂CO₃ addition, the rate of H₂ evolution decreased gradually to zero and it was no longer recovered by pumping away the evolved gases. Oxygen evolution was not observed.

After the irradiation terminated, evolved H₂ and O₂ in the gas phase were not consumed, this means that the backward reaction to form H₂O scarcely proceeded in the gas phase of this experiment. In contrast to our results, it was reported that evolved H₂ and O₂ were consumed immediately in the case of the NaOH coated Pt-TiO₂ catalyst system.⁹

Table 1 shows the initial activities which are constant after several runs of photocatalytic H₂ and O₂ evolution from the reaction mixture. In the case of no additive, a small amount of H₂ was evolved, however, O₂ evolution was not observed. By the addition of NaOH, NaCl, Na₂SO₄, Na₃PO₄ and NaHPO₄ as additive respectively, H₂ evolution rate increased in comparison with the case of no additive, but it decreased to zero with reaction time. Also, there was no O₂ evolution in the gas phase for long periods. On the other hand, in case of Na₂CO₃, K₂CO₃ and NaHCO₃ additions, the H₂ evolution

rate increased dramatically. Furthermore, at the same time, O₂ evolution occurred with a nearly stoichiometric ratio of H₂O decomposition, that is, H₂:O₂ = 2. It is also noted that H₂ and O₂ evolution rates depend on the concentration of Na₂CO₃ additive. The maximum evolution rate was obtained in case of 0.76 mol Na₂CO₃ addition to 350 ml of water. In order to conclude that the photodecomposition of water proceeds 'catalytically', it is very important to confirm that stoichiometric ratio of evolved H₂ and O₂ (H₂/O₂) is two. Our data show this reaction proceeds catalytically.

In this reaction system, it is suggested that CO₃²⁻ or HCO₃⁻ contributes to the photocatalytic overall splitting of water, however, the role of these carbonates is not clear at this moment and is under investigation.

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