

Effect of carbonate addition on the photocatalytic decomposition of liquid water over a ZrO_2 catalyst

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Abstract

The stoichiometric photodecomposition of water into H_2 and O_2 proceeds over ZrO_2 powder suspended in aqueous solutions in the absence of loaded metals such as Pt, RuO_2 and NiO_x . The activity is affected significantly by the pressure of the reaction system, the types of additive and the pH of the solution. Specifically, the addition of carbonate, such as $NaHCO_3$ and Na_2CO_3 , leads to a remarkable increase in the activity and stability of the gas evolution rate vs. the reactor pressure. The surface of ZrO_2 was covered with carbonate species by the addition of carbonate salt. It is thought that carbonate species on ZrO_2 play an important role in the desorption of O_2 via the carbonate radical. In contrast, the promotion effect of platinum loading on water splitting is negligible. This behaviour can be explained in terms of the backward reaction (H_2O formation from H_2 and O_2) on Pt and the barrier height of the semiconductor–metal junction at which electrons in the conduction band migrate. Furthermore, it is concluded that the suppression of the backward reaction on Pt is essential for overall water splitting into H_2 and O_2 , and this is one of the important functions of $NaHCO_3$ and Na_2CO_3 . Pt on ZrO_2 in carbonate solutions exists as an oxide; therefore the effect of the backward reaction is suppressed.

Keywords: Photocatalytic decomposition; Liquid water; ZrO_2 catalyst; Carbonate addition

1. Introduction

As a method for the direct conversion of photon energy to chemical energy and for energy storage similar to photosynthesis, the photodecomposition of water into H_2 and O_2 using semiconductor photocatalysts has been investigated in detail. However, successful catalyst systems which enable stoichiometric water decomposition (ratio of H_2 to O_2 is two) to occur are rare, and their characteristics are very different. For example, RuO_2 – TiO_2 catalyst [1] and NaOH-coated M– TiO_2 (M \equiv Pt, Rh [2] and NiO_x [3]) catalysts lead to the decomposition of water vapour in a gas phase reaction, but the backward reaction ($2H_2 + O_2 \rightarrow 2H_2O$) on the noble metal is very fast in the gas phase and these catalyst systems cannot work in the liquid phase. For M– $SrTiO_3$ (M \equiv NiO_x [4] and RhO_x [5]), the decomposition of pure water in the liquid phase occurs, and the activity is increased by addition of NaOH. M– $A_4Nb_6O_{17}$ [6] (M \equiv RuO_2 , NiO_x and Pt, A \equiv K and Rb), RuO_2 – $Na_2Ti_6O_{13}$ [7] and RuO_2 – $BaTi_4O_9$ [8] are unique photocatalysts, which have layered and tunnel structures. It is assumed that the loaded metal is located in the interlayer spaces or pockets of the tunnel structure. The pho-

tocatalytic activities of these systems are also affected by the solution conditions, such as the pH and additives. All semiconductor photocatalysts reported so far for the stoichiometric photodecomposition of water require loaded metals or metal oxides, such as Pt, Rh, RuO_2 and NiO_x .

Recently, we have found that the addition of a large quantity of carbonate salts, such as Na_2CO_3 , K_2CO_3 and $NaHCO_3$, to a Pt– TiO_2 suspension leads to efficient photocatalytic decomposition even in the liquid phase [9]. This effect is associated with the CO_3^{2-} (or HCO_3^-) anion and not with the cation or pH. We have carried out experiments on the catalysts mentioned above in Na_2CO_3 solution, and have found that the activities of most of the catalysts increase on addition of carbonate salts [10,11]. Furthermore, many kinds of metal–semiconductor photocatalyst have been screened using the “ Na_2CO_3 method”, and new photocatalysts, such as M– Ta_2O_5 (M \equiv NiO_x and RuO_2), Pt– $Na_2Ti_6O_{13}$, Pt– $K_2Ti_6O_{13}$ and M– ZrO_2 (M \equiv Pt, RuO_2 , Cu and Au) have been discovered for stoichiometric water decomposition [11,12]. Of these, the ZrO_2 catalysts have special characteristics. The photodecomposition of pure water proceeds over ZrO_2 in the absence of loaded metals [12]. The splitting of water over ZrO_2 is a catalytic reaction, because the ratio of H_2 to O_2 is exactly two and the rate of gas evolution is constant over a

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long period. ZrO_2 semiconductor has a wide band gap ($E_g = 5.0$ eV) and a highly negative flat band potential ($E_{fb} = -1.0$ eV vs. normal hydrogen electrode (NHE), pH 0 [13]) compared with TiO_2 ($E_g = 3.0$ eV, $E_{fb} = +0.05$ eV vs. NHE, pH 0 [14]) and $SrTiO_3$ ($E_g = 3.2$ eV, $E_{fb} = -0.2$ eV vs. NHE, pH 0 [15]). The activity of ZrO_2 is increased on addition of carbonate salts; furthermore, the evolution of CO (photocatalytic reduction product of CO_2) is observed from $NaHCO_3$ aqueous solution. The mechanism of the photodecomposition of water over ZrO_2 seems to be simpler than that of the metal–semiconductor systems. Therefore it is inferred that we will obtain more fundamental information on the effect of additives using only the semiconductor itself. Furthermore, the function of loaded metals will become clearer by comparison between ZrO_2 and $M-ZrO_2$.

In this study, on the basis of the concepts mentioned above, we report the effect of additives, including several carbonate salts, the pressure in the reaction system, the function of loaded metals and the mechanism of the photocatalytic decomposition of water in a semiconductor catalyst system.

2. Experimental details

The photocatalytic reaction was performed using a closed gas circulating system with an inner irradiation-type reactor. The light source was a 400 W high-pressure Hg lamp (Riko Kagaku) covered with a quartz jacket to keep the reactor temperature constant (20 °C) by cooling water, which was recircled through a thermostatic bath. ZrO_2 semiconductor powder was supplied by Soekawa Chemicals (99.9%). Catalyst loaded with Pt was prepared by an in situ photochemical deposition method using H_2PtCl_6 . The reaction mixture was prepared by the introduction of semiconductor powder (1 g), a fixed amount of additives and distilled water (350 ml) into

a quartz reactor. They were mixed well using a magnetic stirrer and deaerated thoroughly. Argon gas was introduced up to 35 Torr into the gas circulating reaction system, and the first run was started by irradiation. The pressure of 35 Torr represents the sum of the argon pressure (approximately 18 Torr) and the water vapour pressure (approximately 17 Torr). After several hours of irradiation, the gases evolved in the first run were pumped away and argon was introduced again, and the next run was started. The rates of evolution of H_2 , O_2 and CO were measured by an on-line gas chromatograph (TCD, molecular sieve 5 Å, Ar carrier gas) and a volumetric measurement using a pressure sensor. The dead volume of the gas phase was 270 ml.

The zeta potential of ZrO_2 aqueous suspensions and the conductivity of the solutions were measured by a Lazer Zee meter (FEN KEM, model 501). The Fourier transform IR (FT-IR) spectrum was measured using a Shimadzu DR-8000. X-Ray photoelectron spectra (XPS) and ultraviolet–visible diffuse reflectance spectra (UV-DRS) were obtained by a Shimadzu ESCA 850 and a Shimadzu MPS-2000. X-Ray fluorescence (XRF) was measured by a Seiko SEA 2010 to confirm the amount of platinum loading.

3. Results and discussion

3.1. Effect of additives on the photocatalytic activity of ZrO_2

Table 1 shows the rate of H_2 and O_2 evolution from ZrO_2 aqueous suspensions containing several additives. Water can be decomposed over ZrO_2 catalyst stoichiometrically independent of the additives, i.e. the ratio of H_2 to O_2 evolution is almost two in all cases. However, the additives have a major effect on the rate of gas evolution. In particular, the

Table 1
Rate of H_2 and O_2 evolution from ZrO_2 aqueous suspensions containing several additives; the zeta potential of ZrO_2 and the conductivity of the solutions are also given

Additive ^a	Rate of gas evolution ($\mu\text{mol h}^{-1}$) ^b		Zeta potential (mV)	Conductivity (mS cm^{-1})	pH
	H_2	O_2			
None	72	36	-29	<0.001	7.9
NaOH	242	120	-36	6.3	12.7
Na_3PO_4	228	113	-49	4.1	12.0
Na_2CO_3	378	190	-44	3.5	11.2
$NaBO_2$	164	84	-37	2.6	10.9
Na_2HPO_4	129	65	-53	2.7	9.2
$NaHCO_3$	607	319	-42	3.0	8.4
Na_2SO_4	112	56	-11	3.6	7.5
NaCl	91	48	-4	3.9	6.0
HCl	46	19			2.9
H_3PO_4	65	33			2.8
H_2SO_4	85	39			2.6

ZrO_2 , 1.0 g; water, 350 ml; inner irradiated quartz cell; high-pressure Hg lamp (400 W).

^a Concentration of Na^+ and H^+ was 0.012 mol per 350 ml of water.

^b Initial activity in the second run. CO evolution was negligible.

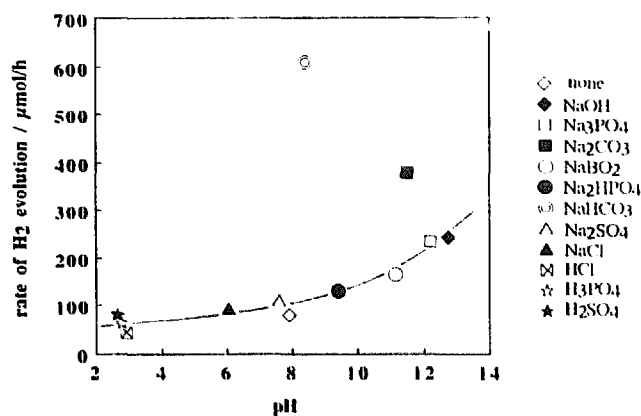


Fig. 1. Relationship between the rate of H_2 evolution and the pH of several kinds of solution over ZrO_2 . The activity was measured as the initial H_2 evolution rate in the second run. Na^+ : 0.012 mol in 350 ml of water. Plot of the evolution of O_2 was omitted.

addition of $NaHCO_3$ increases the rate by a factor of eight, and this factor is five in the case of Na_2CO_3 addition. In the case of $NaHCO_3$ addition, the rate of gas evolution is constant for a long period, and the total amount of evolved gas (90 mmol of H_2 for 150 h) is more than that of the catalyst (8.1 mmol) and additive (12 mmol) in the system. No change is observed in the ZrO_2 catalysts used (X-ray diffraction (XRD) and gravimetric measurement). Thus the splitting of water over ZrO_2 is indeed a catalytic reaction. Fig. 1 shows the relationship between the rate of H_2 evolution and the pH of the solution. The activities with all additives, except for carbonate salts, increase with increasing pH of the solution; furthermore, these evolution rates (symbols in Fig. 1) are located on one line. As a result, it is suggested that both HCO_3^- and CO_3^{2-} anions improve the gas evolution rate significantly, but other anions hardly affect the activity. The activity is controlled by the pH of the solution, and a high pH improves the activity in dilute aqueous solutions.

In the case of the electrolysis of $NaCl$ and HCl solutions, the Cl^- ion is more susceptible to oxidation than the OH^- ion. The ratio of H_2/O_2 increases by more than twofold with an increase in the concentration of $NaCl$ and HCl in the photocatalysis over ZrO_2 . These results indicate that the evolution of O_2 decreases and the evolution of Cl_2 increases with increasing concentration of Cl^- . O_2 evolution precedes Cl_2 evolution under these dilute solution conditions.

The conductivity of the solution and the zeta potential of ZrO_2 are also shown in Table 1. The conductivity is dependent on both the concentration and species of the ion. The activity of ZrO_2 increases slightly on addition of Na_2SO_4 and $NaCl$, while the conductivity of the solution is much improved (more than three orders of magnitude compared with the pure water system). Therefore it is suggested that there is no meaningful relationship between the photocatalytic activity and the conductivity of the solution. The zeta potential is a factor which represents the in situ surface condition of the oxide powder in aqueous solution. The zeta potential of the oxide is affected by both the pH of the solution and the specific

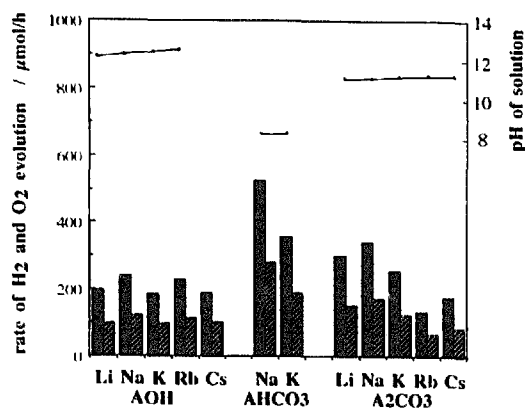


Fig. 2. Effect of alkaline ion on the rate of gas evolution over ZrO_2 (A = alkaline ion, 0.012 mol in 350 ml of water): ■, H_2 ; ▨, O_2 ; ---, pH.

adsorption of the anions. A high pH reduces the zeta potential because of the dissociation of surface hydroxyl groups. The zeta potentials of ZrO_2 suspended in $NaHCO_3$, Na_2CO_3 , Na_3PO_4 and Na_2HPO_4 aqueous solutions are more negative than those in pure water and $NaOH$ solution. The pH values of the carbonate and phosphate aqueous solutions are located between those of pure water and $NaOH$; therefore it is concluded that anions such as HCO_3^- , CO_3^{2-} , PO_4^{3-} and HPO_4^{2-} adsorb on the ZrO_2 surface.

Fig. 2 shows the effect of several alkaline cations on the rate of gas evolution over ZrO_2 . The shifts in pH by the substitution of cations in AOH , $AHCO_3$ and A_2CO_3 (A = Li, Na, K, Rb and Cs) are negligible. The activities of ZrO_2 in AOH aqueous solutions (AOH concentration, 0.012 mol in 350 ml of water) are affected slightly by the substitution of cations. In the case of $AHCO_3$ and A_2CO_3 , the Na salts show the highest activity.

The addition of inorganic salts to ZrO_2 suspensions leads to a change in pH, conductivity of the solution, presence of anions and cations, ionic strength and zeta potential of ZrO_2 . It is clear that the carbonate anions (HCO_3^- and CO_3^{2-}) and pH of the solution (concentration of H^+ and OH^-) are important factors in the activity of the photocatalytic decomposition of water over ZrO_2 . In contrast, the conductivity of the solution and alkaline cations and anions other than carbonate anions are minor, secondary factors.

3.2. Effect of pressure in the reaction system

Fig. 3 shows the time dependence of H_2 evolution over the ZrO_2 catalyst suspended in several solutions. There are large differences in the time dependence between carbonates and other salts. The addition of $NaHCO_3$ or Na_2CO_3 leads to a constant rate of gas evolution up to atmospheric pressure. However, the rate of gas evolution from the other aqueous solutions and pure water decreases gradually with increasing reaction time. It is believed that this decrease in activity is caused by the increase in pressure in the reaction system and is not related to the deactivation of the catalyst. The results in Fig. 4 and Table 2 demonstrate that this explanation may

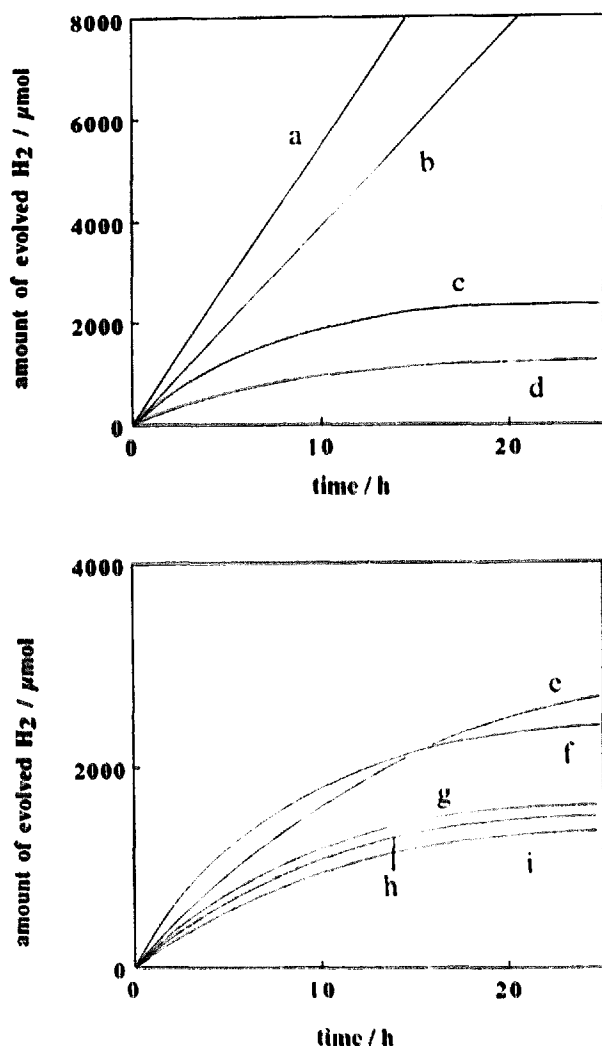


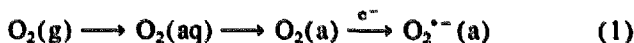
Fig. 3. Time course of H₂ evolution over ZrO₂ in several solutions: (a) NaHCO₃; (b) Na₂CO₃; (c) NaOH; (d) pure water; (e) NaBO₂; (f) Na₃PO₄; (g) Na₂HPO₄; (h) Na₂SO₄; (i) NaCl. Plot of the evolution of O₂ was omitted.

be reasonable. (a) Initially, the reactor was evacuated to remove air and was then filled with argon up to 35 Torr; the first run was started by irradiation. The rate of gas evolution decreased gradually with time. (b) After 30 h, the evolved gas was pumped away and argon was introduced again up to 35 Torr. The initial rate was almost the same as that in the first run. (c) After 50 h, the gas phase was pumped away again and argon was introduced up to 600 Torr. The evolution of H₂ and O₂ was depressed significantly. (d) Next, the gas phase pressure was adjusted to 35 Torr, and the activity was recovered as in (a) and (b). Table 2 shows the comparative ratio of the activities at 600 Torr and 35 Torr (reactor pressure of argon) in ZrO₂ suspension with various kinds of additives. The pressure in the reactor significantly affects the rate of gas evolution, and the addition of carbonate salts leads to the stability of the activity vs. the gas phase pressure. This influ-

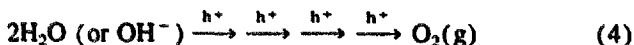
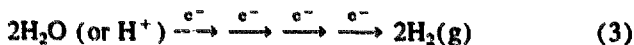
ence of reactor pressure was also observed in Pt-TiO₂ [9], RuO₂-Ta₂O₅ and NiO_x-Ta₂O₅ [11].

It is unexpected and very interesting that the activity is affected by the inert argon gas. The same experiments were performed using He and N₂ instead of argon, and the same pressure dependence was observed in all cases. The dependence of the activity on the pressure of the inert gas can be explained as follows: (i) the gases produced suffer backward reactions on the catalyst; (ii) the gases produced diffuse as bubbles or gaseous molecules which possess a certain volume.

With regard to point (i), ZrO₂ itself cannot catalyze water formation from H₂ and O₂ because H₂ dissociation on the ZrO₂ surface is negligible. Therefore we must emphasize the importance of the photoadsorption of O₂ with an electron. The electron in the conduction band of semiconductors, such as TiO₂ and ZrO₂, has the potential to reduce O₂ to O₂^{•-}. In practice, this phenomenon has also been reported over TiO₂ catalysts as the photoadsorption of O₂ [16-18]. This reaction is reversible, and O₂^{•-} (a) (adsorbed species on ZrO₂, no volume) is oxidized by the hole in the valence band



O₂(g) represents the gaseous O₂ molecule which has a certain volume, and O₂(aq) represents the dissolved O₂ molecule which, ideally, has no volume. The decomposition of water is represented as



Reaction (2) is part of reaction (4). Electrons are consumed by reactions (1) and (3). Therefore it is suggested that electrons react with H⁺ and O₂(a) competitively. If the rate of reaction (1) increases, the rate of reaction (3) will decrease, and the rate of decomposition of water will decrease. In other words, O₂(a) and O₂^{•-}(a) act as recombination sites for electrons (e⁻) and holes (h⁺) due to the repetition of the reversible reaction between O₂(a) and O₂^{•-}(a). For effective water splitting it is necessary to suppress the photoadsorption of O₂.

With regard to point (ii), it is considered that some of the gases produced diffuse as bubbles, because the evolution of many bubbles was observed during the photoreaction. The mechanism of gas evolution accompanied by bubbles is very complicated. The total gas pressure (*P*) of the gas phase above the liquid phase is expressed as $P = P_{\text{H}_2\text{O}} + P_{\text{Ar}} + P_{\text{H}_2} + P_{\text{O}_2}$. The total gas pressure in the bubble (*P^b*) is $P^b = P_{\text{H}_2\text{O}}^b + P_{\text{Ar}}^b + P_{\text{H}_2}^b + P_{\text{O}_2}^b$. *P* and *P^b* are the same as the total pressure in the closed system ($P = P^b$), and moreover $P_{\text{H}_2\text{O}} = P_{\text{H}_2\text{O}}^b$. It is considered that the amount of argon in the bubble is very small compared with that in the gas phase ($P_{\text{Ar}}^b \approx 0$), because the concentrations of H₂(aq) and O₂(aq) close to ZrO₂ are much greater than that of Ar(aq) and the

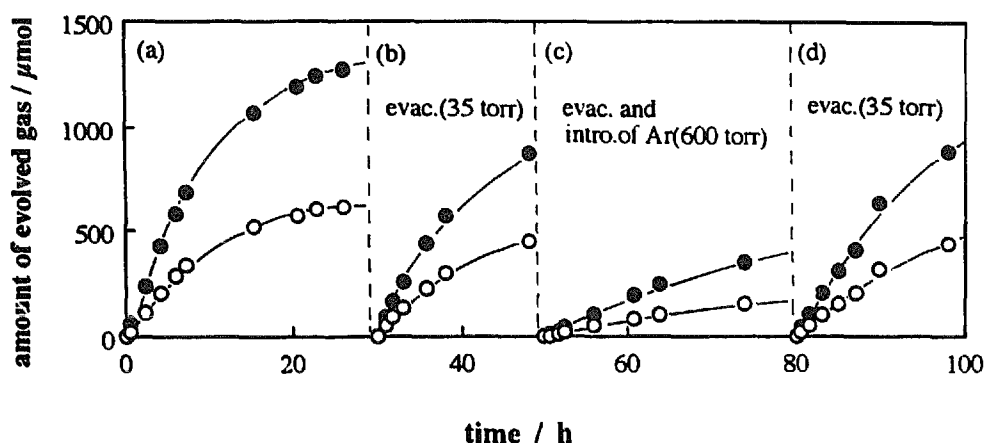


Fig. 4. Time course of H₂ (●) and O₂ (○) evolution over ZrO₂ in pure water. Initial pressure of the system in (a), (b) and (d) was 35 Torr. Initial pressure in (c) was 600 Torr adjusted by argon.

Table 2
Comparative ratio of the activity at 600 Torr and 35 Torr of pressure in the reaction system over ZrO₂ suspended in various solutions

Additive	Rate of gas evolution at 600 Torr ($\mu\text{mol h}^{-1}$)		$R_{\text{H}_2}(600 \text{ Torr})/R_{\text{H}_2}(35 \text{ Torr})^a$
	$R_{\text{H}_2}(600 \text{ Torr})$	$R_{\text{O}_2}(600 \text{ Torr})$	
None	19	8	0.26
NaOH	24	10	0.10
Na ₃ PO ₄	39	17	0.17
Na ₂ CO ₃	386	190	1.02
NaBO ₂	69	28	0.42
Na ₂ HPO ₄	19	9	0.15
NaHCO ₃	606	305	1.00

Pressure was adjusted by the introduction of argon.

^a $R_{\text{H}_2}(35 \text{ Torr})$ is the activity in Table 1.

rate of gas evolution is faster than the diffusion rate of argon through the liquid phase. Therefore $P_{\text{H}_2}^b + P_{\text{O}_2}^b \approx P_{\text{Ar}} + P_{\text{H}_2} + P_{\text{O}_2}$. This means that the partial pressures of H₂ and O₂ molecules in the bubble increase on introduction of argon above the liquid phase; therefore the conversion rate from O₂(aq) to O₂(g) decreases with an increase in the total pressure of the system. The O₂ molecule is nearer to the ZrO₂ surface, and is more susceptible to reaction with an electron. Furthermore, the dissolved O₂(aq) is more susceptible to reaction with an electron than gaseous O₂(g). Therefore the escape rate of gaseous O₂(g) and bubbles from the liquid phase to the gas phase is slower with an increase in the total pressure. Consequently, the photoadsorption of O₂ onto ZrO₂ increases with increasing total pressure of the system and the rate of water splitting decreases because of the recombination of h⁺ and e⁻.

3.3. Effect of carbonate addition

The significant effects of carbonate salts on the activity of ZrO₂ were studied in detail. The dependence of both the activity and pH on the amount of additives is shown in Fig. 5. The activity of ZrO₂ suspended in Na₂CO₃ (a) and NaHCO₃ (b) aqueous solutions increases with increasing

amount of salt up to 0.012 mol of Na⁺ in 350 ml of water, and then gradually decreases with increasing amount of salt. ZrO₂ in NaHCO₃ solution has a higher activity than that in Na₂CO₃ at all concentrations. The evolution of CO is observed only from NaHCO₃ aqueous solution. The rate of CO evolution increases with increasing amount of NaHCO₃, and further reduces products such as HCOOH, CH₄, CH₃OH and carbon is not detected. No CO is observed from Na₂CO₃ solution. Fig. 6 shows the dependence of the activity over ZrO₂ on the pH in the presence of carbonate. The pH was adjusted by mixing NaHCO₃, Na₂CO₃ and NaOH; the total amount of carbonate salts was constant ($\text{CO}_3^{2-} + \text{HCO}_3^- + \text{H}_2\text{CO}_3 = 0.012 \text{ mol per } 350 \text{ ml of water}$). The activity gradually decreases with increasing pH. Fig. 7 shows the concentrations of OH⁻, CO₃²⁻, HCO₃⁻ and H₂CO₃ derived from theoretical calculations in the reaction solution shown in Fig. 6. The concentration of HCO₃⁻ decreases with pH and that of CO₃²⁻ increases.

The observations of a decrease in activity at high concentrations of carbonate salts and a higher activity of ZrO₂ in NaHCO₃ solution then in Na₂CO₃ solution can be interpreted on the basis of the UV absorption of the carbonate anion itself. Fig. 8 shows the UV absorption spectra of several solutions and the diffuse reflectance spectrum of ZrO₂. The

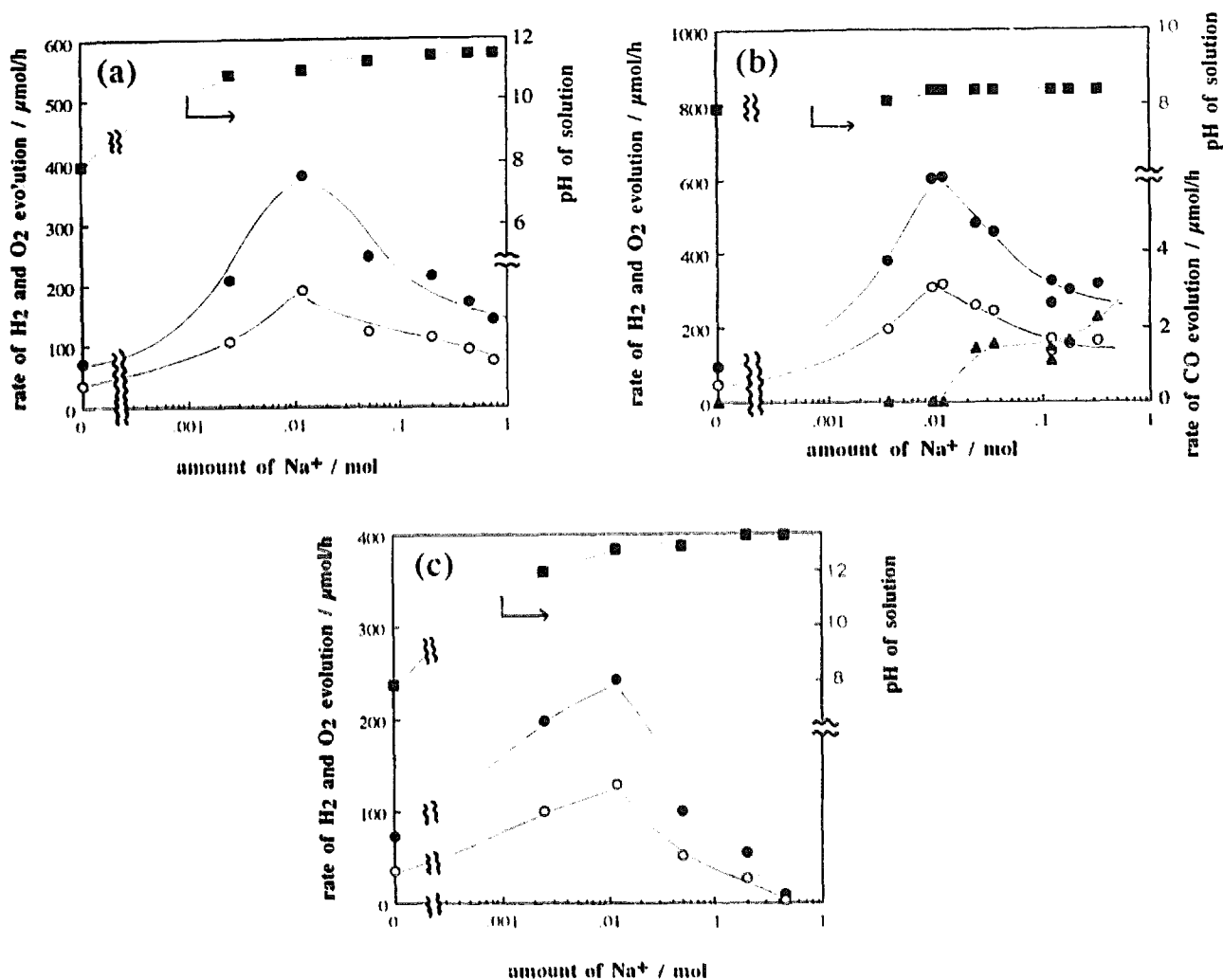


Fig. 5. Dependence of the activity and pH on the amount of salt: (a) Na₂CO₃; (b) NaHCO₃; (c) NaOH; ●, H₂; ○, O₂; ▲, CO; ■, pH.

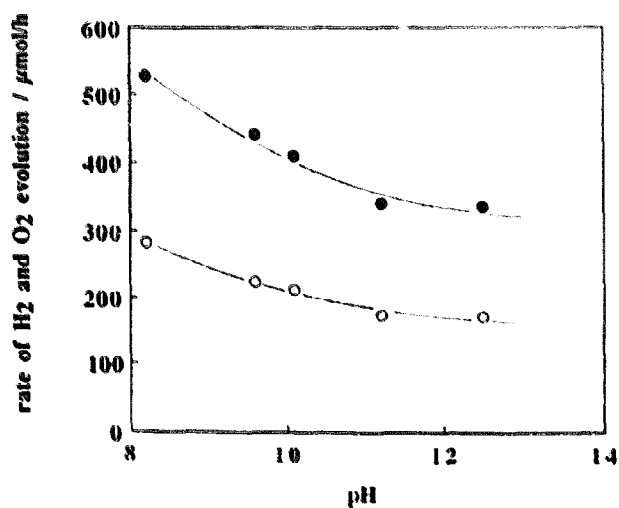


Fig. 6. Dependence of the activity over ZrO₂ on the pH (total amount of carbonate salts was constant (CO₃²⁻ + HCO₃⁻ + H₂CO₃ = 0.012 mol in 350 ml of water)): ●, H₂; ○, O₂.

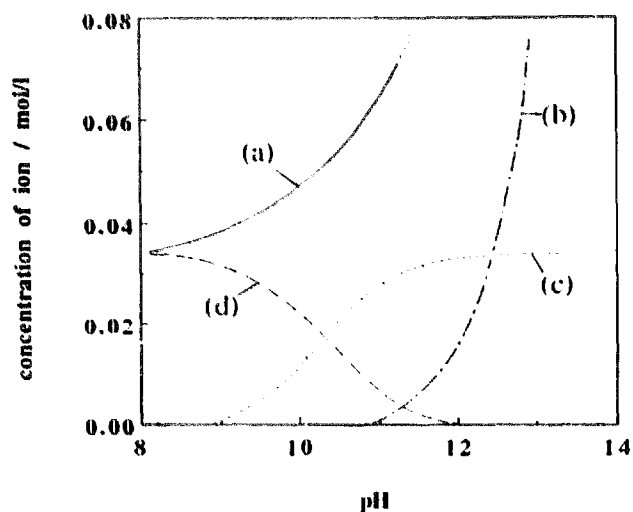


Fig. 7. Ion concentration at different pH values: (a) Na⁺; (b) OH⁻; (c) CO₃²⁻; (d) HCO₃⁻.

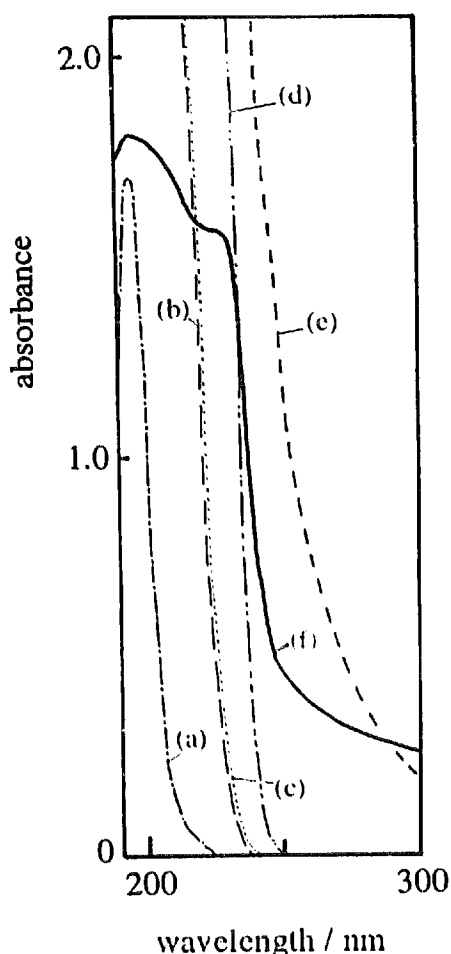


Fig. 8. UV absorption spectra of solutions and diffuse reflectance spectrum of ZrO_2 . (a) NaHCO_3 (0.034 mol l^{-1}); (b) NaHCO_3 (0.94 mol l^{-1}); (c) Na_2CO_3 (0.034 mol l^{-1}); (d) Na_2CO_3 (0.94 mol l^{-1}); (e) $\text{Na}_2\text{C}_2\text{O}_6$ solution; (f) ZrO_2 .

band gap of ZrO_2 is approximately 5.0 eV and ZrO_2 can absorb light below 248 nm [13] (main line spectra at 237.8 and 240.0 nm from the high-pressure Hg lamp). The peaks of the UV absorption spectra of HCO_3^- and CO_3^{2-} ions are both at 193 nm; however, the absorption coefficient of CO_3^{2-} is tenfold larger than that of HCO_3^- . Moreover, the shape of the absorption spectrum of CO_3^{2-} is broader, and the threshold of the spectrum extends to longer wavelengths than that of HCO_3^- . Table 3 shows the rates of gas evolution over ZrO_2 suspended in pure water on UV irradiation through several solution filters. These solutions were passed through the water cooling jacket of the inner irradiation-type reactor. The activity decreases with an increase in concentration of the carbonate salt and with an increase in pH. A blank test (UV irradiation of Na_2CO_3 or NaHCO_3 solutions without ZrO_2) was carried out and no evolution of H_2 , O_2 or CO was observed. From these results, it is suggested that, at higher concentrations of carbonate and pH in the reaction solution, the amount of light absorbed by ZrO_2 is smaller, and the rate of gas evolution decreases.

Table 3

Rate of gas evolution over ZrO_2 suspended in pure water on UV irradiation through several solution filters

Solution filter ^a	Rate of gas evolution ($\mu\text{mol h}^{-1}$)	
	H_2	O_2
Pure water	66	32
NaHCO_3 (0.034 mol l^{-1})	63	30
NaHCO_3 (0.94 mol l^{-1})	34	15
NaHCO_3 (0.94 mol l^{-1}) + NaOH (0.3 mol l^{-1})	18	8

^a The solutions were passed through the water cooling quartz jacket of the inner irradiation-type reactor. The cooling solutions were recycled through a thermostatic bath. ZrO_2 (1.0 g) was suspended in pure water (350 ml).

In the case of NaOH addition (Fig. 5(c)), the optimum concentration is almost the same as for NaHCO_3 and Na_2CO_3 ; however, the activity reaches zero on addition of more than 0.45 mol of NaOH in 350 ml of water. The UV absorption of NaOH solution above 200 nm is negligible. ZrO_2 itself is unchanged in NaOH solution because, after photoreaction, the ZrO_2 used in concentrated NaOH solution shows the usual activity in pure water. The effect of a high concentration of NaOH on the photodecomposition of water has been reported, i.e. the activities of $\text{NiO}_x\text{-SrTiO}_3$ [4], $\text{NiO}_x\text{-TiO}_2$ [3] and $\text{RhO}_x\text{-SrTiO}_3$ [5] increase on addition of a large amount of NaOH , in contrast with ZrO_2 . It is speculated that NaOH may have a positive effect on the loaded metals, such as NiO_x and RhO_x , rather than the semiconductors, because high concentrations of NaOH depress the activity of ZrO_2 .

For the other salts, such as Na_3PO_4 , Na_2HPO_4 , NaBO_2 and Na_2SO_4 , the UV absorption of the solutions above 200 nm is negligible. The rate of gas evolution over ZrO_2 catalyst increases slightly on addition of these salts up to the saturated condition.

3.4. Functions of the carbonate ions

The photocatalytic decomposition of water over ZrO_2 proceeds even in pure water, whose conductivity is very low, suggesting that the activity is not related to the conductivity of the solution. Therefore it can be speculated that the transfer of electrons (e^-) and holes (h^+) occurs on the ZrO_2 surface. Therefore the surface condition is important for the activity.

The possibility that many anions, such as HCO_3^- , CO_3^{2-} , PO_4^{3-} and HPO_4^{2-} , are adsorbed on the ZrO_2 surface under our reaction conditions has been mentioned previously from the results of the zeta potential measurements. Furthermore, adsorbed species on ZrO_2 under a CO_2 atmosphere are observed by FT-IR spectroscopy as shown in Fig. 9. The absorption at 1618, 1431 and 1221 cm^{-1} can be assigned to bicarbonate species [19], and thus the ZrO_2 surface easily adsorbs bicarbonate under a CO_2 atmosphere. In the case of NaHCO_3 solution, CO_2 gas is evolved from the solution as a result of the following equilibrium

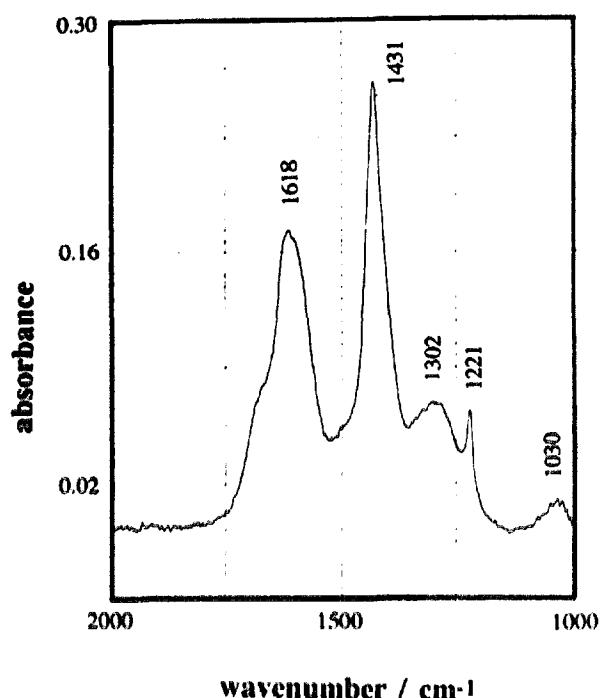


Fig. 9. FT-IR spectrum of surface species on ZrO_2 . CO_2 and water were introduced (10 Torr respectively) to the IR cell.

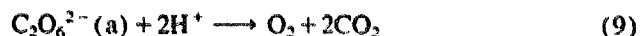
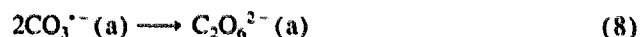
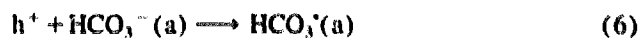


Therefore it is suggested that the ZrO_2 surface in $NaHCO_3$ aqueous solution is covered with bicarbonate species at neutral pH, and these play a specific role in the reaction mechanism.

The presence of carbonate ions in the solution leads to a constant gas evolution rate vs. the pressure of the reactor. It is speculated that the surface carbonate species may have two functions: the inhibition of O_2 photoadsorption to the ZrO_2 surface due to steric hindrance by the adsorbed anions, and acceleration of O_2 desorption from the ZrO_2 surface. However, the former function seems to be a minor factor because the adsorption of phosphoric and sulphate anions, which have very bulky structures, on ZrO_2 has little influence on the activity in Na_3PO_4 , Na_2HPO_4 and Na_2SO_4 solutions. Taking into account the specificity of carbonates, the latter seems to be a more probable function, i.e. the desorption pathway of O_2 may change in the presence of carbonates. Eriksen and Lind [20] studied the behaviour of HCO_3^{\cdot} and $CO_3^{\cdot-}$ radicals in $NaHCO_3$ aqueous solution (0.1 mol l^{-1} , pH 8.2) using a pulse radiolysis system. They demonstrated that most OH^{\cdot} radicals were consumed by HCO_3^- , and that the self recombination of $CO_3^{\cdot-}$ radicals to form peroxy carbonate had a negative apparent activation energy. $Na_2C_2O_6$ was synthesized from Na_2CO_3 and H_2O_2 at low temperature [21], and the UV absorption spectrum of an $Na_2C_2O_6$ solution is shown in Fig. 8. The threshold of the absorption spectrum is 330 nm. Vigorous O_2 evolution from the $Na_2C_2O_6$ solution is observed on UV irradiation. Furthermore, the peroxy carbon-

ate can also be synthesized by electrolysis of highly concentrated carbonate aqueous solutions at low temperature [22]. From these results, we propose the following reaction mechanism via carbonate radicals and peroxy carbonate.

A hole (h^+) reacts with bicarbonate species on the ZrO_2 surface ($HCO_3^-(a)$) and bicarbonate radicals ($HCO_3^{\cdot}(a)$) are formed. This reaction accelerates the charge separation of e^- and h^+ , because the surface HCO_3^- anion is a good trap for h^+ . The $HCO_3^{\cdot}(a)$ radical dissociates into H^+ and $CO_3^{\cdot-}(a)$ radical. Two $CO_3^{\cdot-}(a)$ radicals couple to give the peroxy carbonate species ($C_2O_6^{2-}(a)$), which is easily decomposed into O_2 and CO_2 by reaction with h^+ or photons, yielding desorption of O_2 gas from the surface. After gas desorption, the CO_2 gas soon dissolves and is converted to HCO_3^- . The O_2 desorption process by Eq. (9) is irreversible, whereas that of Eq. (2) is reversible. Therefore the desorption of O_2 via peroxy carbonate is much easier than O_2 desorption via other peroxide species vs. the photoadsorption of O_2 .



3.5. Effect of Pt loading on ZrO_2 catalyst

For TiO_2 and $SrTiO_3$, it is essential to load metals or metal oxides, such as Pt, RuO_2 and NiO_x , onto the semiconductors in order to achieve overall water splitting. In the case of H_2 evolution from sacrificial reagent solution, such as methanol solution, loading of a metal on the semiconductor also increases the activity. The loaded metals accelerate the charge separation and decrease the overvoltage for H_2 evolution [23,24]. Pt is very popular because of the small overvoltage for H_2 production. However, the activity of ZrO_2 is not increased by Pt loading as shown in Table 4. Pt- ZrO_2 suspended in pure water exhibits no activity because a fast backward reaction occurs on the Pt particles. The Pt- ZrO_2 catalyst leads to the decomposition of water on addition of a large amount of $NaHCO_3$ and Na_2CO_3 ; however, Pt- ZrO_2 in $NaHCO_3$ solution shows a lower activity than ZrO_2 without Pt under the same conditions. The activity of ZrO_2 in Na_2CO_3 solution is increased slightly on loading with Pt. A mixture of Pt- ZrO_2 (0.5 g) and ZrO_2 (1.0 g) catalysts was suspended in pure water and irradiated, but no activity was observed. This result suggests that the gases evolved from some ZrO_2 particles can be easily reacted to form H_2O at Pt on other catalyst particles. Therefore it is concluded that sufficient depression of the backward reaction on Pt is essential to achieve overall water splitting in the presence of Pt-loaded semiconductor catalysts, and that the depression of the backward reaction is one of the most important functions of $NaHCO_3$ and Na_2CO_3 .

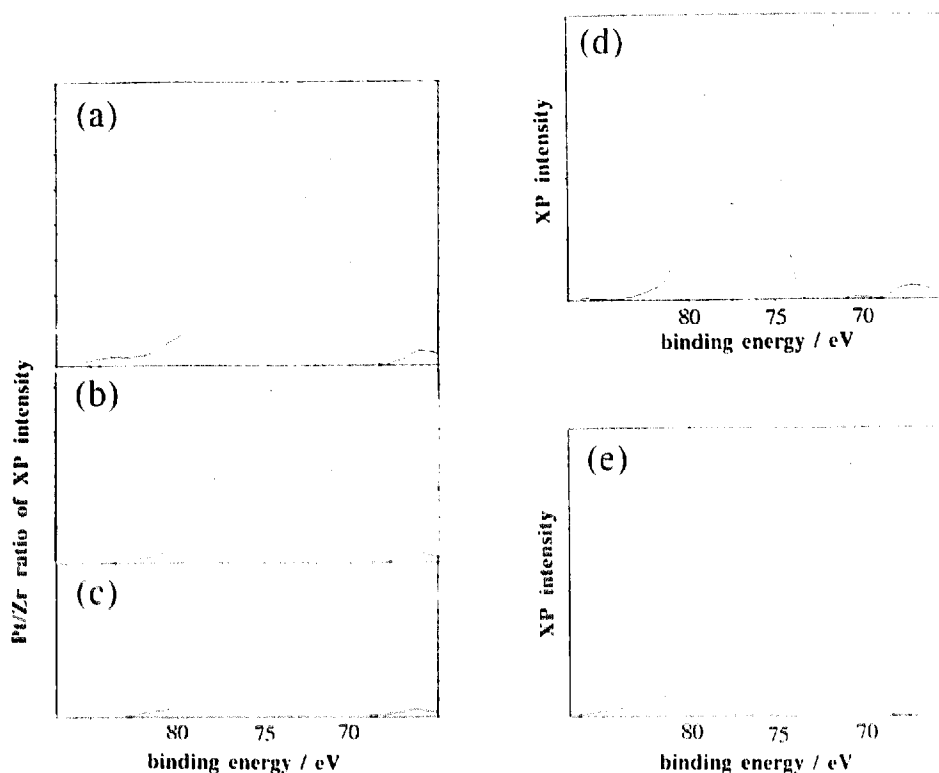


Fig. 10. XPS of Pt $4f_{5/2}$ and $4f_{7/2}$ over Pt(3 wt.%)–ZrO₂ after photoreaction in several solutions (0.33 mol per 350 ml of water): (a) pure water; (b) NaHCO₃; (c) Na₂CO₃. References: (d) PtO₂; (e) Pt black.

Table 4
Rate of H₂ and O₂ evolution from several solutions over ZrO₂ and Pt(0.1 wt.%)–ZrO₂

Catalyst	Additive	Rate of gas evolution ($\mu\text{mol h}^{-1}$)			
		Amount (mol)	H ₂	O ₂	CO
None	NaHCO ₃	0.33	0	0	0
ZrO ₂	None	–	72	36	0
	NaHCO ₃	0.33	309	167	3.0
	Na ₂ CO ₃	0.33	142	75	0
Pt–ZrO ₂	None	–	tr	0	0
	NaHCO ₃	0.33	120	61	0
	Na ₂ CO ₃	0.33	179	88	0
ZrO ₂ + Pt–ZrO ₂ ^a	None	–	tr	0	0

Catalyst, 1.0 g; water, 350 ml; inner irradiation quartz cell; high-pressure Hg lamp (400 W).

^a Catalyst was a mixture of Pt(0.1 wt.%)–ZrO₂ (0.5 g) and ZrO₂ (1.0 g).

The state of the Pt particle on ZrO₂ suspended in several concentrated solutions was measured by XPS. Fig. 10 shows the XPS of Pt $4f_{5/2}$ and $4f_{7/2}$ over Pt(3 wt.%)–ZrO₂. After photoreaction for 3 days in several solutions (0.33 mol per 350 ml of H₂O), these samples were filtered, washed well and dried. The amount of Pt loading was 2.9 ± 0.1 wt.% confirmed by XRF. The spectrum of Pt in pure water agreed with that of Pt black (zero valent metal). The existence of

Pt⁰ causes the fast backward reaction in pure water. However, on addition of NaHCO₃ and Na₂CO₃, the peak attributed to the metallic state decreases and a higher valent peak increases. It is considered that part of the Pt on ZrO₂ exists in the oxide state (PtO_x) in concentrated and high pH solutions.

Platinum accelerates H₂ evolution due to the decrease in the overvoltage for H₂ production and the promotion of charge separation; however, the backward reaction to form water from H₂ and O₂ is also accelerated. The activity of water splitting is determined by the ratio of the forward and backward reactions. The promotional effect of Pt loading on H₂ evolution from methanol solution as hole scavenger is small for ZrO₂ compared with TiO₂ [11]. Pt–ZrO₂ suspended in pure water shows no activity because most of the Pt exists as metallic Pt⁰ which is very active for the backward reaction. For Pt–ZrO₂ suspended in Na₂CO₃ solution, the backward reaction is suppressed because the Pt surface is oxidized as shown in Fig. 10. Therefore the activity is increased slightly by Pt loading because the charge separation is promoted. However, the activity of ZrO₂ suspended in NaHCO₃ solution is decreased by Pt loading because part of the Pt exists in the metallic state.

In the case of TiO₂ catalyst, it is considered that charge separation is promoted by Pt loading because electrons migrate from the conduction band of TiO₂ to the loaded Pt. However, in the case of ZrO₂, it is speculated that the barrier height of the Pt–ZrO₂ junction is higher than that of the Pt–TiO₂ junction because the difference between the Fermi level

of Pt and ZrO_2 is large [25]. Therefore the migration of electrons from ZrO_2 to Pt is rare and the promotional effect of Pt loading is small. If electrons can be supplied sufficiently to Pt from ZrO_2 , oxidized PtO_x may not exist. It is inferred that PtO_x may be produced by migration of holes in the valence band of ZrO_2 . The potential of the valence band of ZrO_2 is very positive (approximately 4.0 eV vs. NHE, pH 0), and the hole in the valence band can oxidize Pt sufficiently. In the case of the NiO_x - $SrTiO_3$ photocatalyst, the oxidation of loaded nickel during the photoreaction has been reported [26].

The reason why PtO_x is more stable in Na_2CO_3 and $NaHCO_3$ aqueous solution than in pure water is unclear. It is speculated that the oxide types are changed by the pH and concentration of the solution. For example, PtO_2 is stabilized by alkali ion, and the reduction of PtO_2 by pure H_2 gas at room temperature shows an induction period of several seconds because the rate of H_2 adsorption on the oxidized PtO_2 surface is very slow [27].

4. Conclusions

The following conclusions can be drawn from the results of this study.

(1) Both HCO_3^- and CO_3^{2-} anions dramatically improve the activity of the photocatalytic decomposition of water over ZrO_2 ; however, other anions, such as PO_4^{3-} , HPO_4^{2-} , BO_2^- , SO_4^{2-} and Cl^- , have little effect on the activity. A high pH promotes increased activity, with the exception of the carbonate salt systems. The influences of alkaline cations and the conductivity of the solution on the activity are negligible.

(2) The rate of gas evolution is affected by the total pressure in the reaction system. This behaviour can be explained on the basis of the photoadsorption of O_2 and gas evolution accompanied by bubbles. However, the addition of $NaHCO_3$ or Na_2CO_3 leads to a constant rate of gas evolution vs. reactor pressure. The maximum activity of ZrO_2 is obtained in 0.034 mol l^{-1} $NaHCO_3$ aqueous solution. The surface of ZrO_2 is covered with bicarbonate anion species, which are effective traps for holes. It is considered that this species on ZrO_2 promotes O_2 desorption via carbonate radicals and peroxy-carbonates.

(3) The effect of Pt loading on ZrO_2 on the activity is negative for the following two reasons. Firstly, the backward reaction (H_2O formation) on metallic Pt is a serious problem. Secondly, the high barrier of the ZrO_2 -Pt junction prevents electron transfer from ZrO_2 to Pt. The sufficient depression of the backward reaction on Pt is essential for the simulta-

neous evolution of H_2 and O_2 . Highly concentrated $NaHCO_3$ or Na_2CO_3 solutions stabilize the oxide state of the Pt surface to avoid the backward reaction.

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