CHEMISTRY LETTERS, pp. 253-256, 1992.

Remarkable Effect of Na_2CO_3 Addition on Photodecomposition of Liquid Water into H_2 and O_2 from Suspension of Semiconductor Powder Loaded with Various Metals

Kazuhiro SAYAMA and Hironori ARAKAWA*
National Chemical Laboratory for Industry, Higashi 1-1, Tsukuba, Ibaraki 305

An addition of Na_2CO_3 played the excellent role for the stoichiometric photodecomposition of liquid water over TiO_2 and $SrTiO_3$ loaded with various metals such as Pt, RuO_2, and NiO_x. The addition of Na_2CO_3 for TiO_2 catalysts was more effective than that for $SrTiO_3$ catalysts. It was suggested that the stoichiometric photodecomposition of water was associated with CO_3^{2-} ion and neither with Na^+ nor pH.

Photocatalytic decomposition of water into H_2 and O_2 using semiconductors loaded with various metals have been widely studied.[1,2] Some catalyst systems such as RuO_2-TiO_2 catalyst[3] and NaOH coated M-TiO_2 (M = Pt[4a], Rh[4b], and NiO_x[5]) were reported for photodecomposition of water vapor in gas phase reaction, however, they could not work for stoichiometric photodecomposition in aqueous suspension. In most cases, only small amount of H_2 was evolved but O_2 was not evolved stoichiometrically.[6-8]

Recently, we found that Na_2CO_3 addition into Pt-TiO_2 suspension was significantly effective to stoichiometric photodecomposition of liquid water.[9] Furthermore, it was found that this procedure was also applicable to other photocatalyst systems for water decomposition. Here, we would like to report to the usefulness of Na_2CO_3 addition to photocatalyst systems which composed of many combinations of various metals and semiconductors.

Semiconductor powders of TiO_2 and $SrTiO_3$ were supplied from Nihon Aerosil (anatase P-25) and Wako Junyaku respectively. Precursors of noble metal were chlorides and those of other metals were nitrates. In case of preparation of Pt, Rh, and Pd catalysts, in situ photochemical deposition method was used. A reaction mixture was prepared by introduction of semiconductor powder (0.3 g), precursor of noble metal (0.3 wt% of metal to semiconductor) and a certain amount of Na_2CO_3 (or NaOH) into distilled water (350 ml) in a quartz reactor. Then, they were mixed well and deaerated. Argon gas was introduced up to 4.6 kPa into this circulating system, and then the first run was started by irradiation at room temperature. After about 14 hours irradiation, the evolved gases at first run were pumped away and argon was introduced again, and then next run was started. In case of catalysts loaded with other metals (Ni, NiO_x, Cu, Ag, Pb, and RuO_2), they were prepared by impregnation method. Catalysts loaded with Ni, Cu, Ag, and Pb were reduced by H_2 at 723 K for 3 hours. RuO_2 loaded catalyst was oxidized by O_2 at 773 K for 3 hours, NiOx loaded catalyst was reduced by H_2 at 773 K for 2 hours and oxidized by O_2 at 473 K for 1 hour. Reaction procedure after mixing of catalyst with distilled water and Na_2CO_3 was same as mentioned above. The evolutions of H_2 and O_2 were measured by both on line gaschromatgraphy (TCD, molecular sieve 5A, Ar carrier gas) and pressure sensor.

Table 1 shows the rates of H_2 and O_2 evolution over various kinds of metal supported TiO_2 and $SrTiO_3$ photocatalysts. The rates of evolved gases in Table 1 were represented by the initial activity in the second run. This is because that ratio of H_2 and O_2 evolved in the first run was often larger than stoichiometric ratio of water decomposition ($H_2/O_2=2$) due to some reasons such as impurites, partially reduced semiconductors or trapping of oxygen. In case of no Na_2CO_3 addition, only small amount of H_2 were evolved , but O_2 evolution were not observed over all TiO_2 catalysts. In case of Na_2CO_3 addition, over the TiO_2 catalysts loaded with Pt, Rh, RuO_2, Ni, NiOx, and Cu, rate of H_2 evolution increased considerably and O_2 began to evolved. Especially H_2 and O_2 were evolved stoichiometrically over the combination of Pt-TiO_2, RuO_2-TiO_2, and NiO_x-TiO_2. Figure 1 shows a time course of H_2 and O_2 evolution over RuO_2 (1 wt%)- TiO_2 catalyst. When catalyst was suspended in distilled water without Na_2CO_3 addition, very small amount of H_2 evolved, but O_2 did not evolved even after 40 hours irradiation. In case of Na_2CO_3 addition, H_2 and O_2 were evolved stoichiometrically. It was found that 0.76 mol of Na_2CO_3 addition was more effective than that of 0.38 mol. The rates of H_2 and O_2 were constant up to 60 hours. Therefore it was concluded that addition of Na_2CO_3 played the excellent role for the effective photodecomposition of water over several TiO_2 catalysts. Furthermore, it should be noteworthy that Cu supported TiO_2 catalyst proved to have the activity of evolution of H_2 and O_2 simultaneously.

Effect of NaOH addition on photodecomposition of water were often reported[10a,11a] and we tried to check the effect of addition of NaOH instead of Na_2CO_3 ((d) in Table 1). The rate of H_2 evolution increased up to only two times by the addition of NaOH. In addition, O_2 evolution could not be observed. This shows that the effect of Na_2CO_3 addition is different from that of NaOH addition.The pH of Na_2CO_3 solution was 11 and this value was between those of NaOH and pure water (NaOH: pH=13, pure water: pH=8). From these results, it was considered that stoichiometric photodecomposition of water was associated with CO_3^{2-} and neither with Na^+ nor pH. However, it is not fully clarifyed at this moment that why addition of Na_2CO_3 leaded to the remarkable and stoichiometric evolution of H_2 and O_2. It is now under investigations.

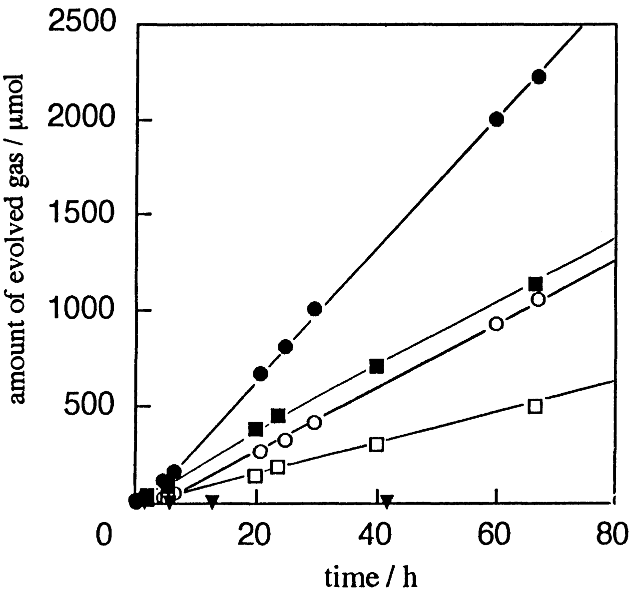

Fig. 1. Time course of H_2 and O_2 evolution over RuO_2(1 wt%)-TiO_2; with 0.76 mol (H_2: ● , O_2: ○) and 0.38 mol (H_2: ■ , O_2: □) of Na_2CO_3, and without Na_2CO_3 (H_2: ▼ , O_2: ▽).

Over $SrTiO_3$ catalysts loaded with Pt, Rh Ni, and NiO_x, both H_2 and O_2 were evolved simultaneously from distilled water without Na_2CO_3 addition. Same results were already reported by Lehn[10b] and Domen el al.[11b] On

Table 1. The rate of H_2 and O_2 evolutions over various kinds of photocatalysts a)

Catalyst b)	Amount of Na_2CO_3 / mol	Rate of gas evolution / $\mu mol\cdot h^{-1}$ c) H_2	O_2	H_2/O_2 ratio
Pt(0.3wt%)-TiO_2	0	2	0	-
	0.38	40	17	2.4
	0.76	78	38	2.1
	0.76 d)	5	0	-
Rh(0.3wt%)-TiO_2	0	2	0	-
	0.38	12	trace	-
	0.76	16	3	5.3
Pd(0.3wt%)-TiO_2	0	1	0	-
	0.76	2	0	-
RuO_2(1wt%)-TiO_2	0	trace	0	-
	0.38	21	9	2.3
	0.76	34	17	2.0
	0.76 d)	7	0	-
Ni(1wt%)-TiO_2	0	2	0	-
	0.38	55	8	6.9
	0.76	78	29	2.7
	0.76 d)	5	0	-
NiO_x(1wt%)-TiO_2 e)	0	1	0	-
	0.76	64	32	2.0
	0.76 d)	10	0	-
Cu(1wt%)-TiO_2	0	1	0	-
	0.76	13	3	4.3
	0.76 d)	6	0	-
Ag(1wt%)-TiO_2	0.76	1	0	-
Pb(1wt%)-TiO_2	0.76	0	0	-
Pt(0.3wt%)-$SrTiO_3$	0	9	2	4.5
	0.38	11	trace	-
	0.76	10	4	2.5
Rh(0.3wt%)-$SrTiO_3$	0	20	4	5.0
	0.38	48	14	4.4
	0.76	5	trace	-
	0.76 d)	1	0	-
RuO_2(1wt%)-$SrTiO_3$	0	2	0	-
	0.76	2	0	-
Ni(1wt%)-$SrTiO_3$	0	10	2	5.0
	0.76	8	2	4.0
NiO_x(1wt%)-$SrTiO_3$ e)	0	9	4	2.3
	0.76	41	20	2.1
Cu(1wt%)-$SrTiO_3$	0	2	0	-
	0.76	3	trace	-

a) Catalyst: 0.3 g, water: 350 ml, an inner irradiation type quartz cell, high pressure Hg lamp(400 W).
b) Pt, Rh, and Pd catalysts were prepared by photo-deposition method.
Other catalysts were prepared by impregnation method.
c) Initial activity in the second run.
d) Amount of NaOH instead of Na_2CO_3.
e) H_2 reduction at 773 K following O_2 oxidation at 473 K.

the other hand, the additions of Na_2CO_3 for $SrTiO_3$ catalysts were not so effective as that for TiO_2 catalysts. Promoted effects by Na_2CO_3 was not observed over Pt, RuO_2, and Ni catalysts at all. As for Rh-$SrTiO_3$, the activity increased two times and became a maximum at 0.38 mol of Na_2CO_3. While the activity of NiO_x-$SrTiO_3$ increased four times at 0.76 mol of Na_2CO_3.

Semiconductors such as TiO_2 and $SrTiO_3$ are widely studied for photodecomposition of water because of the chemical stability and the suitable potential level of the conduction band, however, observed behavior in Na_2CO_3 addition was very different from each other. In connection with this, Sato et al. reported that the promoting effect of NaOH coating over metal supported $SrTiO_3$ for photodecomposition of water vapor was not so remarkable as in case of metal supported TiO_2.12) They inferred that the contact of $SrTiO_3$ with a high concentrated NaOH leaded to the inactivation. Lehn et al. also described the solubility of $SrTiO_3$ even in pure water.10) From these results, it is suggested that the instability of $SrTiO_3$ in high concentrated Na_2CO_3 solution might lose photocatalytic activity in the present study.

Other semiconductor materials such as ZnO, WO_3, Fe_2O_3, and SiC have been also tested. However, the promoted effect of Na_2CO_3 on water decomposition was not found.

References

1) M. A. Grätzel, "Energy Resources Through Photochemistry and Catalysis," Academic Press, Inc., New York, (1983).
2) M. Schiavello, "Photoelectrochemistry, Photocatalysis and Photoreactors: Fundamentals and Developments," Reidel, Dordecht, (1985).
3) T. Kawai and T. Sakata, *Chem. Phys. Lett.*, **72**, 87 (1980).
4) a) S. Sato and J. M. White, *Chem. Phys. Lett.*, **72**, 83 (1980) ; b) K. Yamaguchi and S. Sato, *J. Chem. Soc., Faraday Trans. 1*, **81**, 1237 (1985).
5) A. Kudo, K. Domen, K. Maruya, and T. Onishi, *Chem. Phys. Lett.*, **133**, 517 (1987).
6) J. C. Escudero, S. Cervera-March, J. Giménez, and R. Simarro, *J. Catal.*, **123**, 319 (1990).
7) J. Kiwi and M. Grätzel, *J. Mol. Catal.*, **39**, 63 (1987).
8) G. Munuera, J. Espinos, A. Fernández, P. Malet, and A. Gonzalez-Elipe, *J. Chem. Soc., Faraday Trans.*, **86**, 3441 (1990).
9) K. Sayama and H. Arakawa, *J. Chem. Soc., Chem. Commum.*, in press.
10) a) J. Lehn, J. Sauvage R. Ziessel, and L. Hilaire, *Isr. J. Chem.*, **22**, 168 (1982); b) J. Lehn, J. Sauvage, and R. Ziessel, *Nouv. J. Chim.*, **4**, 623 (1980);
11) a) K. Domen, S. Naito, T. Onishi, and K. Tamaru, *Chem. Phys. Lett.*, **92**, 433 (1982); b) K. Domen, A. Kudo, and T. Onishi, *J. Catal.*, **102**, 92 (1986).
12) K. Yamaguchi and S. Sato, *Nouv. J. Chim.*, **10**, 217 (1986).

(Received November 16, 1991)