Synergy Effect of Graphite Silica and TiO_2 on Photocatalytic Hydrogen Production

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(Received May 16, 2005; CL-050645)

The photocatalytic production of hydrogen gas from water–methanol mixtures was performed in contact with a suspended mixture of titanium dioxide (TiO_2) and graphite silica (GS), one of natural minerals. A drastic synergy effect for hydrogen production was found for GS in collaboration with TiO_2. It is suggested that the clay fraction in GS is one of the key components for the synergy effect.

The practical hydrogen production using a photocatalyst is one of dreams for mankind. For the practical production of hydrogen gas,[1–5] it is necessary to find a low-cost cocatalyst instead of expensive one such as platinum. We are strongly concerned with GS as a low-cost cocatalyst. GS is a natural mineral. It is mined in the hills in Kaminokuni Town, Hokkaido, Japan.[6] The cost of GS is much lower than platinum. Table 1 shows the typical specific composition of GS which was estimated by using the norm method,[7] on the basis of X-ray diffraction[6] and X-ray fluorescence analysis.

Here we report the photocatalytic hydrogen production drastically enhanced by GS in collaboration with TiO_2 in water–methanol mixtures and propose a plausible mechanism for the synergy effect of GS and TiO_2. To our best knowledge, this is the first report showing the drastic synergy effect by using a naturally produced mineral, GS.

The amount of photocatalytic hydrogen production from water–methanol mixtures was measured by following procedures. 1) A mixture of powdered TiO_2 (15 mg, Nippon Aerosil P25) and an additive such as GS (15 mg) was added to 40 vol % aqueous methanol (20 cm^3) in a batch photoreactor of a cylindrical flask (154 cm^3) whose top was sealed with a silicone rubber septum. 2) To remove oxygen gas, the suspended solution was bubbled with Ar gas (about 1 mL/min) for 1 h after sonication for 1 min. 3) Photoirradiation was carried out under an Ar atomosphere of about 1 atm with stirring. 4) The evolved gas was sampled through the silicone rubber septum by using a locking-type syringe at a constant time interval, usually 15 min. 5) The sampled gas was quantitatively analyzed by a gas chromatograph (detector; TCD, column packing; MS5 Å or Porapak N, carrier gas; Ar). The photoirradiation was provided by a super-high-pressure mercury lamp (Ushio 500-W USH-500SC) with an optical band pass filter (300–400 nm, Toshiba ATG UV-D33S).

Table 1. Composition of GS

Name	Chemical formula	Content/wt %
Quartz	SiO_2	67.9
Sericite	$K_2Al_6Si_6O_{22}$	18.9
Carbon[a]	C	5.80
Dolomite	$(Ca,Mg)CO_3$	3.50
Kaolinite	Al_2SiO_2	1.77
Hematite	Fe_2O_3	0.87
Rutile	TiO_2	0.77
Pyrite	FeS_2	0.48

[a]Contains graphite.

Figure 1 shows the amount of hydrogen gas from suspended mixtures of TiO_2 with GS, Pt, SiO_2, calcined GS or clay in GS. The results on TiO_2 alone and platinized TiO_2 (0.3 wt % Pt/TiO_2)[8] alone are also included in Figure 1. Here it should be noted that GS itself produces negligible H_2 gas. The amount of hydrogen gas was increased by a factor of ca. 100 by adding GS to TiO_2 suspension. This shows that the photocatalytic hydrogen production was enhanced by the synergy effect of TiO_2 and GS. The hydrogen evolution in the presence of platinized TiO_2 under our experimental conditions was studied for comparison. The evolution rate of H_2 gas with the powdered GS–TiO_2 mixture was about one-eighth of that with Pt/TiO_2. Since GS could not be deposited on TiO_2 in this study, the mixture of powdered Pt and TiO_2 was also examined. The synergy effect by GS was comparable to that by powdered Pt. Therefore, the GS powder is considered to bear comparison with cocatalytic Pt in the photocatalytic activity.

SiO_2 is the main chemical composition of GS. An addition of powdered SiO_2 (Wako) to TiO_2 suspension did not enhance the photocatalytic hydrogen production, but it was rather detrimental as seen in Figure 1.

The powder of GS with almost negligible carbon was prepared by calcination in air. The pale-pink colored powder was obtained by calcination at 923 K. The calcined GS had ability to enhance the hydrogen gas evolution, almost equal to the untreated powder of GS. This result suggests that the carbon in GS does not play an important role in the synergy effect between TiO_2 and GS.

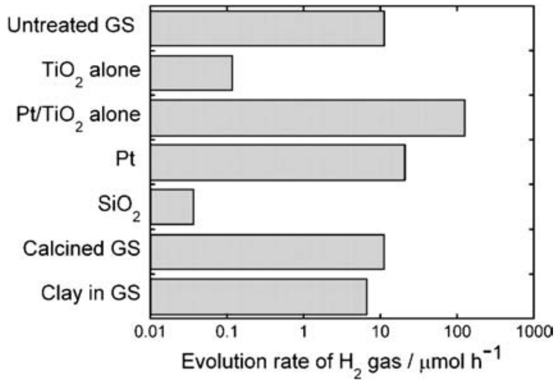

Figure 1. Comparison of hydrogen production. Each powdered additive (15 mg) was added to powdered TiO_2 (15 mg). For TiO_2 alone and Pt/TiO_2 alone systems, the total amount of 30 mg was used. Note the logarithmic abscissa.

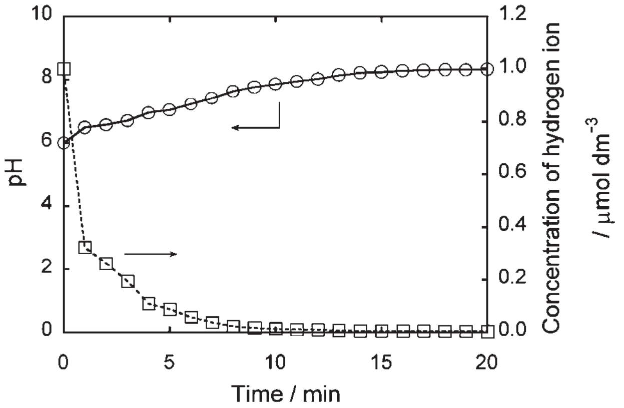

Figure 2. Time variation of pH of water containing the GS powder.

The clay fraction in GS such as kaolinite was separated by the following method.[9] At first, the powder of GS was calcined at 923 K for 5 h in air. Then, the calcined powder was dispersed in water by ultrasonication for 30 min. After the suspension was allowed to stand in a dark place for 6 h, its suspension was separated into two layers of the supernatant and the sediment. The supernatant was centrifuged at 3500 rpm for 15 min. After the precipitate was dried on standing, the pale-pink colored clay was obtained. The clay in GS showed the synergy effect comparable to the powders of calcined and uncalcined GS as shown in Figure 1. This fact indicates that the clay in GS is mainly responsible for the synergy effect of GS and TiO_2 for the hydrogen production.

Clay is one of the functional materials in nature. It is generally known that clay has an ion-exchange property. To investigate the ion-exchange property of the clay in GS, the variations of pH with time and the amount of GS were measured. Figure 2 shows the time variation of pH of 40-cm^3 water containing 30 mg of GS. The pH increased with time and reached equilibrium pH of about 8 after ca. 10 min. This pH variation strongly suggests that the presence of GS results in the exchange of cations between the metal ions in the clay and hydrogen ions in water.

Figure 3 shows the GS-amount dependence of the equilibrium pH and the amount of the exchanged hydrogen ions (M_p) which was estimated from the pH values. The M_p increased with the amount of GS and became nearly constant at about 1.5 $\mu mol\,cm^{-3}$ at about 100 mg of GS. This result suggests that the metal ions at all active ion-exchange sites are replaced by the hydrogen ions in the solution used for hydrogen evolution.

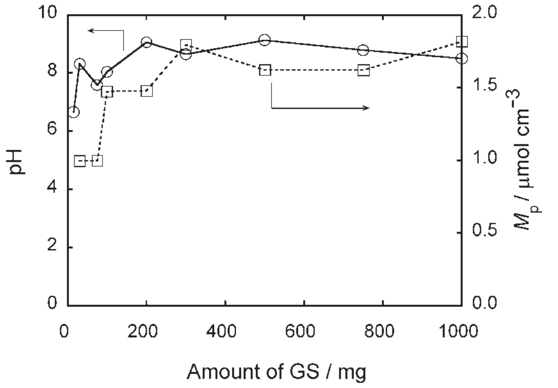

Figure 3. The dependence of the equilibrium pH and M_p on the amount of GS.

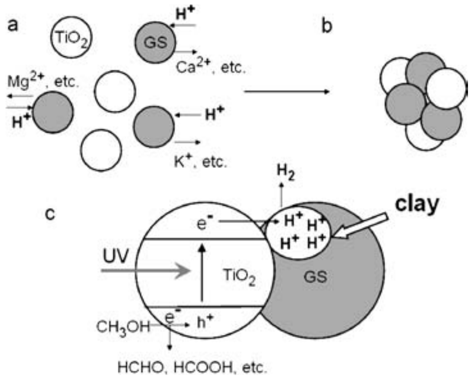

Figure 4. a: Ion exchanges between metal ions and hydrogen ions by the clay in GS. b: Aggregation of both particles of GS and TiO_2. c: Increment of hydrogen production by the photocatalytic reduction of hydrogen ions held in the clay. e^-: Electron. h^+: Positive hole.

Taking these results into consideration, the reaction model composed of the various stages is illustrated as shown in Figure 4. In Figure 4a, the clay in GS exchanges cations between the metal ions in the clay and the hydrogen ions in water. In Figure 4b, the hydrophilic particles of GS will be agglutinated with the particles of TiO_2 bearing the superhydrophilic surface under photoirradiation.[10] In Figure 4c, it is considered that the hydrogen ions held in the clay are the main source of hydrogen gas.

Though 15 mg of GS contains the clay components of about 3 mg, the cocatalytic property of GS itself was comparable to that of 15 mg of the clay. This suggests that the synergy effect of GS and TiO_2 is not fully induced by the clay alone. Further studies are needed to clarify all aspects of the mechanism of the synergy effect and the surface structure of GS.

The authors are grateful to Emeritus Professor Katsutoshi Tomita and Dr. Masamichi Hoashi for helpful discussions. We thank Nishi-Nihon Environmental Engineering Inc. for their kind supply of the GS powder.

References

1 T. Kawai and T. Sakata, *J. Chem. Soc., Chem. Commun.*, **1980**, 694.
2 T. Sakata and T. Kawai, *Chem. Phys. Lett.*, **80**, 341 (1981).
3 M. Kawai, S. Naito, and K. Tamaru, *Chem. Phys. Lett.*, **98**, 377 (1983).
4 M. Kawai, T. Kawai, S. Naito, and K. Tamaru, *Chem. Phys. Lett.*, **110**, 58 (1984).
5 K. Domen, S. Naito, T. Onishi, and K. Tamaru, *Chem. Lett.*, **1982**, 555.
6 J. Sato, J. Kohno, and S. Ono, "Chikyuu-no-megumi," (1990), p 255.
7 K. L. Currie, *Comput. Geosci.*, **17**, 77 (1991).
8 S. Sato and M. White, *Chem. Phys. Lett.*, **72**, 83 (1980).
9 C. R. Schmitt and S. T. Benton, *Powder Technol.*, **6**, 109 (1972).
10 A. Fujishima, K. Hashimoto, and T. Watanabe, in "TiO_2 Photocatalysis, Fundamentals and Applications," BKC, Inc., Tokyo (1999), p 65.