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Effect of graphite silica on TiO_2 photocatalysis in hydrogen production from water–methanol solution

Miyuki Ikeda, Yoshihumi Kusumoto *, Shouichi Somekawa,
Pascaline Ngweniform, Bashir Ahmmad

Department of Chemistry and Bioscience, Faculty of Science, Kagoshima University, 1-21-35 Korimoto, Kagoshima 890-0065, Japan

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Abstract

The photocatalytic production of hydrogen gas from water–methanol mixtures was performed in contact with a suspended mixture of powdered titanium dioxide (TiO_2) and graphite silica (GS), a naturally available mineral. A drastic synergy effect for hydrogen production was found for GS in collaboration with TiO_2. The amount of hydrogen gas evolved from water–methanol mixtures was increased by a factor of ca. 100 simply by mixing GS with TiO_2. The synergy effect is attributed to the enrichment of hydrogen ions in the clay components of GS and aggregation of GS and TiO_2 particles.

Keywords: Graphite silica; Titanium dioxide; Hydrogen gas; Water–methanol mixture; Photocatalysis

1. Introduction

Co-catalysts are indispensable for the hydrogen production using photocatalytic semiconductors. At present, expensive noble metals such as platinum (Pt) and ruthenium (Ru) are used as the co-catalysts. The Pt metal shows especially outstanding performance for photocatalytic hydrogen production, but it is a fairly rare metal. To realize a hydrogen-based society, the co-catalysts derived from abundant natural minerals seem to be interesting and important as a co-catalyst in low cost.

We are strongly concerned with graphite silica (GS, also called “black silica” and “silica black”), one of natural minerals, as a low cost co-catalyst. Here, it should be emphasized that the GS is much cheaper and more abundantly available than metals such as Pt. The GS is siliceous ore containing several percent of carbon in a black mudstone of pre-tertiary. It is mainly composed of quartz, clay and carbon. The GS is usually used as an addition to concrete blocks and an adulterant for soil improvement or snow melting. In industrial application, it has been studied as a source for the preparation of β-SiC or α-Si_3N_4 whiskers [1,2].

Generally, co-catalysts are roughly classified into two types. One is a support-type in which co-catalysts are deposited on photocatalysts. The other is a mixing-type in which co-catalysts are mixed with photocatalysts in suspension. The support-type has high efficiency, but the supporting process is complicated. The mixing-type has lower efficiency than the support-type, but the mixing process is very easy and convenient for practical use. For the support-type, many metals such as Pt, Ni and Ru are used [3–8]. On the other hand, Cu, Ni, Ag, Co, etc. are known as mixing-type co-catalysts [9,10]. For both types, roles of the co-catalysts are summarized as follows: (1) the co-catalysts efficiently accept electrons or holes from TiO_2 to avoid recombination of the electron and hole; (2) the co-catalysts adsorb reactants on the surface which is the reaction field of electrons (or holes) and the reactants. In case of the mixing-type, the frequency of collisions and the degree of aggregates are important factors. Moreover, it is needed that the co-catalysts hold the reactants sufficiently.

In this paper, the co-catalytic ability of GS itself and its components was studied. We obtained the following significant results. The clay component in GS showed good co-catalytic performance close to that of as-powdered GS. The pH values of water increased by adding GS, irrespective of whether the TiO_2 powder was present. Both TiO_2 and GS particles were aggre-

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* Corresponding author. Tel.: +81 99 285 8914; fax: +81 99 285 8914.
E-mail address: kusumoto@sci.kagoshima-u.ac.jp (Y. Kusumoto).

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gated in suspension. On the basis of these experimental results, we here report the role of GS as a co-catalyst for the hydrogen production from water–methanol suspension containing powdered GS and TiO_2 and propose a plausible mechanism of the synergy effect between GS and TiO_2.

2. Experimental

2.1. Reagents and materials

2.1.1. TiO_2

The photocatalyst was TiO_2 (Degussa, P 25) with a mainly anatase structure (ca. 80%) under the shape of non-porous polyhedral particles of ca. 20 nm mean size with a surface area of 49.9 m^2/g.

2.1.2. GS

The GS powder was obtained from Nishi-nihon Environmental Engineering Inc. The GS powder has a surface area of 11.1 m^2/g.

The typical composition of GS is shown in Table 1. It was estimated by using the norm method based on X-ray diffraction and X-ray fluorescence analysis [11,12]. Main components are quartz, carbon, and several kinds of clay such as sericite and kaolinite.

Fig. 1 shows a typical example of thermogravimetry–differential thermal analysis (TG–DTA) curves of GS. A weight loss of about 4% was observed at around 923 K on the TG curve. One exothermic peak was observed on the DTA curve, which was accompanied by the weight loss. The loss mainly corresponds to the total mass of carbon in GS as seen in Table 1. These results suggest that most of carbon was removed by heat treatment at around 923 K. As shown in Fig. 2, the GS color changed from black to pale-pink after the measurement of TG–DTA.

Table 1
A typical example of 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] Contain graphite.

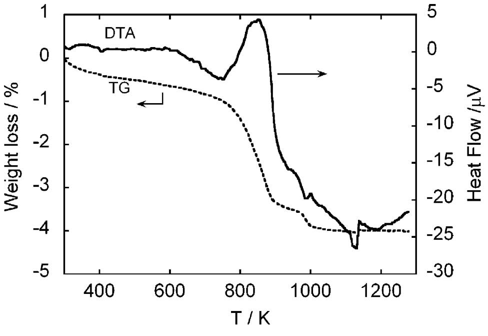


Fig. 1. Typical DTA–TG curves of GS.

Fig. 2. The color change of GS by heat treatment. Left and right: before and after heating at around 923 K, respectively.

2.1.3. Calcined GS

The calcined GS was obtained by heat treatment for 5 h at 923 K in air. The pale-pink colored GS contains negligible carbon, as mentioned above.

2.1.4. Separation of clay and quartz from calcined GS

The clay fraction in the calcined GS was separated by the following method [13]. The calcined GS 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.

After supernatant was removed, the sediment was washed to remove the clay fraction remaining on the GS surface. The sediment was then treated ultrasonically for 20 min in water of 160 cm^3. The obtained suspension was centrifuged at 3500 rpm for 15 min, and the supernatant was removed. This process was repeated 19 times. The ash-like colored powder was obtained after drying. The powder containing mostly quartz was thus obtained from the calcined GS.

2.1.5. Other chemicals

Graphite (99%, Nacalai Tesque), activated carbon (for chromatography, Wako), quartz (99%, Wako), and platinum (99.98%, Nilaco) were used without further purification. Methanol (Wako) was of the highest grade available and was used as received. Laboratory deionized water was distilled twice.

2.2. Methods

2.2.1. Hydrogen production

The amount of hydrogen gas evolved photocatalytically from water–methanol mixtures was measured by following procedures. (1) A mixture of powdered TiO_2 and an additive such as GS, several kinds of GS components, or Pt powders was added to 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 with stirring after ultrasonication for 1 min. (3) Photoirradiation was carried out under an Ar atmosphere 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. (5) The sampled gas was quantitatively analyzed by a gas chromatograph (detector; thermal conductivity detector (TCD), column packing; molecular sieve 5 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, Asahi Techno Glass, UV-D33S).

2.2.2. *Hydrogen production using recycled TiO_2 and GS*

The co-catalytic properties of recycled GS were examined in the following manner. After the hydrogen production experiment was finished, the suspension used was centrifuged at 1000 rpm for 7 min, and then the supernatant was removed. A fresh water–methanol mixture was added to the remaining sediment. Again, the hydrogen production experiment was performed. These recycling processes were repeated consecutively five times.

2.2.3. *PH of GS suspension and eluting metals from GS*

The variations of pH and the eluting metals from GS in water were measured by following procedures. Proper amounts of GS were added to 50 cm^3 of water with or without TiO_2. The suspension was stirred for 20 min. The pH of the suspension was measured using a pH meter (Horiba, D-51). Then the suspension was filtered and the filtrate was analyzed by inductively coupled plasma emission spectroscopy (Thermo Elemental, IRIS).

2.2.4. *Size distribution of particles and aggregates in suspension*

To investigate the aggregation of TiO_2 and GS particles in water, the size distribution of particles was measured by a laser diffraction particle size analyzer (Shimadzu, SALD-3100). The measurement was carried out with and without ultrasonication. The images of aggregates of TiO_2 and/or GS were taken with a scanning electron microscope (Hitachi S-4100).

3. Results

Fig. 3 shows the GS content dependence of the evolution rate of hydrogen gas from 40 vol.% aqueous methanol suspension. The GS content of the GS–TiO_2 mixture was varied in the range of 0–100 wt.%, keeping the total amount of the mixture at 30 mg. The maximum production rate of hydrogen gas, 22.3 μmol h^{-1}, was observed at a GS content of 50 wt.%. On the other hand, TiO_2 or GS only resulted in 0.23 and 0.03 μmol h^{-1}, respectively. By adding GS to TiO_2 suspension, the amount of hydrogen gas was increased by a factor of ca. 100 (a ratio of 22.3 and 0.23 μmol h^{-1}). These results show that the photocatalytic hydrogen production was enhanced by the synergy effect of GS and TiO_2.

Fig. 4 shows the hydrogen production by recycled TiO_2 and GS. The amount of hydrogen gas under 1 h irradiation in the 2nd cycle was larger approximately two times than that in the initial cycle. Furthermore, the amount of H_2 gas was larger than that of the initial cycle in all runs. The cleaning effect of the GS and TiO_2 surfaces in the recycling process may be responsible for the increment of hydrogen production.

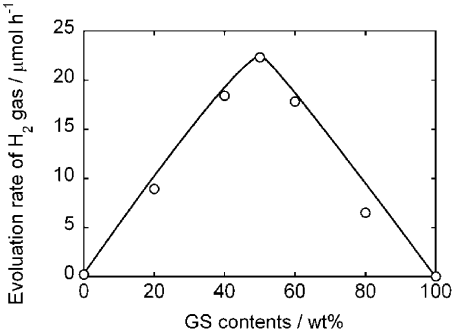


Fig. 3. The GS content dependence of the evolution rate of H_2 gas from water–methanol mixtures containing 40 vol.% methanol under UV irradiation (35 mW cm^{-2}).

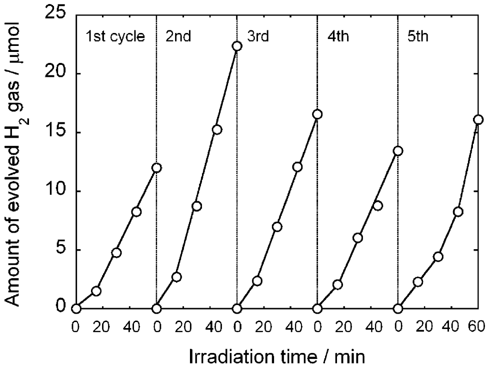


Fig. 4. Hydrogen production by recycled TiO_2 and GS. Methanol: 40 vol.%, UV strength: 15 mW cm^{-2}.

Fig. 5 shows the irradiation-time course of hydrogen production from suspension of TiO_2 with GS or Pt powder. The hydrogen evolution from platinized TiO_2 (0.3 wt.% Pt/TiO_2) was also studied for comparison [14]. The amount of H_2 gas evolved with the powdered GS–TiO_2 mixture was about one-eighth of that evolved with 0.3 wt.% Pt/TiO_2. Since GS could

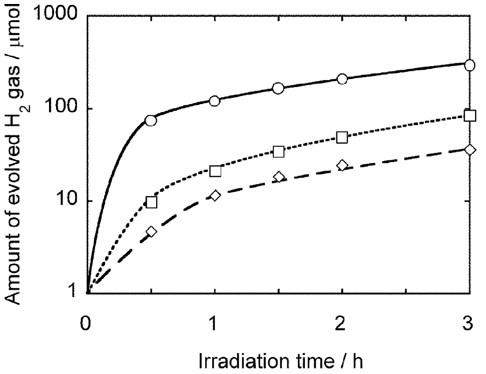


Fig. 5. Comparison of hydrogen production from various kinds of suspensions: (○) Pt/TiO_2, (□) Pt and TiO_2, (◇) GS and TiO_2. Methanol: 40 vol.%, UV strength: 15 mW cm^{-2}. Note the logarithmic ordinate.

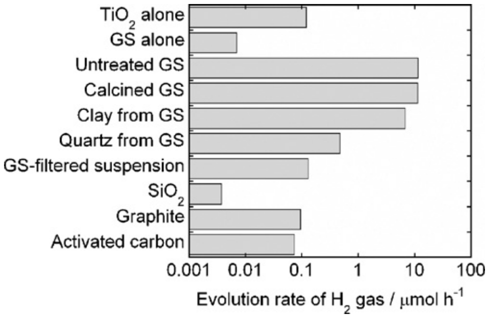


Fig. 6. Comparison of hydrogen production. Each powdered additive (15 mg) was added to powdered TiO_2 (15 mg). For TiO_2 alone and GS alone systems, the total amount of 30 mg was used. Methanol: 40 vol.%, UV strength: 15 mW cm^{-2}. Note the logarithmic abscissa.

not be deposited to TiO_2, the mixture of powdered Pt and TiO_2 was also examined. The synergy effect by the powdered GS was comparable to that by the powdered Pt. Therefore, the GS powder is considered to bear comparison with the co-catalytic Pt in the photocatalytic activity.

Fig. 6 shows the amount of hydrogen gas evolved from various suspended mixtures of TiO_2 with untreated GS, SiO_2, graphite, activated carbon, calcined GS, clay from GS, or quartz from GS.

An addition of powdered SiO_2 to TiO_2 suspension did not enhance the photocatalytic hydrogen production, but it was rather detrimental. The quartz from GS was also insufficient to enhance the hydrogen evolution. These indicate that the SiO_2 fraction is not effective for the photocatalytic reaction.

The suspended mixture of TiO_2 with graphite or activated carbon (Fig. 6) showed no enhancement effect for hydrogen production. However, the calcined GS with negligible carbon maintained ability to enhance the hydrogen gas evolution. The ability was almost equal to that of the untreated powder of GS. These results strongly suggest that the carbon in GS dose not play an important role in the synergy effect between GS and TiO_2.

The clay fraction separated from GS showed the synergy effect comparable to both powders of untreated and calcined GS as shown in Fig. 6. This fact indicates that the clay in GS is mainly responsible for the synergy effect of GS and TiO_2 for the hydrogen production.

Table 2 shows the metal species eluted from GS. We can see that various metal species are eluted from GS. As shown in Fig. 6 (see "GS-filtered suspension"), the presence of these metal species alone in the absence of the GS particles was not effective in the photocatalytic hydrogen production by TiO_2. This means that the interaction between GS and TiO_2 particles is important for the synergy effect.

Fig. 7 shows the time variation of pH after adding 30 mg of GS to 40 cm^3 of water containing no TiO_2. The pH values increased with time and reached equilibrium pH of about 8 after ca. 10 min from starting pH of 6, resulting in pH increments of about 2. The very similar pH increment by the presence of GS was also observed in water containing TiO_2. The pH increment and the elution of metal ions strongly suggest that GS particles exchange their metal ions for hydrogen ions in water.

Table 2
Metal species eluted from GS (30 mg) in water (50 cm^3)

Eluting species[a]	Amount (μmol)
Na	2.44
K	1.46
Ca	1.20
Ga	0.68
Si	0.61
Al	0.28
Mg	0.16
Nb	0.08
Mn	0.07
Hf	0.05

[a] Main species are listed.

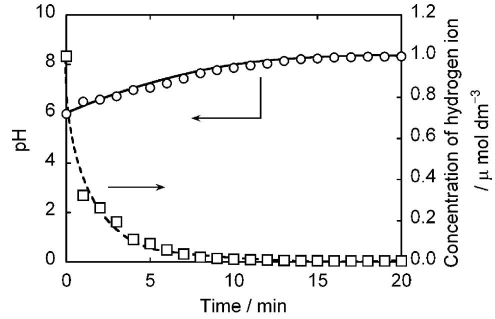


Fig. 7. Time course of pH variation of 40-cm^3 water containing 30 mg of the GS powder.

Fig. 8 shows the GS amount dependence of both the equilibrium pH and the exchanged hydrogen ions per 1-mg GS (Cp) which were estimated from the equilibrium pH. The Cp decreased steeply by the addition of GS and became nearly constant at around 0.1 μmol mg^{-1} at around 600 mg of GS. This suggests that most metal ions at active ion-exchange sites are replaced by the hydrogen ions in the suspension used for hydrogen production.

Sayama and Arakawa reported that an addition of carbonate salts to Pt-loaded TiO_2 suspensions leads to highly efficient stoichiometric photocatalytic decomposition of liquid water into H_2 and O_2 [15]. They found that neither the pH nor cation

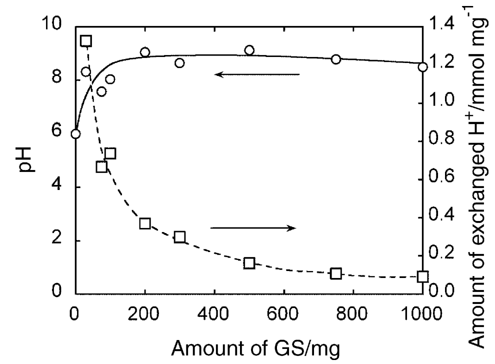


Fig. 8. The dependence of both the equilibrium pH and the exchanged hydrogen ions per 1-mg GS on the amount of GS. Various amounts of GS were added to 50 cm^3 of water.

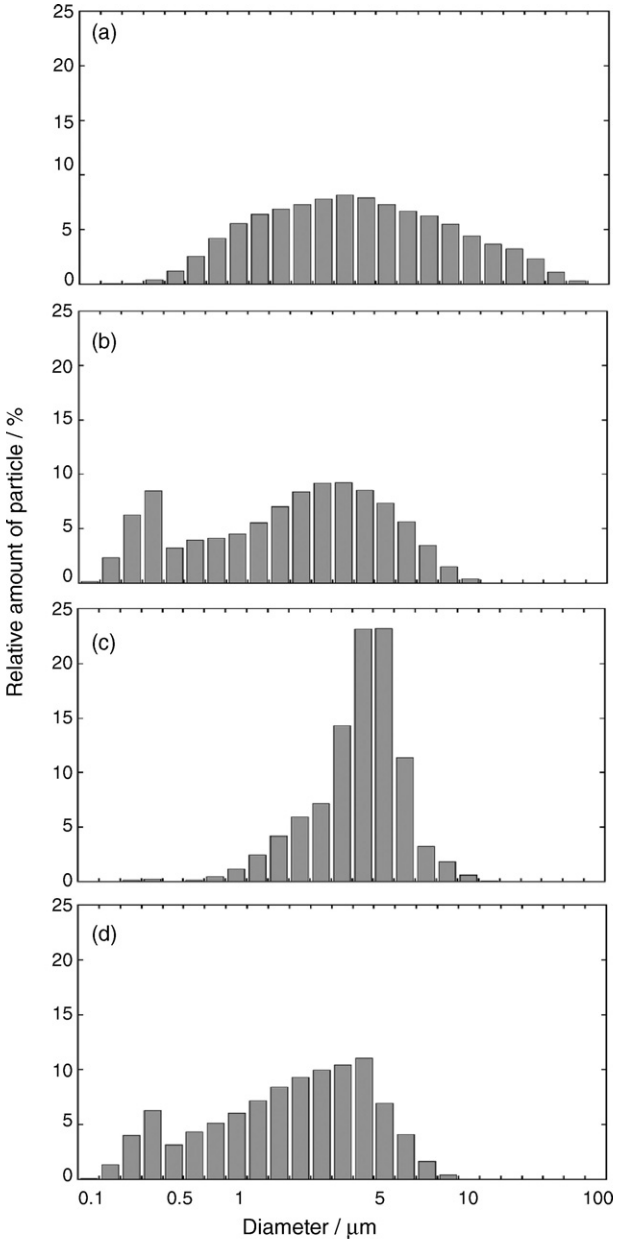


Fig. 9. Particle size distribution of several kinds of powders in water. (a) GS alone, (b) TiO_2 alone, (c) GS–TiO_2 mixture, and (d) after ultrasonication of GS–TiO_2 mixture. Note the logarithmic abscissa.

directly contributes to the water splitting, but the presence of a high concentration of carbonate ions is essential for the catalytic photodecomposition of water. This also strongly suggests that a simple shift of pH to higher values and the presence of cations are not effective, but the coexistence of GS and TiO_2 powders is essential for the photocatalytic hydrogen production in the present system.

Fig. 9 shows the particle size distribution of various suspensions. Fig. 9(a) and (b) are size distributions of GS and TiO_2 particles, respectively, which were added to water and allowed to stand for 1 day. It is considered that some particles of GS or TiO_2 are self-agglutinated. The size distribution of the GS–TiO_2 mixture is shown in Fig. 9(c). The pattern of distribution differs from a simple composite of those shown in Fig. 9(a) and (b). This result shows that the self-aggregates of GS or TiO_2 were reconstructed to co-aggregates of GS and TiO_2 by mixing them together. Fig. 9(d) shows the size distribution of the GS–TiO_2 mixture after ultrasonication. Some of co-aggregates were separated into small particles below around 1 µm in diameter by ultrasonication. Fig. 10 shows SEM images of samples after drying suspensions. Fig. 10(A) and (B) are photographs of GS and TiO_2 samples, respectively. The SEM images of the GS–TiO_2 mixture are shown in Fig. 10(C) and (D). We can see that TiO_2 particles agglutinate with certain parts of GS surface, especially as seen in Fig. 10(C). All the obtained data reveal that there is the strong interaction between GS and TiO_2.

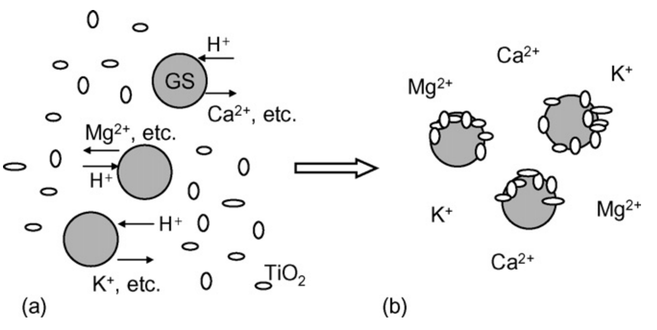
4. Discussion

Scheme 1 shows a plausible aggregation process between GS and TiO_2 in a stirring step before irradiation. The GS particles elute several kinds of metal ions and exchange them for hydrogen ions in suspension. The ion–exchange makes the surface of GS to a more hydrophilic and hydrogen-ion-rich one. The surface of a TiO_2 powder (Degussa, P 25) is hydroxylated (–TiOH) at around pH 6.6 [16,17]. However, the $–TiO^-$ groups coexist and become dominant at pH values higher than 6.6. Hence, GS clumps together with negatively charged TiO_2 to give the particles centered at a particle size of about 4 µm.

Taking these results into consideration, the reaction model is illustrated as shown in Scheme 2. It is considered that the hydrogen ions held in the clay are the main source of hydrogen gas evolved.

Though 15 mg of GS contains the clay components of about 3 mg, the co-catalytic 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.

In this connection, we also studied the addition effect of commercially and naturally available clay to TiO_2. The addition of the clay such as Kunipia F (99% sodium montmorillonite), Kunigel-V1 (natural Na-type bentonite) and Sumecton SA (synthesized smectite) of Kunimine Industries Co. Ltd., Bengel A (purified montmorillonite, Hojun Co. Ltd.) and kaolin (natural clay, mostly kaolinite) instead of GS to TiO_2 did not enhance the hydrogen production at all. This suggests that clay itself may not have the active sites for the hydrogen production and also



Scheme 1. (a) Ion exchange between metal ions and hydrogen ions by the clay in GS. (b) Aggregation of both particles of GS and TiO_2.

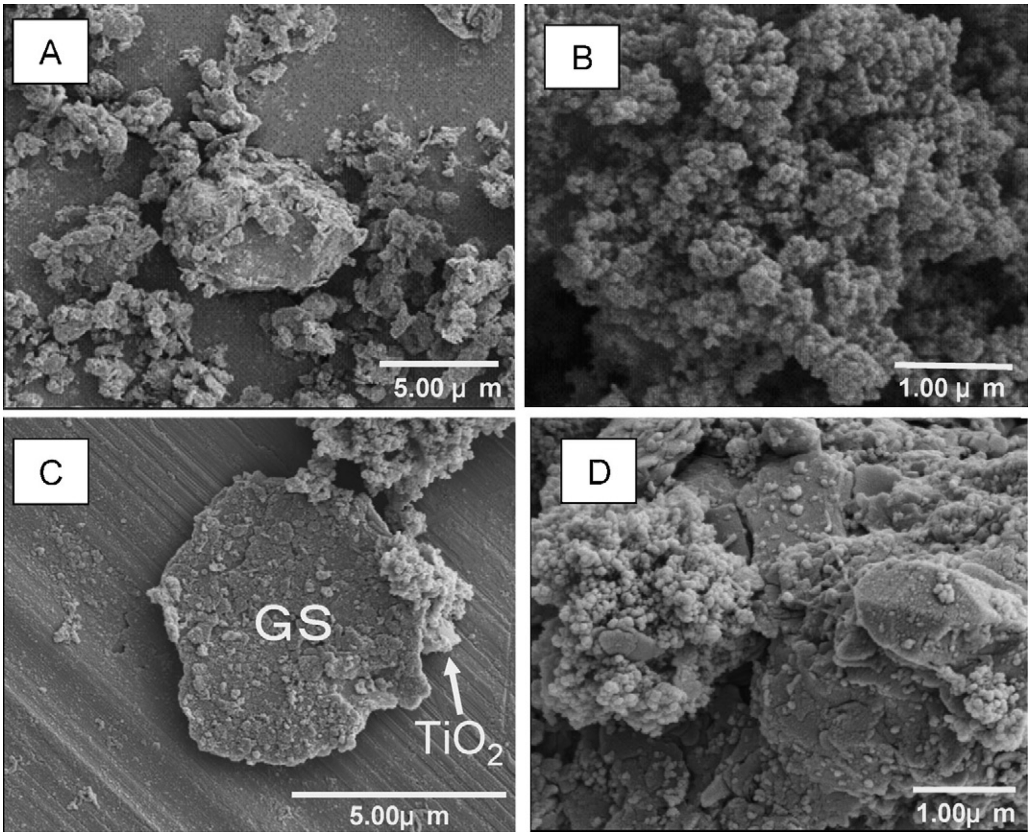
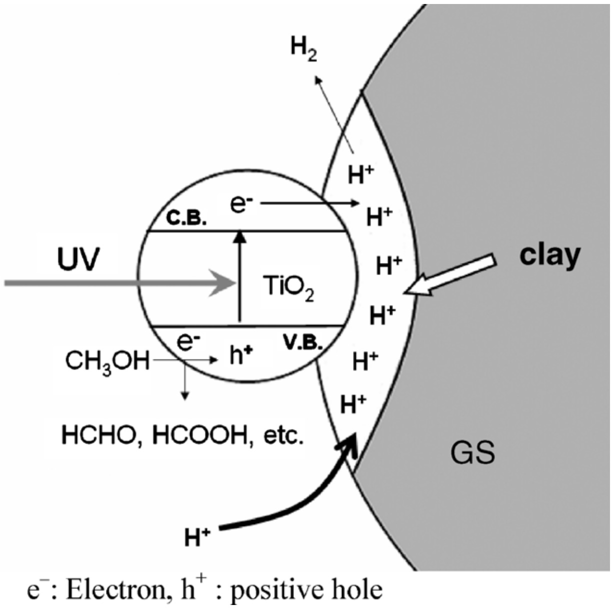


Fig. 10. SEM images of samples after drying suspensions. (A) GS, (B) TiO_2, (C), and (D) GS–TiO_2 mixture.



Scheme 2. Increment of hydrogen production by the photocatalytic reduction of hydrogen ions held in the clay in GS.

that the clay may play the lead in the hydrogen production when it is in GS.

Further studies are needed to clarify all aspects of the mechanism of the synergy effect and the detailed surface structure of GS.

5. Conclusions

A drastic synergy effect for hydrogen production from water–methanol mixtures was found for GS in collaboration with photocatalytic TiO_2. The amount of evolved hydrogen gas was increased by a factor of ca. 100 simply by mixing GS with TiO_2. To reveal the key component of the drastic synergy effect, the amount of evolved hydrogen gas was measured from various suspended mixtures of TiO_2 with untreated GS, SiO_2, graphite, activated carbon, calcined GS, clay from GS, or quartz from GS. The experimental results obtained showed that the clay in GS was a key component. It was concluded that the synergy effect is attributed to the enrichment of hydrogen ions in the clay components of GS and aggregation of GS and TiO_2 particles. The present study may be expected to contribute to the novel development of the practical co-catalyst in the photocatalytic production of hydrogen gas.

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