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Paper

Preparation of TiO_2 Fine Particles Supported on Silica Gel as Photocatalyst

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シリカゲル担持 TiO_2 微粒子光触媒の作製

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The composite silica gel which supported nanometer-size TiO_2 fine particles with platinum was prepared by the sol-gel method in order to obtain a high photocatalytic activity and to discuss the mechanism of photocatalytic hydrogen generation by TiO_2 fine particles in aqueous solution. The heat-treated composite gel showed hydrogen generation rate almost 4 times larger than that of TiO_2 sol in aqueous ethanol solution. However, little hydrogen was generated from pure deionized water. The photocatalytic activity of the composite gel is considered to be affected by both the surface condition and the crystalline phase of TiO_2 fine particles when the correlation among the changes with heat treatment in hydrogen generation rate was examined, the amount of photogenerated Ti^{3+} ions and the structure of composite gel. The superiority of the hydrogen photogeneration rate of the composite gel compared with a TiO_2 suspension system is attributed to its controllability of the crystallite size and the crystalline phase of semiconductor fine particles since they remain in a highly dispersive condition during heat treatment.

Key-words : *Photocatalyst, TiO_2, Silica gel, Fine particles, Sol-gel method, Hydrogen*

1. Introduction

Studies on photocatalytic properties of oxide semiconductors have been advanced since the photodecomposition of water using the photoelectrode of titanium dioxide (TiO_2) was reported,[1] because such materials are expected to be very effective for solar energy conversion such as hydrogen generation by photodecomposition of water and photosynthesis of organic molecules.[2)-4)]

For generation of hydrogen from water using photocatalysts, TiO_2 has been widely investigated because of its high efficiency of hydrogen generation and also its high photostability in an aqueous solution, even though it is activated only by irradiation of UV light.[5),6)]

When fine semiconductor particles are utilized as photocatalysts, they have various advantages such as the increment of surface area of photocatalysts and facility in diffusion of excited electrons and holes toward a reaction surface before their recombination. On the other hand, the quantum size effect of fine semiconductor particles is also notable in photocatalytic reactions. Anpo et al. reported that the photogeneration rate of hydrogen from water using TiO_2 fine particles steeply increased when the particle size was less than about 10 nm in diameter.[7]

This size effect was considered to be due to the decrement of the recombination rate of the photo-excited electrons and holes with the increment of band-gap energy of TiO_2.[8] However, the reaction mechanism of photogeneration of hydrogen from oxide semiconductor fine particles in aqueous solution has not clearly been established.

Heat treatment of TiO_2 fine particles is an effective procedure to alter their characteristics such as the number of surface Ti-OH groups, the surface area and the crystalline phase of TiO_2.

The investigation of the photocatalytic mechanism of semiconductor fine particles requires prevention of particle aggregation during heat treatment in order to maintain their nanometer size. When the fine particles are supported in porous materials, it will be possible to prevent particle aggregation and growth during heat treatment.

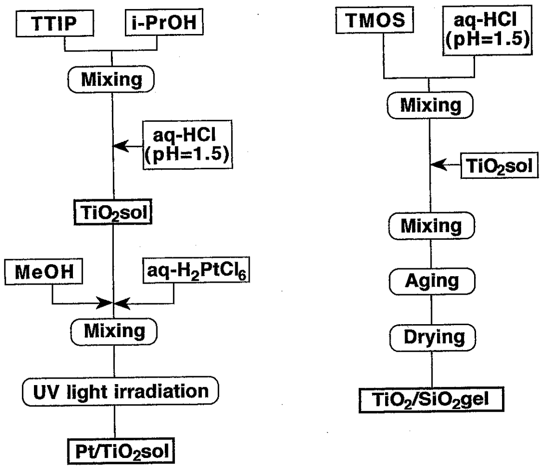
Various oxide semiconductors supported on SiO_2 particles or porous materials have been prepared in order to achieve the highly dispersive condition of catalysts or to investigate the mechanism of photocatalytic reactions.[9)-13)]

In this study, nanometer-size TiO_2 fine particles supported on silica gel, which has a large surface area, nanometer-size pores and high optical transparency in the UV/Vis region, were prepared in order to achieve the highly dispersive condition of nanometer-size semiconductor particles. The photocatalytic and structural properties of such composite materials were investigated and the mechanism of hydrogen photogeneration from TiO_2 fine particles was discussed.

2. Experimental

2.1 Sample preparation

TiO_2 fine particles were prepared by the hydrolysis of titanium iso-propoxide (TTIP), which is generally used for making TiO_2 fine particles by the sol-gel method.[14] Figure 1(a) shows the flow chart of the process for making TiO_2 fine particles. One hundred



(a) (b)

Fig. 1. Flow charts for the sample preparation.

ml of HCl aqueous solution (pH=1.5) was added dropwise to 4.05 ml of TTIP in 10 ml of iso-propanol (*i*-PrOH). The mixture solution initially became opaque but became a transparent sol upon storing at room temperature for 1 week.

The rate of photocatalytic hydrogen generation from TiO_2 sol is well-known to be accelerated with platinum because platinum facilitates the reduction of H^+.[15] Therefore, platinum was supported on TiO_2 fine particles by photocatalytic deposition of hydrogen hexachloroplatinate (Ⅳ) ($H_2PtCl_6 \cdot 6H_2O$).[16] The nominal composition of the prepared Pt-loaded TiO_2 (Pt/TiO_2) fine particles was 1 Pt–99 TiO_2 (wt%).

The silica gels supporting TiO_2 fine particles were prepared as shown in Fig. 1(b); 6.00 ml of silicon-tetramethoxide (TMOS) was hydrolyzed by 3.00 ml of HCl aqueous solution (pH=1.5) for 1 h. The obtained silica sol was mixed with 3.00 ml of TiO_2 sol or 3.25 ml of Pt/TiO_2 sol. The mixtures gelled and were dried at 60°C. The nominal composition of final composite gels supporting Pt-loaded TiO_2 fine particles ($Pt/TiO_2/SiO_2$ gel) and non-Pt-loaded TiO_2 fine particles (TiO_2/SiO_2 gel), excluding platinum, was 1 TiO_2–99 SiO_2 (mol%).

Both gels were subjected to heat treatment at various temperatures in the range from 120 to 800°C. First, each gel was kept at 60°C in vacuo and at 120°C in oxygen flow both for 1 h, in order to remove water and alcohol adsorbing in the micro pores of the composite gel. Then, the gels were heated at the rate of 1.5°C/min to 450°C in order to decompose the residual organic compound, and further heated to 800°C in vacuo.

2.2 Sample characterization

Dried Pt/TiO_2 sol at 60°C and $Pt/TiO_2/SiO_2$ gel heat-treated at 120°C were also observed by transmission electron microscopy (TEM; Hitachi, type H-9000) in order to determine the particle size and the microscopic structure of the gel.

Changes of the pore size distribution and the specific surface area of the samples upon heat treatment were measured by the nitrogen adsorption technique with the Quantachrome AUTOSORB-1 system.

The shift of the UV absorption edge on the composite gels from that of a pure silica gel was measured using the JASCO UVIDEC-610 spectrometer in order to obtain the band-gap energy of TiO_2 fine particles.

2.3 Photocatalytic properties

Photocatalytic activity of the heat-treated sample was evaluated by the measurement of the hydrogen generation rate in aqueous ethanol solution under UV light irradiation. Five grams of the heat-treated gel was immersed in 20 ml of 10 mol% aqueous ethanol solution or pure deionized water. The UV light from a 300 W Xe lamp passing through a water cell was irradiated onto the sample in Ar atmosphere for up to 2 h at room temperature. The amount of hydrogen generated was measured by gas chromatography (Shimadzu, type GC-6AM with TCD detector and 2-m silica gel column with Ar carrier gas).

Photoexcited electrons as Ti^{3+} ions are well-known to be intermediates of the photocatalytic reaction. Therefore, the amount of Ti^{3+} ions is taken as an indicator of the photocatalytic activity of TiO_2.[7] The amount of Ti^{3+} ions in the samples was measured by use of the ESR spectrometer, JEOL type JES-FE2XG. Various heat-treated gels were exposed to the vapor of aqueous ethanol solution or pure deionized water in advance. UV light was irradiated onto the samples for 10 min at room temperature. The samples were immediately cooled in liquid nitrogen and thus subjected to the ESR measurement at 77 K.

3. Results

3.1 Properties of TiO_2 particles and silica gel

The TEM micrograph of dried TiO_2 sol shows that the size of primary TiO_2 particles was 3–5 nm in diameter, as shown in Fig. 2(a). The TEM micrograph of the $Pt/TiO_2/SiO_2$ gel (Fig. 2(b)) shows that the gel consisted of particles of 20 to 40 nm. However, no independent primary TiO_2 particles of 3–5 nm were found in the micrograph of the composite gel. It has been reported that an alkoxy-derived silica gel is composed of 20 to 30-nm SiO_2 secondary particles which consist of <8-nm SiO_2 primary particles.[17] Therefore, the dispersive condition of TiO_2 fine particles in silica gel was difficult to establish from TEM observation because the particle sizes of primary TiO_2 and SiO_2 particles were very similar.

The TiO_2/SiO_2 gels were bulky, transparent and colorless and the Pt-loaded gels showed slight dark grayish color. The diameter of most pores in the Pt/

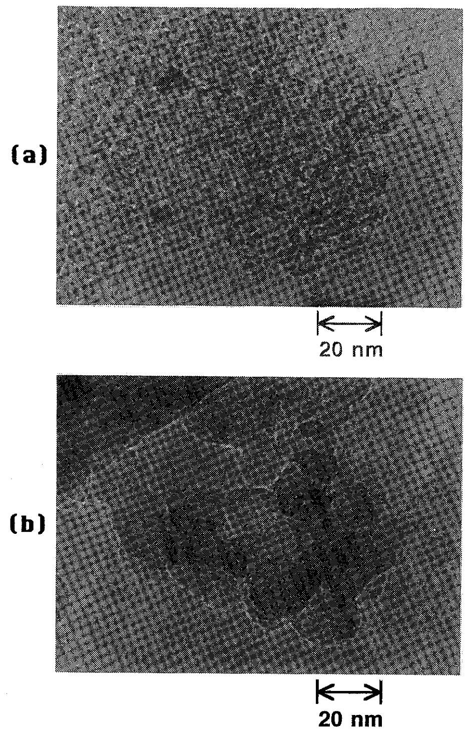


Fig. 2. TEM micrographs of (a) dried TiO_2 sol and (b) as-prepared $Pt/TiO_2/SiO_2$ gel.

TiO_2/SiO_2 gel was less than 2 nm, from the pore size distribution curve. Figure 3 shows the changes of specific surface area (S_g) of both samples upon heat treatment.

No difference of S_g or the shape of the pore size distribution curve was observed between the gels supporting Pt-loaded TiO_2 and non-Pt-loaded TiO_2 at 120°C. S_g of the $Pt/TiO_2/SiO_2$ gel was unchanged up to 450°C and decreased gradually at higher temperature. On the contrary, S_g of the TiO_2/SiO_2 gel had already decreased by about 85% of the initial value at 450°C, but the decreasing behavior of S_g at higher temperature was almost the same as that of the $Pt/TiO_2/SiO_2$ gel.

Figure 4 shows the UV/Vis spectra on the TiO_2/SiO_2 gel. The absorption edge of pure silica gel was about 280 nm. The absorption edge of TiO_2/SiO_2 gel was 360 nm after the heat treatment at 120°C and slightly blueshifted to 350 nm after the heat treatment at over 450°C. The blueshift of the absorption edge of the TiO_2/SiO_2 gel from those of anatase (383.7 nm=3.23 eV) and rutile (410.4 nm=3.02 eV) indicates the increment of band-gap energy of TiO_2 caused by the quantum size effect.[18] No appreciable shift of the absorption edge upon crystalline phase transformation of TiO_2 was observed in the range over 450°C. The absorption edge of $Pt/TiO_2/SiO_2$ gel was similar to that of the sample without platinum, though the transmittance decreased because of the scattering and absorption by platinum.

3.2 Photocatalytic properties

Hydrogen photogeneration was observed in all $Pt/TiO_2/SiO_2$ gels immersed in aqueous ethanol solution. The amount of photogenerated hydrogen increased linearly with exposure to UV light, at least up to 2 h. Figure 5 shows the change of hydrogen generation rate of the $Pt/TiO_2/SiO_2$ gels upon heat treatment. The rate had the maximum value of about 40 ml/h·TiO_2 g at around 450 or 500°C, which was almost 4 times as large as that of as-prepared Pt/TiO_2 sol.

On the other hand, when the sample was immersed in pure deionized water, the hydrogen generation rate of even the gel heat-treated at 450°C was very low, i.e., about 0.1 ml/h·TiO_2 g.

The samples without platinum heat-treated at 120 and 450°C showed only a trace (<0.01 ml/h·TiO_2 g) of photogenerated hydrogen even in aqueous ethanol solution, although the gel changed into a bluish color after UV light irradiation, which was caused by the formation of Ti^{3+} ions.[19] This color change suggests that a significant amount of Ti^{3+} ions was generated

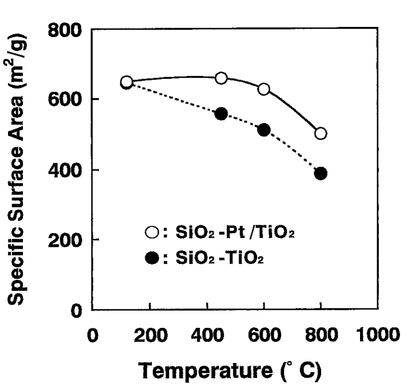


Fig. 3

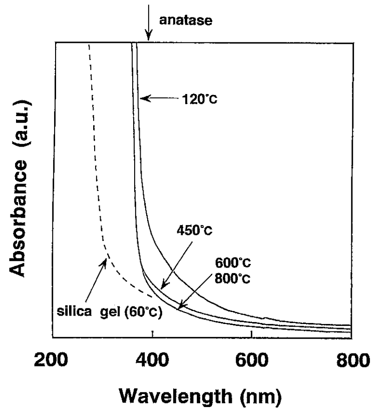


Fig. 4

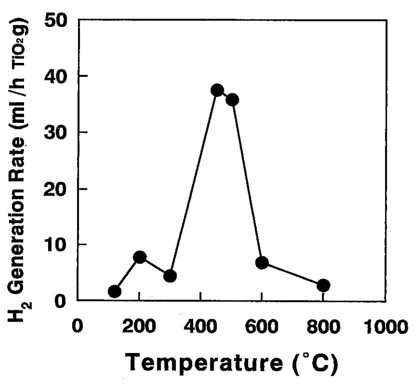


Fig. 5

Fig. 3. Changes of specific surface area of the $Pt/TiO_2/SiO_2$ and TiO_2/SiO_2 gels.
Fig. 4. Change of UV/Vis spectra of the TiO_2/SiO_2 gel with heat treatment.
Fig. 5. Change in hydrogen generation rate of the $Pt/TiO_2/SiO_2$ gel with heat treatment.

but H^+ ions were not reduced.

Figure 6 shows the ESR spectra of the samples heat-treated at 450°C. The signal at around 3400 Gauss ($g=1.94$) is assigned to Ti^{3+} ions and that at around 3270 Gauss ($g=2.01$) is considered to be attributed to oxygen radicals.[7] It was found that the Ti^{3+} signal of the sample adsorbing aqueous ethanol solution was much stronger than that of the sample adsorbing pure deionized water. The change in the ratio of Ti^{3+} ions to total Ti ions with heat treatment is shown in **Fig. 7**. In the $Pt/TiO_2/SiO_2$ gel adsorbing aqueous ethanol solution, the ratio of Ti^{3+} ions once decreased and then increased over 300°C, and the ratio had the maximum value at around 500°C. This temperature was almost the same that at which the hydrogen generation rate was a maximum. Only 0.6% of Ti ions in the gel heat-treated at 500°C changed into Ti^{3+} ions upon UV light irradiation. This indicates that the electrons of TiO_2 ions at or near the surface of the particles were photoexcited. The signal of oxygen radicals increased markedly over 600°C.

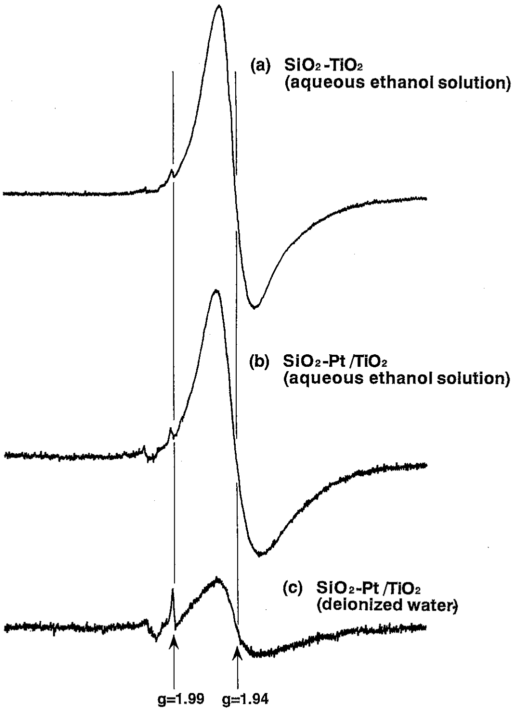


Fig. 6. ESR spectra of various samples heat-treated at 450°C.

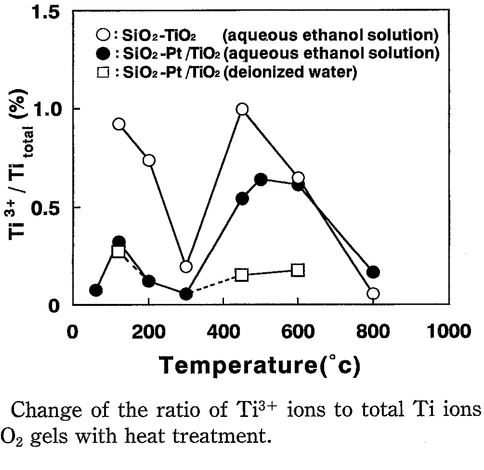


Fig. 7. Change of the ratio of Ti^{3+} ions to total Ti ions in the TiO_2/SiO_2 gels with heat treatment.

In TiO_2/SiO_2 gel samples, larger amounts of Ti^{3+} ions were generated, especially at 120 and 200°C in comparison with the sample containing platinum, but the change of the ratio was similar to that of samples with platinum. On the contrary, few signals of Ti^{3+} were detected for $Pt/TiO_2/SiO_2$ gel samples adsorbing not ethanol but only pure deionized water.

4. Discussion

In the present study, some notable results for photocatalytic reaction were obtained.

(a) The hydrogen photogeneration rate of $Pt/TiO_2/SiO_2$ gel in aqueous ethanol solution was much higher than that in pure deionized water.

(b) Without loading platinum onto the TiO_2 fine particles, only a trace of hydrogen photogeneration was observed, even in aqueous ethanol solution.

(c) Among the $Pt/TiO_2/SiO_2$ gels subjected to various temperatures, the gel yielding the highest concentration of Ti^{3+} upon UV light irradiation showed the largest hydrogen generation rate.

Various mechanisms of hydrogen photogeneration on Pt-loaded TiO_2 in aqueous solution have been proposed. In a water–ethanol or iso-propanol system, it was reported that $\dot{O}H$ radical species, especially surface $Ti-\dot{O}H$ groups, are involved in the mechanism of hydrogen photogeneration and that hydrogen photogeneration occurs not by photodecomposition of water but by photo-deprotonation of alcohol.[20),21)] Therefore, the reaction of hydrogen photogeneration in a water–ethanol system is explained as

$$Ti^{4+}\text{-}OH^- \xrightarrow{h\nu} Ti^{3+}\text{-}\dot{O}H \qquad (1)$$

$$2Ti^{3+}\text{-}\dot{O}H \longrightarrow 2Ti^{4+}\text{-}\dot{O}H+2e^-(\text{on Pt}) \qquad (2)$$

$$Ti^{4+}\text{-}\dot{O}H+C_2H_5OH \longrightarrow Ti^{4+}\text{-}OH^-+C_2H_5\dot{O}+H^+ \qquad (3)$$

$$Ti^{4+}\text{-}\dot{O}H+C_2H_5\dot{O} \longrightarrow Ti^{4+}\text{-}OH^-+CH_3CHO+H^+ \qquad (4)$$

$$2H^++2e^- \longrightarrow H_2 \qquad (5)$$

When platinum is not loaded onto the TiO_2 particles, an excited electron trapped as a Ti^{3+} ion cannot move into platinum. Consequently, not reaction Eq. (5), but the reverse of reaction Eq. (1) proceeds. When ethanol is not present in the reaction system, the following reaction may proceed instead of reaction Eq. (3) :

$$Ti^{4+}-\dot{O}H+H_2O \longrightarrow Ti^{4+}-OH^-+\dot{O}H+H^+ \qquad (6)$$

In this case, the generated $\dot{O}H$ radical and a H^+ ion immediately recombine with an excited electron;

thus, hydrogen will not be yielded.

$$\dot{O}H + H^+ + e^- \longrightarrow H_2O \qquad (7)$$

This difference of these reaction mechanisms can explain our experimental results described in (a) and (b) above.

On the other hand, the characteristics of composite gel, such as the crystalline phase and the particle size of TiO_2, the surface area and the pore diameter of silica gel, are thought to significantly affect the photocatalytic properties. Although the dispersive condition of TiO_2 fine particles in silica gel was not found in our TEM observation, considering that the composite gel consisted of primary silica and TiO_2 fine particles at almost the same size and had large surface area, pore size and porosity, it is considered that the TiO_2 fine particles are sufficiently dispersed in silica gel to maintain their quantum size during heat treatment, and that the gel has pores of sufficient size for photogenerated substances to move out of the gel.

According to Sasamoto et al., TiO_2 particles prepared by the hydrolysis of TTIP were amorphous at temperatures up to about 200°C. Amorphous TiO_2 became anatase at that temperature and was unchanged until it was transformed into the rutile phase at around 600°C.[22] Nishimoto et al. reported that anatase shows high activity for hydrogen photogeneration from aqueous alcohol solution, whereas amorphous TiO_2 and rutile were much less active.[6] This is explained to be due mainly to the low energy level of excited electrons.[8]

Considering our results and the above reports, the change of hydrogen photogeneration rate upon heat treatment is explained as follows.

As-prepared TiO_2 fine particles formed by hydrolysis and polycondensation of TTIP had a significant number of $-OH$ groups and unreacted $-O-C_3H_7$ ($-OR$) groups on their surfaces. Therefore, a considerable amount of Ti^{3+} ions were generated in TiO_2 particles upon UV light irradiation, as represented by reaction Eq. (1). The photogenerated Ti^{3+} ions were stable in the non-Pt-loaded samples because the rate of recombination between excited electrons and holes decreased with the increment of the band-gap energy of TiO_2,[8] whereas Ti^{3+} ions were unstable in $Pt/TiO_2/SiO_2$ gels where the excited electrons moved toward platinum on TiO_2 and reacted with H^+ ions there. Thus, the amount of photogenerated Ti^{3+} ions in $Pt/TiO_2/SiO_2$ gel was less than that in samples without platinum, as shown in Fig. 7.

Polycondensation among adjacent $-OH$ groups in TiO_2 particles proceeds even at low temperature. On the other hand, thermal decomposition of $-OR$ groups normally occurs in the temperature range from 300 to 500°C and they change into $-OH$ groups. Therefore, the marked decrement of Ti^{3+} ions between 120 and 300°C in the sample without platinum may be attributed to the large reduction in the number of Ti–OH groups due to polycondensation. This reduction of Ti–OH groups was represented as the decrement of the specific surface area, in Fig. 3. Also this is the reason why hydrogen generation was not extensive in this temperature range, even though TiO_2 was expected to have changed into photoactive anatase.

Heat treatment at temperatures ranging from 400 to 500°C changed Ti–OR groups on the surface of anatase into Ti–OH groups, and a large number of Ti^{3+} ions were again generated upon UV light irradiation. Some of these Ti^{3+} ions in $Pt/TiO_2/SiO_2$ gel were consumed in the reduction of H^+. The amount of Ti^{3+} ions in the heat-treated sample was, therefore, less than that in TiO_2/SiO_2 gel.

A large number of Ti–OH groups still remained on the surface of TiO_2 after heat treatment at around 600°C because a considerable amount of Ti^{3+} ions were generated. However, the phase of TiO_2 was considered to have already been transformed into rutile, so that the hydrogen generation rate decreased suddenly. Above this temperature, not only did polycondensation of Ti–OH groups proceed, but also, silica gel itself began to be sintered, as represented by the decrement of specific surface area. Therefore, this composite gel no longer functioned as photocatalyst.

Because of the highly dispersive condition of TiO_2 fine particles in silica gel, the composite material showed a good photocatalytic property compared with the suspension system of the same particles. The reason seems to be that the nanometer size of TiO_2 particles, that is, the large reaction surface area with Ti–OH groups, was maintained to higher temperature, and that the energy level of excited electrons became higher and consequently, the frequency of recombination between excited electrons and holes became lower.

In this study, little hydrogen photogeneration was observed from pure deionized water. This seems to be because the reaction between oxidized and reduced substances immediately proceeded at the platinum on the TiO_2 particles. In order to efficiently achieve photogeneration of H_2 and O_2 from pure water, it is necessary that the reduction and oxidation sites on the photocatalyst be completely separated to maintain quantum size in order to prevent the reaction between oxidized and reduced substances on it. Therefore, the composite material which is a semiconductor photoelectrode of a two-dimensional quantum plane supported on a porous substrate will be an efficient photocatalyst which has the desired structure for perfect photodecomposition of water.

5. Summary

The composite silica gel which supported nanometer-size TiO_2 fine particles with platinum was prepared by the sol-gel method in order to obtain a high photocatalytic activity and to discuss the mechanism of photocatalytic hydrogen generation by TiO_2 fine particles in aqueous solution.

The heat-treated composite gel showed a hydrogen generation rate almost 4 times larger than that of the TiO_2 sol in aqueous ethanol solution. However, little hydrogen was generated from pure deionized water.

The photocatalytic activity of the composite gel is considered to be affected by both the surface condition and the crystalline phase of TiO_2 fine particles when the correlation among the changes with heat treatment in hydrogen generation rate, the amount of photo-generated Ti^{3+} ions and the structure of composite gel was examined. The superiority of the hydrogen photogeneration rate of the composite gel compared with a TiO_2 suspension system is attributed to its controllability of the crystallite size and the crystalline phase of semiconductor fine particles since they remain in a highly dispersive condition during heat treatment.

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