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Instructions for use

Asymmetrically modified titanium(IV) oxide particles having both hydrophobic and hydrophilic parts of their surfaces for liquid-liquid dual-phase photocatalytic reactions

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Abstract

Titanium(IV) oxide (TiO_2)-based photocatalyst particles assembled at the phase boundary of a liquid-liquid dual-phase mixture were prepared by partial modification of the external surface of each particle with alkylsilyl groups. Average surface coverage of alkylsilyl groups estimated by elemental analyses of carbon and ash components of the samples and floatability on aqueous ethanol solutions revealed that the hydrophobicity-hydrophilicity of asymmetrically modified samples was comparable to that of samples fully covered with alkylsilyl groups. TiO_2 particles asymmetrically or fully modified with alkylsilyl groups showed photocatalytic activity for benzene oxidation to produce phenol from an aerated benzene-water dual-phase mixture even without agitation, while bare TiO_2 required mechanical agitation to induce the photocatalytic reaction. However, prolonged irradiation precipitated some of the

surface-modified particles in the aqueous layer due to photocatalytic decomposition of surface alkylsilyl groups. The photostability was improved by employment of TiO_2 particles coated with porous silica (SiO_2) as a starting material. Compared with the SiO_2-coated TiO_2 particles fully modified with alkylsilyl groups (o-Si/Ti), the asymmetrically modified SiO_2-TiO_2 particles (w/o-Si/Ti) showed slightly higher photocatalytic activity for benzene oxidation. On the other hand, a notable difference between them was observed in photocatalytic hydrogen evolution in the presence of sacrificial donors from a benzene-water mixture and from an aqueous solution under deaerated conditions; w/o-Si/Ti showed the activity more than two-fold greater than that of o-Ti/Si, presumably because of efficient contact of w/o-Si/Ti with both aqueous and organic phases compared with o-Si/Ti, which was rather difficult to contact with the aqueous phase.

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1. Introduction

Heterogeneous photocatalytic processes are induced by photoexcitation of semiconductor particles such as titanium(IV) oxide (TiO_2) with light of energy greater than the band gap between valence and conduction bands to generate electrons (e^-) and positive holes (h^+) as reductants and oxidants, respectively, for substrates adsorbed on the photocatalyst surfaces [1]. Since both e^- and h^+ are, in principle, consumed in each particle, the particle itself works as a small photoelectrochemical cell, i.e., both oxidation and reduction occur in a one-pot reaction without providing electrolytes, which are requisite for a similar redox reaction, electrolysis [2,3]. This characteristic feature provides various types of redox reactions, e.g., overall water splitting into H_2 (produced through reduction of water by e^-) and O_2 (produced through oxidation of water by h^+) [4-6] and redox-combined processes, including deamino-N-cyclization of L-lysine into pipecolinic acid [7-9].

Photocatalytic reactions using powder photocatalysts are generally performed by photoirradiation of aqueous suspensions containing photocatalyst particles and substrate(s). In cases in which substrates are immiscible in water, organic solvents having relatively high stability toward redox reactions, such as acetonitrile, are used to prepare homogeneous solutions [10-12]. Although it is quite convenient to use such a suspension system for the evaluation of photocatalytic activities of photocatalyst powders, there have been a few disadvantages for practical applications. For instance, when the wavelength range of photoabsorption of solvents and/or substrates is overlapped with that of the photocatalyst, the number of photons absorbed by the photocatalyst must be reduced and, thereby, the rate of the photocatalytic reaction is reduced. Moreover, photoexcitation of solvents and/or substrates may induce unexpected side reactions. Also, a serious problem of the suspension system in practical applications is that filtration or centrifugation is necessary to recover (remove) photocatalysts from the reaction mixtures. Adhesion of photocatalyst particles to

optically transparent materials, such as a glass plate, is one way to overcome these two problems. However, transportation of chemical species across the plate is highly restricted. Another strategy to simultaneously achieve selective photoabsorption of photocatalyst particles and simplified isolation of products from the mixture is to assemble the photocatalyst particles at the interface between gas and liquid phases or, in the case of a mixture of immiscible liquids, aqueous and organic phases. Photoirradiation can be performed from one side of the phase without components interrupting the light, and the reaction solutions can be collected and/or exchanged without filtration or centrifugation to remove photocatalyst particles. Furthermore, this particle membrane system guarantees the transportation of chemicals through it.

Recently, we have found a novel method for assembling zeolite particles at a liquid-liquid phase boundary between aqueous hydrogen peroxide and water-immiscible organic substrates such as 1-octene by partial modification of the external surface of each zeolite particle with alkylsilyl groups [13-16]. The strategy for particle modification was based on aggregation of hydrophilic particles with a small amount of water, which is similar to "impregnation" for metal loading on supports, followed by reaction with a hydrophobic alkylsilylation agent. Since the binding water between particles prevents penetration of the agent into the aggregates, alkylsilyl groups can be attached only on the outer parts of aggregates. Thus, the surfaces of resulting zeolite particles were proved to be bimodal, having both hydroxyl and alkylsilyl faces [15]. One of the most noticeable features is that the assembled particles loaded with small amounts of titanium oxide acted as an efficient catalyst for epoxidation of several alkenes without agitation [14]. The reaction system is thus named phase-boundary catalysis.

From these considerations and facts, we applied the above-mentioned method for partial modification of the external surface of TiO_2 to prepare bimodal TiO_2 photocatalyst particles that can be assembled at a phase boundary. In this paper,

characteristics of the surface and photocatalytic activity of the bimodal TiO_2 particles are described in detail. The usefulness of porous silica (SiO_2)-covered TiO_2 for improving stability against photoirradiation is also discussed.

2. Experimental

2.1 Materials

TiO_2 and SiO_2-coated TiO_2 particles were supplied from Merck (anatase, 11 m^2 g^{-1}) and Taihei Kagaku Sangyo (a mixture of anatase and rutile, 85% of TiO_2, 150 m^2 g^{-1}) [17] and used as received. Here, these hydrophilic bare particles are labeled w-Ti and w-Si/Ti, respectively. Other commercial chemicals were of the highest available grade and used without further purification. Laboratory-grade water was prepared by using a Milli-Q pure water system (Yamato-Millipore).

2.2 Modification of particle surface with an alkylsilylation agent

Functionalization of external surfaces of w-Ti and w-Si/Ti with alkylsilyl groups was carried out using the procedure reported for zeolite particles [13-16]. To 1 g of w-Ti or w-Si/Ti, an appropriate amount of water was added and the mixture was stirred until the added water had been soaked into the aggregates. The amount of water was adjusted depending on the sorption capacity of TiO_2 samples (typically, 0.36 cm^3 for w-Ti and 0.90 cm^3 for w-Si/Ti). Then the thus-obtained aggregates were suspended in 10 cm^3 of toluene containing 500 μmol of octadecyltrichlorosilane (ODS). After shaking the mixtures for 5 min at room temperature, the suspensions were centrifuged and washed with chloroform (50 cm^3) and ethanol (50 cm^3) to remove unreacted ODS and a

by-product, hydrogen chloride. The precipitate was then dried at 383 K overnight. The resulting powders are labeled w/o-Ti and w/o-Si/Ti, respectively. Samples with external surfaces thoroughly covered by alkylsilyl groups were also prepared without addition of water to make aggregates before the reaction with ODS. These samples are called o-Ti and o-Si/Ti, respectively.

2.3 Characterization and analytical procedures

Based on the weight fractions of carbon and ash components obtained by elemental analysis, the amount of surface alkylsilyl groups was determined by assuming that the remaining ash is composed of a mixture of TiO_2 and SiO_2. Since the carbon component was mostly less than 6 wt% and the error in data in elemental analysis was less than 0.3%, the estimated amounts might include a large error. However, we could confirm reproducibility within ±5% for some selected samples. Floatability of w-Si/Ti, w/o-Si/Ti, and o-Si/Ti in various concentrations of aqueous ethanol solutions was evaluated as follows. To 5 cm^3 of a given concentration of aqueous ethanol, a 10-mg portion of w-Si/Ti, w/o-Si/Ti, or o-Si/Ti was added. After shaking for a few minutes, the mixture was centrifuged and the precipitates were collected. The percent fraction of floated particles was calculated as the difference between weights of added and precipitated particles.

2.4 Photoirradiation and product analysis

Each sample (10 mg) was added to (**a**) a dual-phase mixture of benzene (2 cm^3) and H_2O (1 cm^3), (**b**) a mixture containing 1-octanol (0.1 cm^3) and chloroplatinic acid (H_2PtCl_6, 0.4 mg) or (**c**) 5% of aqueous methanol (3 cm^3) containing 0.4 mg of H_2PtCl_6 and phoroirradiated in air (**a**) or argon (Ar) (**b** and **c**). Photoirradiation was performed

using a xenon arc (Ushio UXR-300DU, 300 W) from the bottom of a cylindrical reaction vessel (transparent at >290 nm, 3.2 cm in diameter) at 298 K. When necessary, the reaction mixture was agitated vigorously with a magnetic stirrer with photoirradiation from a side of the reaction vessel. Liberated phenol, carbon dioxide (CO_2), and hydrogen (H_2) were analyzed using a Shimadzu GC-14B gas chromatograph equipped with an FID and a DB-1 column (for phenol) and a Shimadzu GC-8A gas chromatograph equipped with a TCD and an MS-5A column (for H_2) or a Porapak Q column (for CO_2).

3. Results and discussion

3.1 Surface characteristics of modified photocatalysts

Figure 1 shows the apparent locations of samples added to the dual-phase mixture of water and benzene. Since w-Ti and w-Si/Ti are originally hydrophilic owing to their surface hydroxyl groups, they were dispersed only in water upon addition to the water-benzene mixture. By thorough surface treatment with ODS, these particles (o-Ti and o-Si/Ti) became hydrophobic due to the surface coverage of alkylsilyl groups and they were well dispersed in benzene. On the other hand, the alkylsilylated samples prepared *via* ODS treatment of aggregates with water (w/o-Ti and w/o-Si/Ti) were assembled at the liquid-liquid phase boundary. Similar behavior was also observed when toluene, hexane or another solvent immiscible with water was used instead of benzene. These results resembled those obtained by using surface-modified samples derived from NaY zeolite [14,15]. Therefore, as has been proved for NaY zeolite powder, it is assumed that each particle of w/o-Ti and w/o-Si/Ti has an asymmetric surface structure, with both hydroxyl and alkylsilyl faces.

The overall hydrophobicity-hydrophilicity of particles was evaluated by checking their behavior when added to water-ethanol mixtures of various compositions. Figure 2 shows the amounts of floating, floatability, w-Si/Ti, w/o-Si/Ti, and o-Si/Ti particles as a function of weight fraction of ethanol in water. Owing to its surface hydrophilicity, the original bare sample (w-Si/Ti) was precipitated in the whole range of the ethanol fraction as expected. On the other hand, both modified samples (w/o-Si/Ti and o-Si/Ti) floated almost completely, i.e., without any appreciable precipitation, when the weight fraction of ethanol was less than 35%, indicating their hydrophobic surface characters. With increase in the ethanol fraction from 40 to 60%, some of both the w/o-Si/Ti and o-Si/Ti particles settled, and complete sedimentation of both samples was observed when the ethanol fraction greater than 65%. At present, we have no technique to check the floatabilities of particles, which may have different extents of surface modification and properties, e.g., particle size. Hence, in the intermediate ethanol fraction range (ca. 40-60%), the difference between surface coverages of floating and precipitated particles can not be discussed. However, it is clear from these results that w/o-Si/Ti and o-Si/Ti exhibited similar behaviors, suggesting that they have, overall, comparable degree of hydrophobicity-hydrophilicity.

Table 1 shows the amounts of alkylsilyl groups attached to the samples (M_a / μmol g^{-1}) estimated from their carbon and ash compositions. No appreciable amount of carbon was detected in the bare samples (w-Ti and w-Si/Ti), indicating that there was negligible contamination of organic residues on their surfaces. For each TiO_2 sample, w-Ti and w-Si/Ti, asymmetrical and full modification with an alkylsilylation agent gave almost the same M_a; M_a was independent of the modification procedure. The approximately 5-times larger M_a on w/o- and o-Si/Ti than on w/o- and o-Ti was mainly attributable to the differences in specific surface area and in reactivity of hydroxyl groups on their surfaces. The above-described results of floatability tests (Fig. 2) suggest that the overall hydrophobicity of the samples is governed predominantly by

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M_a.

Using M_a (Table 1), external surface area, and the estimated cross section of an alkylsilyl group (0.226 nm^2) [18], surface coverage of w/o-Ti and o-Ti was calculated to be ca. 70%, i.e., ca. 30% of o-Ti surface remained uncovered with alkylsilyl groups in the present preparation procedure. However, as shown in Fig. 1, the sample was well dispersed in the organic phase, while w/o-Ti with almost the same surface coverage of alkylsilyl groups was assembled at the interface. Similar behavior was also observed when M_a was halved (data not shown). These results imply that the mode of distribution of alkylsilyl groups on the surface accounts for the apparent location of the modified particles in a water-oil mixture and that M_a or overall hydrophobicity can not predict the location.

3.2 Phase-boundary photocatalytic reactions

When a dual-phase mixture of benzene and water containing w-Ti, w/o-Ti, or o-Ti was photoirradiated from the bottom of the reaction vessel, phenol and CO_2 were liberated as major products with production of small amounts of other by-products such as hydoroquinone and 1,4-benzoquinone. Table 2 shows the amounts of liberated phenol and CO_2 and the selectivity of phenol production, defined as the molar fraction of phenol in the major products liberated by 20-h irradiation at 298 K. On w-Ti, only small amounts of phenol and CO_2 were detected when photoirradiation was performed without stirring (entry 1), and marked acceleration was observed when the mixture was vigorously stirred (entry 2), i.e., the hydrophilic w-Ti photocatalyst requires mechanical agitation to drive the photocatalytic reaction. On the other hand, comparable amounts of phenol and CO_2 were produced on w/o-Ti and o-Ti even without agitation (entries 3 and 4). Improvement in contact between the hydrophobic substrate (benzene) and particles by their surface alkylsilylation might account for this. It is worth noting that when

compared to the results obtained for w-Ti under stirring, the production of CO_2 was reduced to give relatively high selectivity of phenol production. These facts indicate that there is a potential advantage of the phase-boundary photocatalytic reaction system for partial oxidation of organic compounds, though the phenol yield was lowered to ca. 75%. However, an inevitable disadvantage of the present system is low photostability of the modified particles; some of the w/o-Ti and o-Ti particles settled during the photoirradiation. As has been previously observed using TiO_2 fully modified with several alkylsilane reagents [19], the instability was attributed to photodecomposition of alkylsilyl groups on the surface through the photocatalytic reaction of TiO_2. Actually, elemental analysis of o-Ti after photoreaction, for example, revealed that ca. 50% of alkylsilyl groups were removed from the catalyst surface.

In order to improve the photostability, we employed TiO_2 particles coated with porous silica (w-Si/Ti) and modified their surface with alkylsilyl groups (w/o-Si/Ti and o-Si/Ti). As expected, upon photoirradiation in a dual-phase mixture of benzene and water, neither w/o-Si/Ti particles or o-Si/Ti particles changed their location, i.e., w/o-Si/Ti was assembled at the phase boundary and o-Si/Ti was dispersed in the organic phase after the prolonged irradiation, though ca. 10% of alkylsilyl groups was removed from w/o-Si/Ti after 20-h photoirradiation. Since alkylsilyl groups on w/o-Si/Ti and o-Si/Ti particles were possibly attached to surfaces of both coated SiO_2 and TiO_2 particles, the photoinduced removal of alkylsilyl groups attached to the bare TiO_2 surface might occur without changing the hydrophobicity-hydrophilicity balance.

Similar to the above-mentioned TiO_2 photocatalysts derived from w-Ti, w/o-Si/Ti and o-Si/Ti showed photocatalytic activity for benzene hydroxylation that was greater than that of the original w-Si/Ti powder (Table 2, entries 5-7) when the reaction was performed without mechanical agitation. It is also notable that w/o-Si/Ti gave a slight higher yield of phenol than that obtained from o-Si/Ti. This trend is different from the above-described results for the w-Ti-based system in which o-Ti showed an activity

level that was comparable with, or slightly higher than, that of w/o-Ti. Although the detailed reaction mechanism is unclear at present, control experiments indicated that the production of phenol required the presence of oxygen and a small amount of water (data not shown). Therefore, the higher yield of phenol by w/o-Si/Ti is attributable to its effective contact with both benzene and aqueous phases, while the reaction might proceed in the benzene phase using dissolved oxygen and water. On the other hand, due to the partial decomposition of surface alkylsilyl groups leading to exposure of the hydrophilic surface on w/o-Ti and o-Ti as discussed above, the affinity to both phases might become comparable to exhibit similar photoactivity.

As an extension of the phase-boundary photocatalytic reactions, photoinduced reduction of water to produce H_2 in the presence of sacrificial electron donor under deaerated conditions was conducted using photostable w/o-Si/Ti and o-Si/Ti particles. Figure 3 shows time-course curves of H_2 liberation from the water-benzene mixture in the presence of H_2PtCl_6 in water and 1-octanol in benzene. In this system, photoexcited electrons (e^-) reduce chloroplatinic ions dissolved in water to make platinum deposits which act as a catalyst for reduction of water into H_2 using e^-, and positive holes (h^+) oxidize 1-octanol dissolved in benzene, i.e., reduction and oxidation proceed in aqueous and organic phases, respectively. Due to the absence of electron donor, to be oxidized by h^+, in the aqueous phase, a negligible amount of H_2 was liberated on w-Si/Ti dispersed only in the aqueous phase. On the other hand, w/o-Si/Ti and o-Si/Ti showed appreciable photocatalytic activity, and w/o-Si/Ti showed a rate of H_2 liberation two-times higher than that of o-Si/Ti. These results are again attributed to the efficient contact of both aqueous and organic reagents with w/o-Si/Ti, while the contact with o-Si/Ti sample seems less efficient, especially for the aqueous phase.

In order to prove the difference between affinity of w/o-Si/Ti and that of o-Si/Ti to the aqueous phase, photocatalytic production of H_2 from aqueous methanol solution in the presence of H_2PtCl_6 was performed. Figure 4 shows the results. In this system,

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both w/o-Si/Ti and o-Si/Ti floated on the aqueous solution, i.e., visual observation showed practically no difference between them. However, the rate of H_2 production on w/o-Si/Ti was more than three-times higher than that on o-Si/Ti, indicating that photocatalytic reduction of water into H_2 using e^- and oxidation of methanol by h^+ efficiently occurred at the hydrophilic surface of w/o-Si/Ti facing the aqueous phase. It is notable that o-Si/Ti liberated an appreciable amount of H_2 in this photocatalytic system, as was observed in the dual-phase mixture of benzene and water, even though negligible contact of the TiO_2 surface to the aqueous phase was expected. A possible explanation of this is increase in surface hydroxyls of TiO_2 (Ti-OH) inside the porous SiO_2 shell to increase hydrophilicity of the o-Si/Ti surface during the photoirradiation; the formation of Ti-OH induced by band-gap excitation of TiO_2 has been reported in relation with a phenomenon of photoinduced super hydrophilicity [20]. Another plausible reason for the appreciable photocatalytic activity of o-Si/Ti is that surface modification had not been achieved uniformly, and thereby some of the particles had a bimodal surface structure like w/o-Si/Ti. Anyway, from these results, it is expected that highly efficient photocatalytic systems consisting of liquid-liquid and/or gas-liquid dual-phase mixtures will be constructed using bimodal w/o-Si/Ti, which can be photoirradiated selectively and removed easily after photoirradiation without tedious work-up procedures.

4. Conclusions

The present study has shown that the partial coverage of each particle of a TiO_2 photocatalyst with alkylsilyl groups gave affinity to both water and water-immiscible organic phases, enabling assembly just at their interface to drive photocatalytic reactions of chemical species in both phases. Although the rate of photocatalytic reaction was not

so fast under the present reaction conditions, this system can be improved by optimization of reaction conditions, e.g., appropriate choice of photocatalysts and/or modifier, and can be further extended to other types of reaction such as reaction between water and immiscible gas phase organics and decontamination of water by gaseous molecular oxygen. Studies along these lines are now under way.

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Figure Captions

Fig. 1.   Photographs of several TiO_2 powders added to a water–benzene dual-phase system.

Fig. 2.   Dependence of amount of floating particles on the weight fraction of ethanol in water. Circles, w-Si/Ti; Squares, w/o-Si/Ti; Triangles, o-Si/Ti.

Fig. 3.   Time-course curves of H_2 liberation from a dual-phase mixture of water and benzene containing 1-octanol (0.1 cm^3) and chloroplatinic acid (H_2PtCl_6, 0.4 mg). Symbols are the same as those in Fig. 2.

Fig. 4.   Amount of H_2 liberated from a 5 vol% aqueous methanol solution containing H_2PtCl_6 (0.4 mg) as a function of irradiation time. Symbols are the same as those in Fig. 2.

Table 1

Amount of surface attached alkylsilyl groups on several TiO_2 powders

TiO_2	w-Ti	w/o-Ti	o-Ti	w-Si/Ti	w/o-Si/Ti	o-Si/Ti
M_a / µmol g^{-1}	0	57	59	0	297	317

Table 2.

Photocatalytic activity of several TiO_2 powders for benzene oxidation in a water-benzene dual-phase system[a]

entry	TiO_2		CO_2[c] /μmol	selectivity[d] /%
1	w-Ti	6.7	5.9	53
2	w-Ti[e]	30.0	71.9	29
3	w/o-Ti	22.1	29.8	43
4	o-Ti	23.7	33.6	41
5	w-Si/Ti	5.0	4.5	52
6	w/o-Si/Ti	35.3	44.9	44
7	o-Si/Ti	32.8	41.3	44

[a]Photoirradiation was carried out at 298 K for 20 h with benzene (2 cm^3), H_2O (1

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cm^3) and photocatalyst (10 mg) without agitation.

[b]Amount of phenol.

[c]Amount of CO_2.

[d]Selectivity of phenol production defined as the percentage of the phenol yield to the sum of amount of produced phenol and CO_2.
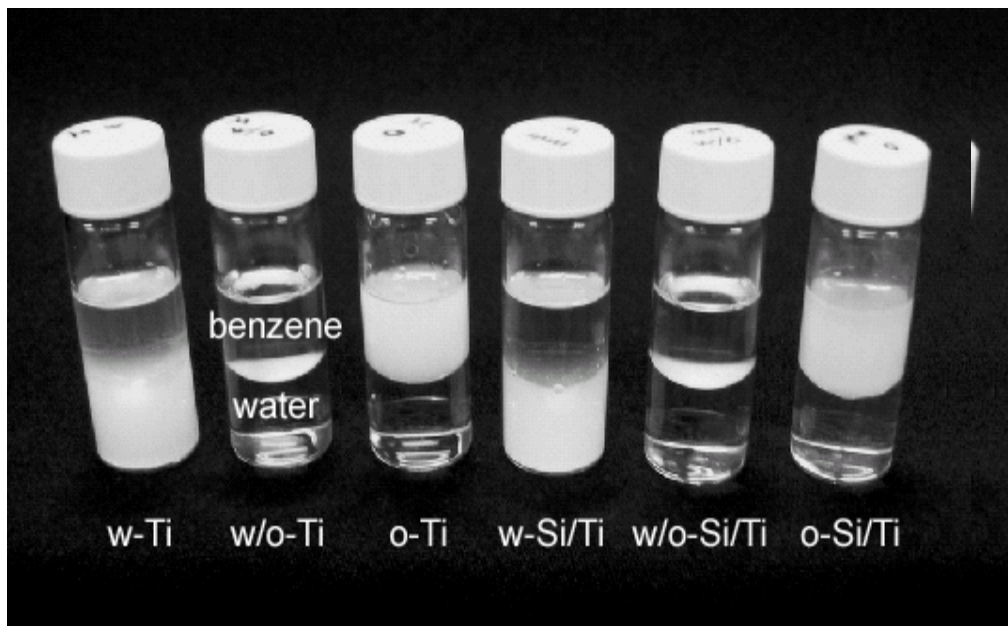
[e]Reaction was carried out with mechanical agitation.

Fig. 1. Photographs of several TiO_2 powders added to a water-benzene dual-phase system.
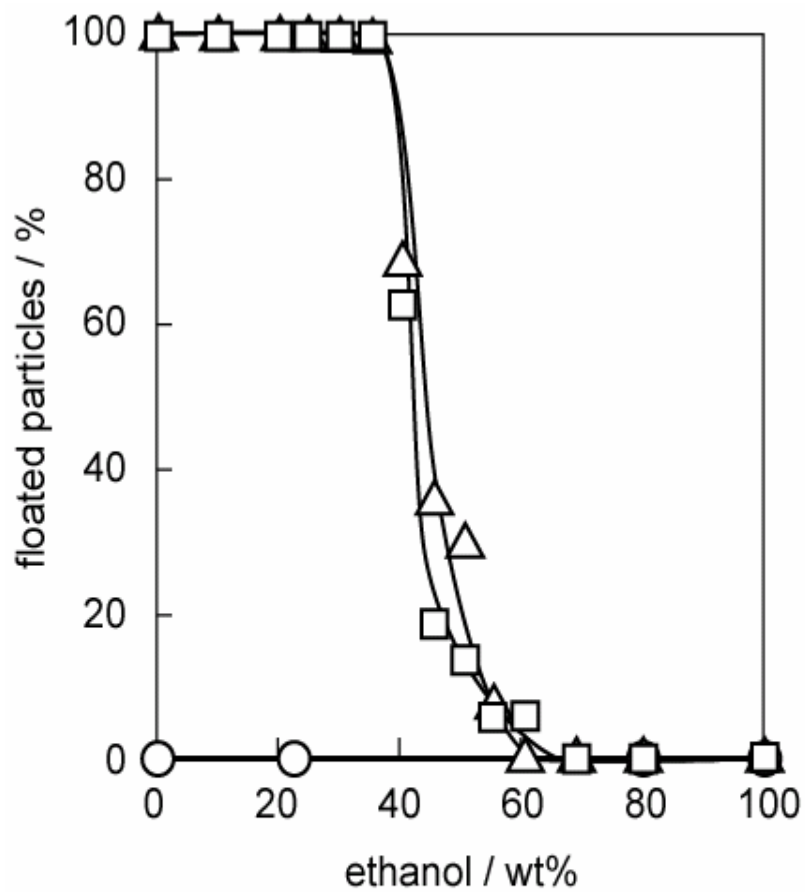
S. Ikeda, Y. Kowata, K. Ikeue, M. Matsumura, B. Ohtani

Fig. 2. Dependence of amount of floating particles on the
weight fraction of ethanol in water. Circles, w-Si/Ti; ;
Squares, w/o-Si/Ti; Triangles, o-Si/Ti.

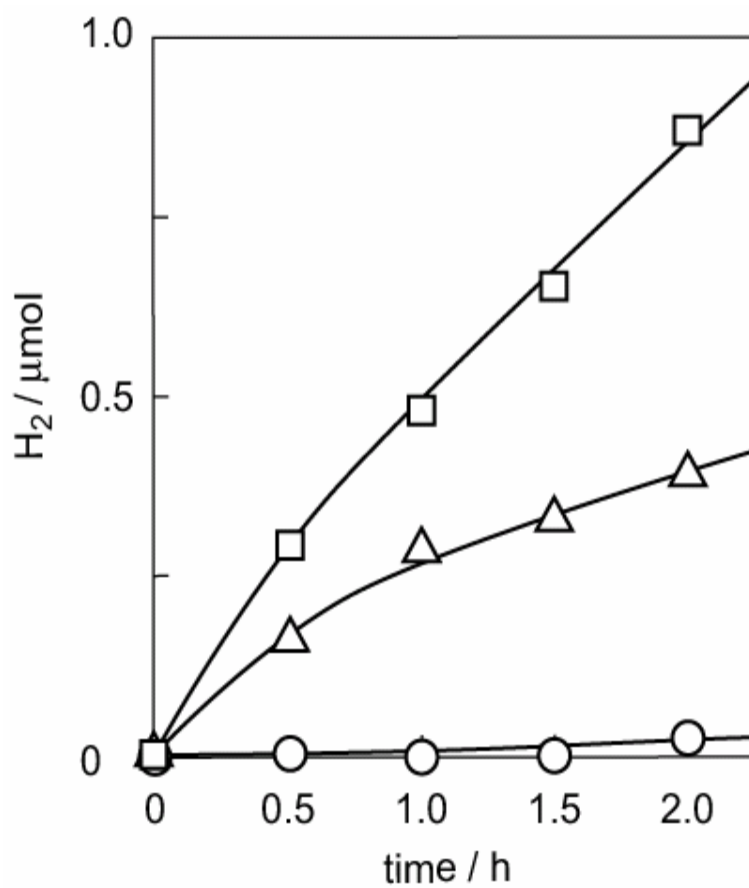S. Ikeda, Y. Kowata, K. Ikeue, M. Matsumura, B. Ohtani

Fig. 3. Time-course curves of H_2 liberation from a dual-phase mixture of water and benzene containing 1-octanol (0.1 cm^3) and chloroplatinic acid (H$_2$PtCl$_6$, 0.4 mg). Symbols are the same as those in Fig. 2.

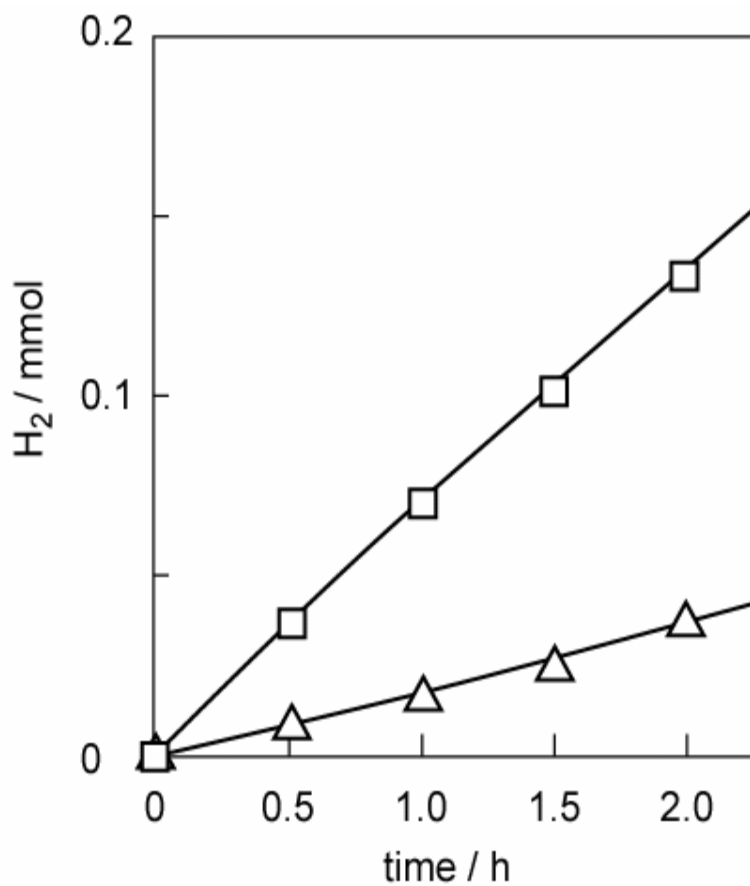S. Ikeda, Y. Kowata, K. Ikeue, M. Matsumura, B. Ohtani

Fig. 4. Amount of H_2 liberated from a 5 vol% aqueous methanol solution containing H_2PtCl_6 (0.4 mg) as a function of irradiation time. Symbols are the same as those in Fig. 2.

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