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Photocatalytic Hydrogen Production from Water with Nonfood Hydrocarbons as Oxidizing Sacrifice Agents

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To enhance photocatalytic water splitting, various oxidizing sacrifice agents (OSA) have been added to the system in order to scavenge the coproduced O_2, and, thus, to hinder the reverse reactions. In the aim of achieving carbon-neutral photocatalytic water splitting, nonfood hydrocarbons of castor- and jojoba-oils were evaluated as OSA. Moreover, various surfactants were tested as emulsifiers for W/O binary solution for promoting photocatalytic water splitting rate. Among the OSA used, the castor-oil was found to be more suitable candidate compared to jojoba-oil, which was attributed to its smaller carbon chain numbers of mainly 18. Without surfactants, around 20 vol %-castor-oil aqueous binary solution with TiO_2/Pt(0.10 wt %) provided the highest water splitting rate of about 30 mL-H_2/(m^2·h). Among tested surfactants, liquid-detergent was the best due to its optical transparency. 40 vol %- or 60 vol %-castor-oil emulsion with a drop of liquid-detergent resulted in a water splitting rate of 125 mL-H_2/(m^2·h), which was four times greater that the aforementioned highest value. © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 2237–2243, 2011
Keywords: catalysis, photochemical reactions, energy, reaction kinetics, aqueous solutions

Introduction

The recent increase in energy demand could soon lead to a disruption in energy supply caused by various factors including the exhaustion of fossil fuels. Hence, the alternative energy sources such as fuel cells are being developed, and there utilization might soon result in a society based on H_2 energy the World Energy Network (WE-NET) project in the period from 1993–2003 provided a great deal of credits on the basic policy of H_2 production by water electrolysis using electric-power generated from renewable energy sources such as hydropower and windpower.[1–3] Despite this fact, present H_2 production still relies on thermochemical conversion of fossil fuels, due to the supply/demand mismatches in terms of time, place, quantity and quality.[4–9]

According to WE-NET,[10] the electrochemical reactions play important roles in H_2 production, and photoelectrochemical reaction known as Honda/Fujishima effect, based on splitting water by Pt/TiO_2 with ultraviolet rays, is of great importance.[11–13] To promote photocatalytic water splitting rates, various oxidizing sacrifice agents (OSA) have been added to water. The role of OSA is to scavenge the coproduced O_2 due to water splitting, and, thus, to prevent the reverse reaction of O_2 with H_2 to H_2O from occurring.[14–21] Typically, the OSA are

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Table 1. Properties of OSA and Surfactant Candidates

OSA	main components	number of carbon in a molecule	solubility to water	color	principal utilizations
castor-oil	ricinoleic acid	18	insoluble	transparent	lubricant purgative
	oleic acid	18			
	linoleic acid	18			
jojoba-oil	eicosenoic acid	20	insoluble	transparent	cosmetics lubricant
	erucic acid	22			
starch	amylose	20000–85000	soluble to hot water	transparent	food
	amylopectin	60000–1700000			

surfactant	natural or artificial	solubility to water	color	cost
lecithin	natural	insoluble	orange	expensive
saponin	natural	insoluble	orange	expensive
liquid detergent	artificial	soluble	transparent	very cheap

eatable hydrocarbons such as saccharides, alcohol and acetic acid, but the use of nonfood OSA such as cellulose, benzoic acids and pyroligneous acid has also been reported.[15,18,22] Given this, saccharides and acetic acid were the preferred OSA in our recent study.[22]

However, the continuing rumors on the possible worldwide food crisis should also be taken into consideration, and, hence, the authors decided to shift attentions to natural nonfood hydrocarbons such as castor-oil and jojoba-oil, which could be used for carbon-neutral photocatalytic water splitting. Unfortunately, these OSA candidates are known to be water-insoluble, and, hence, lower water splitting rates are to be expected due to small W/O (water/oil) interface area in binary mixtures. Assuming that higher water splitting rates can be obtained by altering W/O binary solutions to stabilized emulsified solutions characterized by higher W/O interface areas, the authors had also surveyed natural surfactants such as lecithin and saponin. Tables 1 shows the properties of natural nonfood OSA and surfactant candidates. Starch with extremely high-molecular-weight and soluble in hot-water was selected for optimization of TiO_2/Pt powders. The starch had similar proprieties as natural nonfood OSA candidates but water-soluble; this may lead to a simpler discussion of the obtained results. As a referential surfactant, a commercial liquid-detergent with higher availability was selected because of its extremely low cost.

In this study, optimizations of TiO_2/Pt powders were done at first using starch aqueous solution. Then, the optimized TiO_2/Pt powders were used to assess the feasibility of photocatalytic water splitting from various W/O binary solutions, and to determine the best-performing OSA candidate shown in Table 1. Subsequently, photocatalytic water splitting from W/O emulsified solutions containing a surfactant in Table 1 was carried out in order to clarify the best mixture. Finally, future strategies for the photocatalytic water splitting from W/O emulsified solutions leading to the practical stage applications were declared.

Experimental apparatus and procedures

Figure 1 shows a schematic drawing of the experimental apparatus. Main reactor was made of Pyrex glass in cylindrical shape of 90 mm internal diameter and 40 mm tall, having about 255 mL in volume. The cylinder had two taps for replacing air inside by Ar in order to obtain higher H_2 producing rates[22] and to allow gas-sampling. The top cover was made of solid quartz glass with high transmissivity toward ultraviolet rays. To maintain a constant reaction temperature, a cooling chamber made of Pyrex glass was attached to the bottom of the cylinder, where water at 293 K was circulated throughout the whole experimental period. Since H_2 producing efficiency by water electrolysis is quite high above 95%, the cooling system in the practical application stage should be replaced by radiating fins or other systems consuming no electricity. In the same way, other electrical equipments such as magnetic stirring and temperature monitoring were excluded in the apparatus, imitating the practical operations as much as possible.

TiO_2 powders utilized were P25 (a mixture of 70 mol %-anatase form and 30 mol %-rutile form) produced by Nippon Aerosil Co., Ltd. The P25 indicated superior H_2 producing efficiencies comparing to other commercial products used in our former studies such as famous ST01 produced by Ishihara Sangyo Kaisha, Ltd., and reagents purchased from Wako Pure Chemical Industries, Ltd., in our former studies.[22–24] Next, Pt loading to TiO_2 powders was performed by photodecomposition of hexachloroplatinic acid.[25] Almost the same-size distribution of TiO_2/Pt powders could be obtained owing to powder grinding for sufficiently longer times of more than 60 min in an automatic grinder (ANM1000, Nitto Kagaku Co., Ltd.), independent to TiO_2 type and loaded Pt wt % content up to 0.50. Figure 2 shows a representative particle-size distribution of P25 with 0.10 wt %-Pt loaded, which was measured by a laser diffraction particle-size analyzer (LA-920, Horiba, Ltd.).

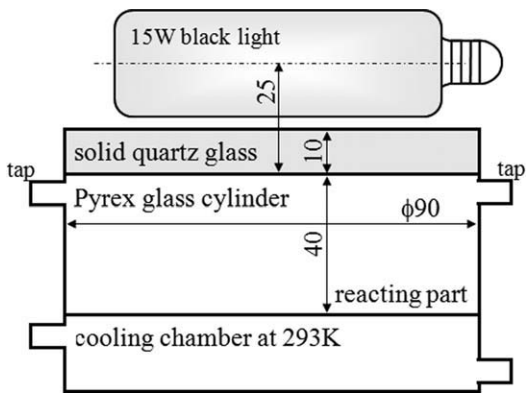

Figure 1. Schematic drawing of experimental apparatus.

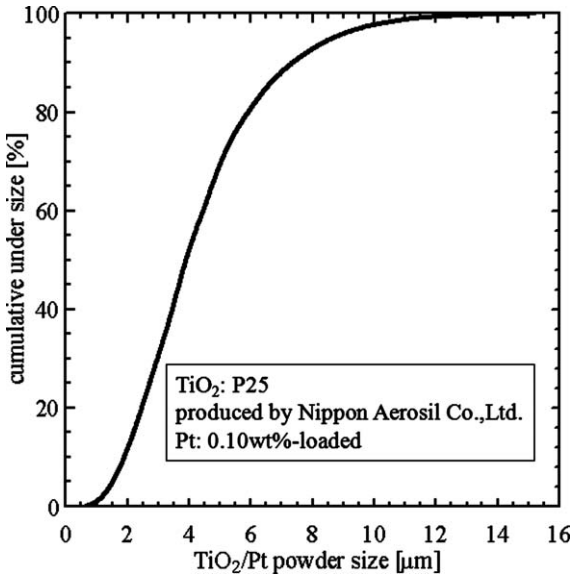

Figure 2. Particle size of TiO_2/Pt powders.

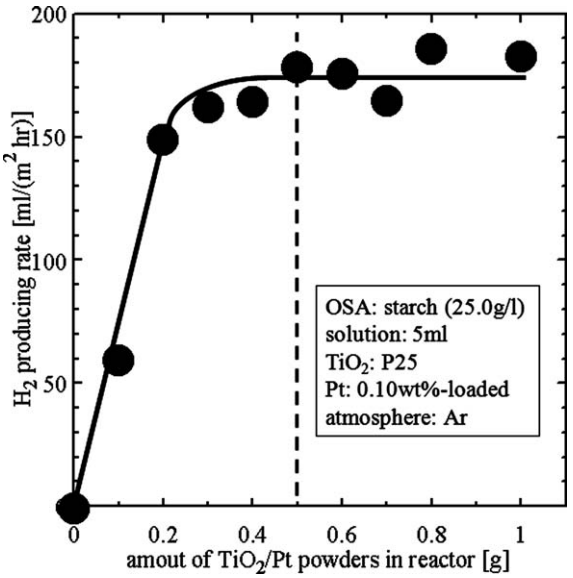

Figure 3. Optimal amount of TiO_2 powders.

Regarding the water splitting experiments, W/O binary solution of 5.0 mL and/or the surfactant prepared in advance according to Table 1 was poured into the reactor along with the TiO_2/Pt powders. Then, the whole apparatus was manually agitated to replace air inside by Ar. Then, after starting the circulation of water (293 K) in the cooling chamber, the light irradiation by 15.0 W black light (EFD15BLB-T, Toshiba Lighting and Technology Corp.) was initiated. The light intensity stated in the catalog is 1.30 W in the ultraviolet region. Finally, H_2 concentration inside the gas phase of reactor was measured by means of TCD gas-chromatography (GC-8A, Shimadzu Corp.). In these procedures, experimental repeatabilities can be conveniently preserved.

Results and Discussion

Optimal TiO_2/Pt powders

Figure 3 shows the H_2 producing rates obtained with various amounts of TiO_2/Pt(0.10 wt %) from starch aqueous solution of 25 g/L. It can be seen that no water splits were obtained without TiO_2/Pt powders, and, thus, there was no H_2 produced by ultraviolet decomposition. Furthermore, when the experiments were carried out in the presence of TiO_2/Pt powder, H_2 generation was clearly observed, and H_2 producing rate was observed to steeply increase with an amount of TiO_2/Pt powders up to around 0.5 g. Above this content, the H_2 producing rate seemed to attain a constant value, which was attributed to plane surface reactions in this system without flowing fluids and solids. Hence, 0.50 g of TiO_2/Pt powders was used as an optimum dosage in the subsequent experiments.

Figure 4 shows H_2 producing rates for different Pt wt % loaded to TiO_2 powders. No water splitting by only TiO_2 indicated that Pt plays an important role of capturing excited electrons, so called Schottky effect. It can be seen that H_2 producing rate increased proportionally to Pt wt % up to about 0.1, and then decreased. This may have resulted from change in Pt dispersing condition as illustrated in the bottom part of this figure. It is well-known that Pt itself has no photocatalytic functions, but can be a catalyst for recoupling of produced H_2 and O_2 to water, so that the extensive amount of Pt resulted in the deterioration of H_2 producing rate. Consequently, the optimum Pt wt % loaded to TiO_2 powders was revealed to be around 0.1 wt %, and this optimum was used for further experiments.

Feasibility of H_2 production from W/O binary solutions

Figure 5 shows time trends of H_2 production from binary solutions of water and castor- or jojoba-oil. First of all, it is found that H_2 can be produced from such heterogeneous W/O binary solutions, concluding that oils can become OSA for photocatalytic water splitting. It is clear that castor-oil is better than jojoba-oil as OSA, resulting from their different

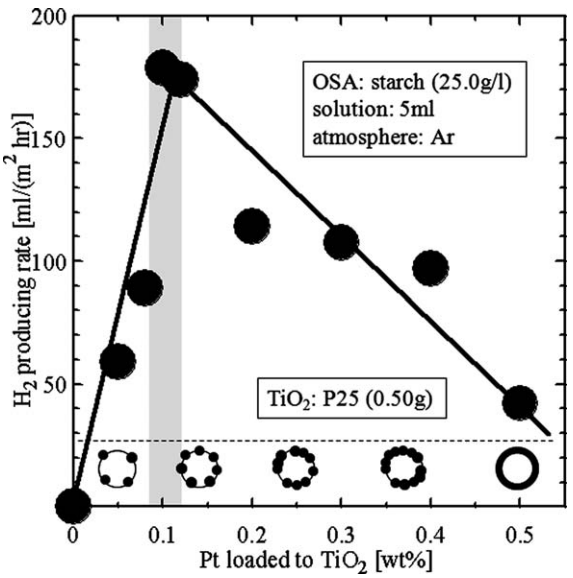

Figure 4. Optimum Pt wt % loaded to TiO_2 powders.

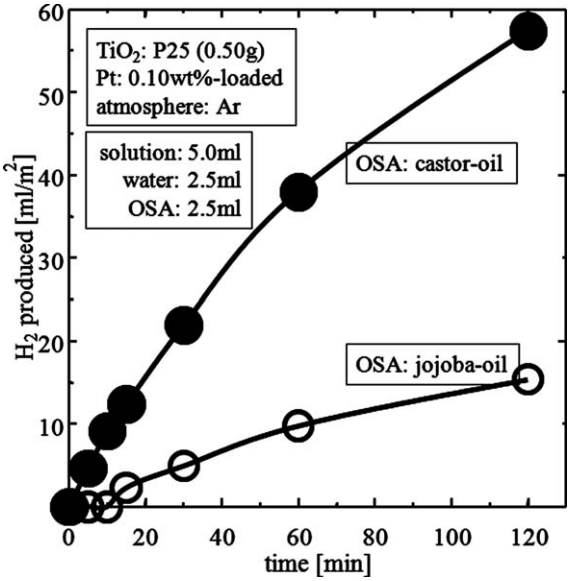

Figure 5. H_2 production from W/O binary solutions.

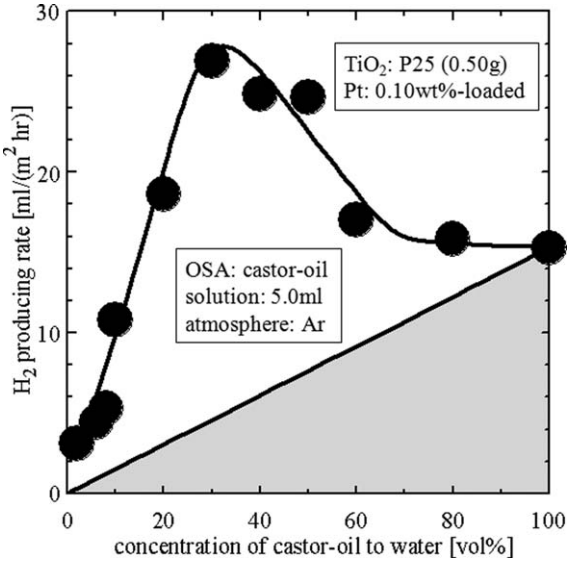

Figure 6. H_2 production from water and castor-oil binary solutions in various concentrations.

carbon chain numbers in Table 1. Therefore, castor-oil is used in latter experiments.

H_2 production from binary solutions of water/castor-Oil

Figure 6 shows H_2 producing rates for various concentrations of castor-oil to water. The most notable point is that H_2 was produced from 100 vol %-castor-oil, i.e., photocatalytic decomposition of castor-oil took place. It is reasonable to assume that the contribution of castor-oil decomposition to the whole H_2 production was directly proportional to its concentration, and such an assumption is represented by the triangulated gray area in this figure. The gray area, thus, corresponds to H_2 produced by direct photocatalytic decomposition of castor-oil itself.

In order to discuss the roles of castor-oil as OSA, the triangulated area was subtracted from Figure 6, resulting in a fine symmetric curve as shown in Figure 7, representing H_2 producing rate by photocatalytic water splitting. To provide clear explanations, a simple illustration based on our observation was added to Figure 7. First, up to 30 vol % of castor-oil, H_2 producing rate was found to increase and it was also noticed that the castor-oil floated on the water surface in the form of droplets. Given the fact that the water splitting takes place at W/O interface, the H_2 producing rate increase was attributed to an increase in W/O interface area. Second, at castor-oil concentrations above 30%, the water surface was completely covered with castor-oil, which resulted in a constant W/O interface area. The thickness of the surface layer of castor-oil grew with the castor-oil concentration, and the decline in H_2 producing rate was most likely caused by absorption of ultraviolet rays by the castor-oil layer and the consequent deterioration in the optical intensity of ultraviolet rays at W/O interface.

Consequently, as long as the oils are utilized as OSA, further expansion of W/O interface area is necessary to bring this system up to a practical stage. Typical ways to enlarge the W/O interface area are mechanical agitations and enforced convections using magnetic stirrers. However, since water electrolysis is known to be efficient above 95%, expansion of W/O interface area must be realized without any electric devices. Therefore, W/O emulsification using surfactants was adopted in the next section.

H_2 production from water/castor-oil emulsions with various surfactants

Figure 8 shows time plots of H_2 production from water/20 wt %-castor-oil emulsions with about 0.1 g of various surfactants in Table 1. In these experiments, a commercially available liquid-detergent was used, and its water content was determined using a thermogravimetric analysis (TGA-50H, Shimadzu Corp.). Subsequently, the water content in

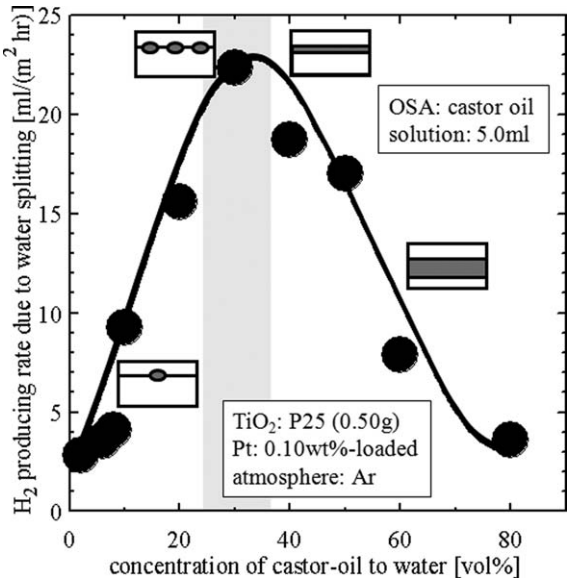

Figure 7. H_2 production by photocatalytic water splitting with castor-oil as OSA.

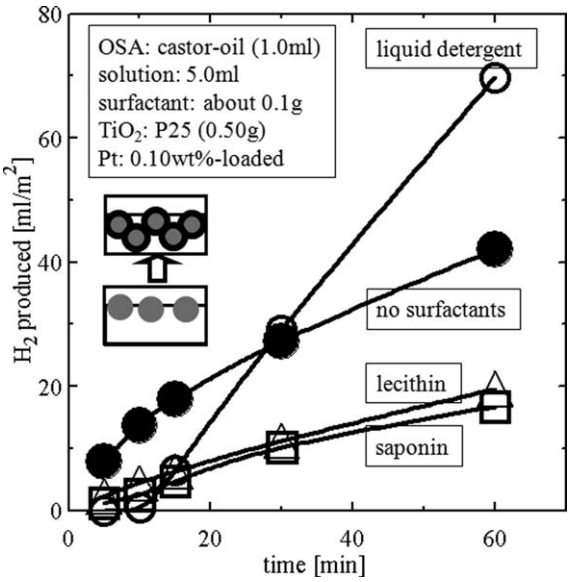

Figure 8. H_2 production from water and castor-oil emulsions with various surfactants.

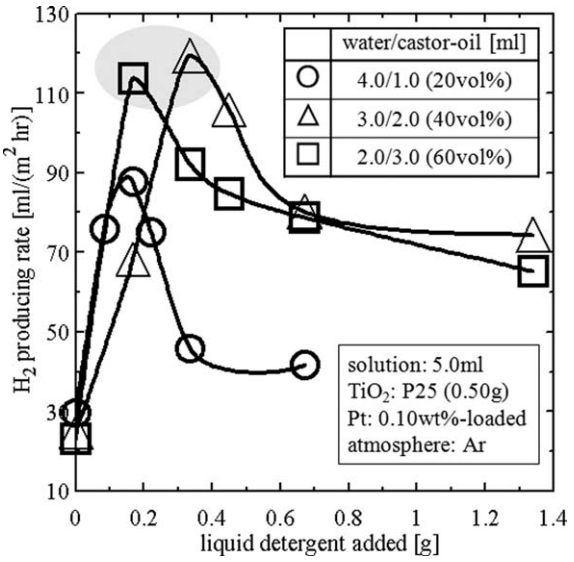

Figure 9. H_2 production from various ratios of water/castor-oil/liquid-detergent emulsions.

the liquid-detergent was found to be 33 wt %, and the dosage of liquid-detergent was corrected accordingly First, it can be seen that H_2 productions from W/O emulsions at the beginning of the experiments were low and without exceptions, comparing with the binary solution. This fact indicates that the surfactants utilized in this study are all improper as OSA. After a while, better H_2 productions were obtained. Such transitions are completely opposite to the cases of W/O binary solutions, leading from finer castor-oil drops fully coated by surfactants as illustrated in this figure. In other words, unsuitable surfactants play roles as OSA and hardly decompose photocatalytically at the beginning, and then higher W/O interface areas contribute H_2 production.

Among tested surfactants, only the liquid-detergent can promote water splitting, compared to W/O binary case. Although other natural surfactants of lecithin and saponin can also stabilize W/O emulsions, no promoting effect for water splitting was attributed to their colorations in orange, which must absorb ultraviolet rays at only upper regions of the W/O emulsions. Therefore, it can be concluded that W/O emulsification using optical transparent surfactants has predominance for photocatalytic H_2 production.

Optimal emulsion of water/castor-oil/liquid-detergent

Figure 9 shows H_2 producing rates from various water/castor-oil/liquid-detergent emulsions. It can be seen that the optimal dosage of liquid-detergent varied with the castor-oil concentrations. This might have resulted form three contra-effects by liquid-detergent; namely expansion of W/O interface area, impropriety as OSA and difficulty for photocatalytic decomposition. H_2 producing rates could be enhanced by adding suitable amount of liquid-detergent to any W/O solutions, up to about four times of respective W/O binary cases. The best H_2 producing rate was acquired from 40 vol %-castor-oil with a drop of liquid-detergent, and almost the same rate was seen from 60 vol %. This fact indicated that W/O emulsified systems suited a wide-range of W/O ratios, compared with the binary systems.

Since the best H_2 producing rate of about 120 mL-H_2/(m^2·h) from W/O emulsified system is almost the same as that from homogeneous starch aqueous solution of about 175 mL-H_2/(m^2·h) in its maximum. Therefore, it can be concluded that liquid-detergent provides a great help to make W/O system homogeneous.

Tip trial of newly developed TiO_2 named P90 by Nippon Aerosil Co., Ltd.

Recently, Nippon Aerosil Co., Ltd. has developed new TiO_2 powders named P90. Figure 10 shows time plots of H_2 production from binary 20 vol %-castor-oil solution by P90

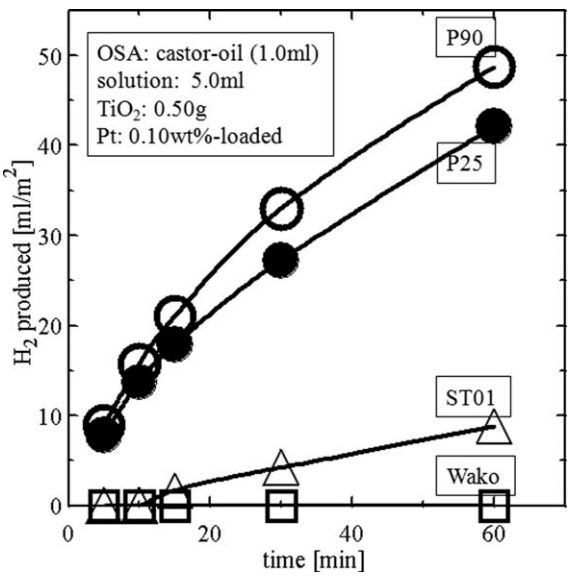

Figure 10. Best TiO_2 powders.

together with ST01, reagent by Wako and P25. As expected, it is seen that ST01 and reagent by Wako were less efficient for water splitting than P25.[22] The most noteworthy is that P90 had a superior H_2 producing capacity of more than 15% compared to P25.

Energy converting efficiency and future strategies

The best H_2 producing rate of 120 mL-H_2/(m^2·h) was obtained from water/40 vol %-castor-oil/liquid-detergent-drop emulsified systems. P90 must raise this best value 15% at least, leading to 138 mL-H_2/(m^2·h). Here, light energy to the reactor from the black light was about 0.6 W, which was a half of the value stated in the catalog. Taking H_2 energy density of 12.8MJ/m^3 into consideration, energy converting efficiency was calculated to be about 0.52%. To increase the energy converting efficiency, the following future strategies are of outmost importance.

First, concerning material strategies, so far only limited numbers of nonfood natural hydrocarbons were tested as OSA, but the tests should be extended toward many other OSA candidates such as humins and terpenes. Similarly, various studies have shown the importance of the selection of TiO_2 powders, and there are many commercially available TiO_2 powders such as Fuji Titanium Industry Co., Ltd., Tayca Corp., and Titan Kogyo, Ltd. Furthermore, the tailor-made TiO_2 powder in nano-orders could also bring an enormous improvement, especially by building-up method of spray pyrolysis.[26,27] Additionally, the authors have recently developed new technology of salt-added super- or subcritical fluid annealing processes that could improve crystallinity of fine metallic powders with restricting their agglomerations.[28] Using this process, TiO_2 powders without lattice defects could be easily obtained. In summary, screening experiments could result in a significant rise in energy converting efficiency drastically.

Secondary, concerning hydrodynamic strategies, the authors have focused on Rayleigh-Benard convection to obtain a medium flow without consuming electricity. Such a medium flow can provoke present plane surface photocatalytic reaction to volumetric one. The authors have already confirmed about thrice as high H_2 producing rate due to Rayleigh-Benard convection induced by waste heats, and our optimizing works in progress are expected to bring about a remarkable promotion of the energy converting efficiency.

Finally, other strategies are related to chemical and process engineering. For example, precise control of pH value,[22] H_2 separation by semipermeable membranes and adding O_2 absorbents such as Ageless produced by Mitsubishi Gas Chemical Co., Inc., could also contribute to an improvement in energy converting efficiency eminently.

Conclusions

As oxidizing sacrifice agents for photocatalytic water splitting, nonfood natural hydrocarbons of castor- and jojoba-oils were evaluated in order to establish a genuine carbon-neutral H_2 producing process. It can be concluded that castor-oil with smaller carbon chains of mainly 18 was better than jojoba-oil with longer carbon chains of mainly 20 and 22. The highest H_2 producing rate of 30 mL-H_2/(m^2·h) was obtained from 20 vol %-castor-oil binary solution. Furthermore, various surfactants were used to emulsify the W/O binary solution, and the optical transparency of these surfactants was found to be critical. In accordance with these findings, 40 vol %-castor-oil emulsified solution with a drop of transparent liquid-detergent gave the best water splitting rate, which was about four times greater than the highest value in W/O binary case.

Acknowledgments

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