

Photocatalytic activity evaluation of granular Pt/TiO₂ for hydrogen production from glycerol aqueous solution with continuous gas bubbling

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Abstract: Photocatalytic activity of Pt/TiO₂ for hydrogen evolution from aqueous glycerol solutions was evaluated by using a batch reactor with continuous gas bubbling. In the suspended condition of the powder photocatalyst, CO₂ was the predominant product under oxygen-containing (20%) nitrogen bubbling, while H₂ was selectively evolved with pure N₂ bubbling. The H₂ production rate achieved with the granular photocatalysts (>40 μm secondary particle size) that settled at the bottom of the reactor with N₂ bubbling was comparable to that attained using the suspended powder photocatalyst. High H₂ selectivity (87%) and production rate was maintained even under oxygen (20%)/nitrogen bubbling condition, indicating the suppression of glycerol oxidation.

Keywords: Photocatalyst, Hydrogen production, Granular Pt/TiO₂.

1. Introduction

Hydrogen production utilizing sunlight as a renewable energy is an important technology for the near future. A novel method of efficient photocatalytic hydrogen production from water containing dissolved oxygen has been proposed [1–3]. This method utilized non-suspended granular Pt/TiO₂ and glycerol, which is a waste from the production of bio-diesel fuel, added to water as a sacrificial reagent. To date, the efficiency of this method has not been compared with the conventional method (suspended powder photocatalyst used and dissolved oxygen removed) under the same photo-irradiation conditions. It has also been difficult to examine the precise activity under a fixed concentration of dissolved oxygen because oxygen is consumed and decreases with time in a small scale batch reaction. A pronounced difference in the effect of dissolved oxygen was observed in this study on comparing the “settled granular” and “suspended powder” modes with a fixed oxygen concentration using a continuous gas bubbling reactor.

2. Experimental

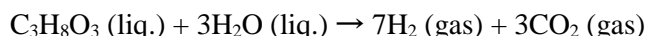
The Pt/TiO₂ (0.3 wt% Pt) catalyst was prepared by the photodeposition method [1]. TiO₂ powder (P25, Japan Aerosil) was dispersed in a 50 vol.% methanol aqueous solution and H₂PtCl₆ was added to the dispersion. After N₂ bubbling for 30 min, the suspension was stirred and irradiated with a 100 W high-pressure Hg lamp. After filtration, washing, and drying at 373 K, the obtained aggregate was crushed and sieved. The granules (40–125 μm) thus obtained were mixed with water and the turbid supernatant was repeatedly removed until it became clear. After collecting and drying, the granular Pt/TiO₂ catalyst was used for the reaction.

The photocatalytic reactor is shown in **Figure 1**. The granular Pt/TiO₂ (50 mg) catalyst was added to an aqueous glycerol solution (1.09 mol L⁻¹, 25 mL) and it settled to the bottom of the reactor. Pure N₂ or O₂ (20%) + N₂ (balance) gas was bubbled at 20 mL min⁻¹ for 30 min, and the reactor was irradiated from the bottom using a Xe lamp (100 W) with continuous bubbling and without stirring (settled granular condition). The control reaction was performed with stirring at 350 rpm and continuous bubbling (suspended powder condition) after the same amount of Pt/TiO₂ powder was suspended in the solution and sonicated for 30 min. Each of these reaction conditions were maintained for at least 30 min and the exit gas was analyzed by GC after stabilization.

3. Results and discussion

GC analysis confirmed that H₂ and CO₂ were the only gas-phase products. The formation rate of these gases is shown in **Figure 2**. H₂ was selectively produced (89% of the gas-phase) under the suspended

powder condition with N₂ bubbling. In the photoreforming of glycerol, H₂ selectivity after full conversion should be 70% according to the following equation.



The higher H₂ selectivity was maintained under the present condition, i.e., at a high concentration and low conversion of glycerol, which meant that glycerol was simply dehydrogenated or partially oxidized and the products of these reactions constituted the liquid phase.

The formation of CO₂ became dominant and H₂ was almost diminished when the oxygen concentration in the bubbling gas increased to 20% (equivalent to air). This change was interpreted as the transfer of the excited electron in the conduction band to the oxygen molecule at the surface of Pt. This led to the formation of the reactive oxygen species such as O₂⁻ radical anion, which attacked the organic molecules to decompose them into CO₂.

A higher H₂ evolution rate and selectivity (90%) was observed with pure N₂ bubbling under the settled granular condition as compared to that achieved under the suspended powder condition. This result implied that the irradiated light was the most effectively utilized in the settled granular condition. Although the rate of H₂ evolution decreased with the increasing O₂ concentration in bubbling gas, the rate achieved under 20% O₂ was equivalent to 70% of that under pure N₂. Moreover, the rate of CO₂ evolution did not increase and the H₂ selectivity (87%) was almost unchanged.

We previously reported [1,2] that the thermal catalytic reaction of product H₂ and dissolved O₂ to regenerate water can easily occur on Pt in the suspended powder photocatalyst, where light is not sufficiently irradiated onto most of the photocatalyst particles. The regeneration of water was effectively suppressed in our method by using the settled granular photocatalyst. Another explanation is possible that the interstitial space between the primary TiO₂ particles in the granules can be oxygen deficient locally, and therefore not susceptible to the dissolved oxygen in the bulk liquid phase. Additional data and further discussions are outlined in the poster.

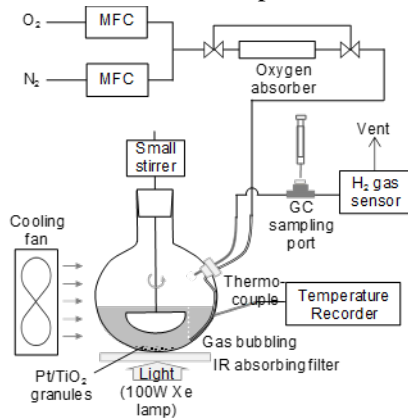


Figure 1. Reactor with continuous gas bubbling.

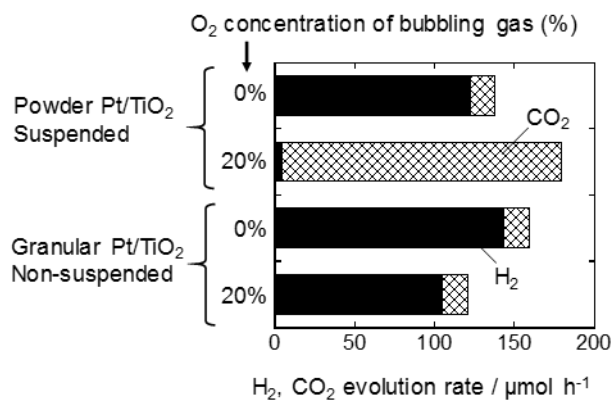


Figure 2. Reaction products in each condition.

4. Conclusions

Selective production of H₂ was possible from aqueous solutions of glycerol containing dissolved oxygen in equilibrium with air using the granular Pt/TiO₂ photocatalyst. The H₂ production rate was comparable to that obtained under conventional suspension conditions, and may be further increased by optimizing the size and porosity of granules, or the irradiation method of light. A new economic method of photocatalytic hydrogen production is proposed in this study, which does not require the inert gas to remove dissolved oxygen nor the energy of stirring suspended solution.

References

1. H. Sakurai, M. Kiuchi, C. Heck, T. Jin, Chem. Commun. 52 (2016) 13612.
2. H. Sakurai, M. Kiuchi, T. Jin, Syokubai (Catalysts & Catalysis), 59 (B) (2017) 44.
3. H. Sakurai, M. Kiuchi, T. Jin, WO 2017/159853 A1 (2017)