Photocatalytic Effect of TiO$_2$ on Hydrothermal Gasification of Glucose

A Nakatani, N Kometani$^1$
Dept. of Applied Chemistry, Graduate School of Engineering, Osaka City University
Sugimoto 3-3-138, Sumiyoshi-ku, Osaka 558-8585, Japan

E-mail: kometani@a-chem.eng.osaka-cu.ac.jp

Abstract. The hybrid process of the hydrothermal gasification method and the TiO$_2$ photocatalysis has been developed and tested for the gasification of glucose. TiO$_2$ powder and those loaded with Pt or Ni were used as photocatalyst. 0.05 M glucose aqueous solutions suspending the photocatalysts were reacted by the flow-type reactor system in the dark or under near-UV illumination with pressure and temperature controlled to be 30 MPa and 350−450 °C, respectively. It was found that the evolutions of hydrogen and methane from glucose could be promoted by the photocatalytic action of TiO$_2$ under hydrothermal conditions, which was further enhanced by supporting Pt and Ni on TiO$_2$.

1. Introduction

Hydrothermal gasification processes have been extensively investigated as a promising means of energy and material conversion from biomass and biodegradable organic wastes because of the advantages over conventional methods in which large energy is required for dehydration of wet raw materials [1,2]. However, hydrothermal gasification processes are usually performed at considerably high reaction temperatures above 500 °C and therefore retain the problem of energy cost for practical applications. On the other hand, it has been known that biomass can be converted into hydrogen, methane and other low molecular gases at room temperature and atmospheric pressure with a help of photocatalytic action of titanium dioxide (TiO$_2$) under near-UV irradiation [3], but the conversion efficiency of this method is quite low compared with hydrothermal gasification processes.

Recently we have revealed that TiO$_2$ exhibits the efficient photocatalytic activity comparable to the one at room temperature even in high-temperature high-pressure water near or above the critical point ($T_c = 374$ °C, $P_c = 22.1$ MPa) [4]. This finding suggests that new processes may be constructible by combining conventional hydrothermal techniques with TiO$_2$ photocatalysis. We actually demonstrated that the oxidative decomposition of chlorinated organic compounds in high-temperature high-pressure water (supercritical water oxidation process) could be effectively accelerated by the photocatalytic action of TiO$_2$ [5]. In this study, we have examined the photocatalytic effect on the hydrothermal gasification of glucose under various conditions by using the flow-type reactor system capable of performing the photocatalytic reaction of aqueous suspensions under high-temperature high-pressure conditions. Glucose was employed as a model biomass because its gasification mechanism has been extensively studied by many researchers [6]-[12]. It is demonstrated that the evolution of both hydrogen and methane can be accelerated by the photocatalysis under hydrothermal conditions.

$^1$ To whom any correspondence should be addressed.
2. Experimental

Three kinds of photocatalysts; TiO$_2$ powder, Pt or Ni supported TiO$_2$ powder, were used in this study. TiO$_2$ powder (JRC-TIO4) was supplied from Catalysis Society of Japan. Pt was supported on TiO$_2$ powder by the conventional photodeposition method [13]. Ni was supported by impregnation of TiO$_2$ powder (1 g) with 5 ml of 0.02 M Ni(NO$_3$)$_2$ aqueous solution followed by the calcination in hydrogen at 300 °C. A 0.02 g of photocatalyst powder was suspended in a 100 ml of 0.05 M glucose aqueous and this suspension was consecutively fed into the reactor (inner volume ~1.0 cm$^3$) through a preheater by a HPLC pump (Pu-20865 Plus, Jasco Co.) with a combination of a piston separator under striring. The flow rate was 1.0 cm$^3$min$^{-1}$. An optical sapphire window (diameter = 6mm) installed to the reactor allowed the light illumination to solutions under hydrothermal conditions. Pressure was adjusted at 30 MPa by a back-up pressure regulator (Model 26-1761-24, TESCOM) and the reactor was kept at room temperature or heated at 350, 400 or 450 °C by an electric furnace. The solutions inside of the reactor were illuminated with near-UV light (300-400 nm) from a Hg-Xe lamp (MUV-202U, Moritex Co.) through a fiber optics. The generated gas was collected in the gas-collecting assembly and the amount of evolved hydrogen was analyzed by a gas chromatography with a TCD detector (GC-7000T, Lesca Co.).

![Diagram](image_url)

**Figure 1.** Schematic illustration of the experimental system used for the examination of the photocatalytic reaction in high-pressure high-temperature water. PG: pressure gauge; PH: preheater; PS: piston separator; TC: thermocouple; IW: iced water bath; TF: tee-type filter; BPR: back-up.

3. Results and discussion

Figure 2 shows the hydrogen yeilds from 0.05 M glucose solution under the typical experimental condition, 30 MPa and 400 °C. In the absence of photocatalyst, the hydrogen yields are less than 13% regardless of light irradiation. It appears that all photocatalysts showed almost no promoting effect on hydrogen evolution under the dark condition. On the other hand, the hydrogen yeild was increased by light irradiation in the presence of each photocatalyst. This observation clearly demonstrates that the
hydrothermal gasification of glucose could be accelerated with a help of photocatalytic actions. Especially, Pt-supported TiO$_2$ and Ni-supported TiO$_2$ showed the remarkable photocatalytic enhancement of hydrogen yield up to about 23–24 %, which may be due to the increased quantum efficiency of photocatalysis resulting from the suppressed hole-electron recombinations in TiO$_2$ by supported Pt and Ni.

Figure 2. Hydrogen yields from 0.05 M glucose solutions at 30 MPa and 400 °C in the absence or presence of photocatalyst in the dark (black bars) or under near-UV irradiation (gray bars). (a), (b) no photocatalyst; (c), (d) TiO$_2$; (e), (f) Ni-supported TiO$_2$; (g), (h) Pt-loaded TiO$_2$.

Figure 3. Methane yields from 0.05 M glucose solutions at 30 MPa and 400 °C in the absence or presence of photocatalyst in the dark (black bars) or under near-UV irradiation (gray bars). (a), (b) no photocatalyst; (c), (d) TiO$_2$; (e), (f) Ni-supported TiO$_2$; (g), (h) Pt-loaded TiO$_2$.

Figure 3 shows the methane yields from 0.05 M glucose solution at 30 MPa and 400 °C. In the absence of photocatalyst, the methane yield was as small as 0.025 % in the dark and slightly increased to 0.038 % by near-UV irradiation. Even in the presence of photocatalyst, it remained about 0.023-0.029 % under dark conditions, whereas the considerable enhancement was found under near-UV irradiation in the presence of each photocatalyst. In particular, Ni-supported TiO$_2$ exhibited the highest photocatalytic activity. These results are similar to those of hydrogen evolution and suggest that the photocatalytic generation of methane from glucose also takes place under hydrothermal conditions.
should be noted that the catalytic ability of Ni in the hydrothermal gasification of glucose has been reported by several researchers [8]-[10], while Ni-supported TiO$_2$ has no catalytic effect in the dark in the present study. However, a simple comparison seems to be inadequate, as the experimental conditions (reaction temperature, pressure, flow rate or residence time, and so on) were quite different between them.

We note that similar observations were found for different reaction temperatures, 350 and 450 °C, too, although the yields of hydrogen and methane are on the whole higher at 450 °C and lower at 350 °C than that at 400 °C. Especially, the hydrogen yields at 400 °C is about one order of magnitude larger than those at 350 °C. The photocatalytic enhancement was also observed for both temperatures, while such enhancement was relatively pronounced for 350 °C and somewhat modest for 450 °C compared with that for 400 °C.

It has been known that glucose decomposition proceeds generally by two reaction pathways; (A) the decomposition into low-molecular-weight compounds like acids and aldehydes that are preferable for the gasification and (B) the unfavorable formation of ring compounds like 5-hydroxymethylfurfural (5-HMF) due to dehydration reaction of glucose. The polymerization of 5-HMF is believed to cause the formation of char or tar [6]-[12]. We have recently reported that the hydrothermal gasification of ethanol to hydrogen and methane could be effectively promoted by the photocatalysis of Pt-supported TiO$_2$ [14]. It is therefore reasonable to assume that the gasification of glucose by reaction pathway (A) has been accelerated with a help of photocatalysis, leading to the enhancement of hydrogen and methane yields as observed in Figures 2 & 3. In addition, the efficient photocatalytic decarboxylation of carboxylic acids like acetic acid has been known to proceeds by Pt-supported TiO$_2$ photocatalyst (photo-Kolbe reaction) [15,16], which may be responsible to the enhancement of methane evolution.

On the other hand, we noticed that the solution ejected from the back-up pressure regulator remained almost colorless when the suspension containing each photocatalyst was illuminated with near-UV light, however it turned to a dark brown color under the dark conditions. Because the solutions containing 5-HMF or char are usually dark brown in color, it is likely that the photocatalytic decomposition of 5-HMF or char takes place. It is thus presumed that such reactions can contribute to the further acceleration of glucose gasification. However, the reaction mechanism of 5-HMF decomposition is rather complicated and the further detailed study will be required for better understanding.

![Figure 4](image_url)

**Figure 4.** Hydrogen yields at 30 MPa and 400 °C for different glucose concentrations. (●): Reaction with TiO$_2$ photocatalyst under near-UV irradiation, (■) reaction without photocatalyst in the dark.

We finally examined the effect of glucose concentration on the gasification efficiency. Figure 4 shows the hydrogen yileds at 30 MPa and 400 °C as a function of glucose concentration ranging from 0.01 M to 0.05 M. It is evident that hydrogen yield increases with decrease in glucose concentration.
and is almost independent of concentration around 0.01–0.025 M. It is also found that the difference in hydrogen yield between photocatalyzed and noncatalyzed reactions becomes smaller with decreasing glucose concentration. A possible reason for the increase of the hydrogen yield with decreasing glucose concentration is the inhibition of formation of 5-HMF or char at low concentrations [9,10], which is favorable for gasification. It is rather difficult to understand why the photocatalytic effect on the hydrogen yield approximately disappeared at low glucose concentrations. As the solid photocatalysts have been used in this study, the adsorption of the reactant or intermediate on the solid surface should be essential for the photocatalytic reaction to be initiated. It is therefore assumed that the insufficient adsorption of glucose or other intermediates on TiO$_2$ at low concentrations may cause the depression of photocatalysis.

4. Conclusion
The present study have revealed that the hydrothermal gasification of glucose at 30 MPa and 350–450 °C can be effectively accelerated with a help of the photocatalysis. In particular, Ni-support TiO$_2$ exhibited the high activity for both hydrogen and methane production. Furthermore, it was found that the formation of 5-HMF or char could be suppressed by the photocatalytic action of each photocatalyst, which is of great significance from the practical point of view. Based on the present results, we have concluded that the hybrid process of the hydrothermal gasification and the photocatalysis of TiO$_2$ has a large potential as the novel gasification method of glucose. The extension of this hybrid process to the gasification of other biomass will contribute to the development of clean and renewable energy resources.

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