Photosynthesis of hydrogen and methane as key components for clean energy system

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Abstract

While researchers are trying to solve the world’s energy woes, hydrogen is becoming the key component in sustainable energy systems. Hydrogen could be produced through photocatalytic water-splitting technology. It has also been found that hydrogen and methane could be produced through photocatalytic reduction of carbon dioxide with water. In this exploratory study, instead of coating catalysts on a substrate, pellet form of catalyst, which has better adsorption capacity, was used in the photo-reduction of carbon dioxide with water. In the experiment, some water was first absorbed into titanium dioxide pellets. Highly purified carbon dioxide gas was then discharged into a reactor containing these wet pellets, which were then illuminated continuously using UVC lamps. Gaseous samples accumulated in the reactor were extracted at different intervals to analyze the product yields. The results confirmed that methane and hydrogen were photosynthesized using pellet form of TiO$_2$ catalysts. Hydrogen was formed at a rate as high as 0.16 micromoles per hour (μmol h$^{-1}$). The maximum formation rate of CH$_4$ was achieved at 0.25 μmol h$^{-1}$ after 24 h of irradiation. CO was also detected.

Keywords: Solar reforming; Photocatalysis; Renewable energy; Hydrogen production; Reduction of CO$_2$

1. Introduction

In the study of hydrogen technology, one should not neglect the fact that molecular hydrogen does not form naturally on the earth but must be produced from other hydrogen-containing materials. This process requires a primary energy source, such as fossil fuel. Thus, hydrogen is not an energy source. Instead, it is just an energy carrier. In the process of hydrogen production involving hydrocarbons such as methane and methanol by a variety of reforming processes, significant amounts of carbon dioxide and carbon monoxide are produced as well. Particularly, production of carbon monoxide is fatal. Thus, hydrogen cannot be called as a “clean” fuel yet because the risk of environmental pollution exists from the production of hydrogen using the current processes. Only if these undesirable greenhouse gases produced can be recycled back into the process of creating fuel, the hydrogen technology may then be considered as an appropriate solution to clean energy systems.

In another aspect of solving carbon dioxide emission, photocatalytic reduction of carbon dioxide is of vital interest. The technologies of recycling CO$_2$, reducing CO$_2$ emission and CO$_2$ sequestration are equally important to tackle the challenge of global climate change. Using the photocatalytic process to reduce CO$_2$ into hydrocarbons has the potential to contribute to the control of CO$_2$ emission from industrial processes and eventually eliminate it. Furthermore, it has been found that H$_2$ could also be produced through the photocatalytic reduction of CO$_2$ with water using titanium dioxide pellets at room conditions [1]. However, the technology of recycling CO$_2$ is currently far from sufficiently mature to make a significant contribution to the reduction of CO$_2$ concentration in the atmosphere and the H$_2$ production for beneficial to the industries and society. More research work has to be done to improve the efficiency before the CO$_2$ recycling.
technology is ready to be part of the clean energy systems in the near future.

Previous work suggested that one of the possible main reasons for the inefficient reforming rate could be the rapid recombination of photo-excited electron/hole (e⁻/h⁺) pairs as well as the reverse reaction. Many researchers have studied various possible effective remediation methods for the photocatalysis process [2]. Some researchers studied the effects of adding sacrificial reagents and positive-hole scavengers to stop the rapid recombination of the e⁻/h⁺ pairs and the reverse reactions. Other studies focused on different forms of TiO₂ catalysts. Instead of coating the catalysts on a substrate, which was mostly done by other researchers, we used pellets form of catalysts in our current experiment to maximize the adsorption capacity in order to enhance the reforming rate of the photocatalysis process.

In our previous study conducted recently [3], the results showed that the pellet form of titanium oxide catalyst could be also feasible for use in photo-reduction of CO₂ with H₂O. It showed that when Short Wave UV (UVC) radiation was used, total yield of CH₄ obtained in the experiment after 65 hours (h) of continuous irradiation was 170 parts per million (ppm), which was fairly good as compared to those obtained from the processes using immobilized catalysts through thin-film techniques and anchoring methods. In this present study, samples of the gaseous product mixtures were extracted at different intervals to analyze the production profiles. This paper aims to analyze the formation rates of all the gaseous products accumulated in the reactor during the illumination.

2. Experiment

A fixed-bed photocatalytic reactor was constructed in the laboratory. A detail schematic drawing of the experimental set-up is shown in Fig. 1. The reactor as the main part of the experimental rig was made of cylindrical quartz tube. A flat glass tray was integrated in the tube to hold the catalysts. The tube has the length of 300 mm and the outer diameter of 74 mm. Stopcocks were attached to both ends with ground-glass joints. It has an internal volume of 1.11. One of the ends was connected to a gas cylinder supplying highly purified (99.999%) CO₂. Three gemicidal UVC lamps were installed above the reactor. The lamps were made of special glass that allowed large amounts of UVC rays, wavelength of 253.7 nanometers (nm), to pass through, with emitting power output of 1.6 W from each lamp. The entire experimental rig was shielded away from ambient light with an opaque insulation throughout the whole experiment cycle to minimize any possible external influence on the experiment outcomes.

The catalysts used were TiO₂ pellets that were cylindrical in shape with dimension of 4 mm in both diameter and height. They were extruded from Degussa’s pyrogenic TiO₂ (P25), 80% anatase and 20% rutile, with particle size of 30 nm and surface area of 50 m²/g. The catalysts were inclined before being used in the experiment to minimize any possible contamination in the porous pellets. After heating up the catalysts to 200 °C in an oven, they were placed in a vacuum desiccator, connected to a conventional vacuum system. The desiccator containing the heated catalysts was degassed for a few hours and then purged with the highly purified CO₂ gas. These degassing and purging processes were repeated three times. Next, a small amount of de-ionized water was sprayed over 100 g of pre-treated TiO₂ catalyst pellets. The pellets were then weighed again to determine the actual amount of water absorbed before being spread onto the flat tray in the reactor.

After the whole rig was properly setup, the air inside the reactor was first evacuated using a vacuum pump and flushed with the highly purified CO₂ gas. The processes were repeated a few times to ensure that no air but only CO₂ was present in the reactor. Finally, it was isolated at ambient pressure. The reactor and its contents were allowed to settle for a few hours before UV light was switched on to start the experiment and remained on continuously for the next 24 h. Gaseous samples accumulated in the reactor were extracted after 6, 12 and 24 h of illumination to analyze the product yields using gas chromatography with thermal conductivity detectors (GC-TCD) so as to obtain the production profile and study the effectiveness of this photocatalytic process. The instrument has four columns. Three of them were molecular sieve type for separation of He, H₂, O₂, N₂, CH₄ and CO. The fourth was a plot U-type for separation of CO₂, C₂H₄ and C₂H₆. All columns have their own thermal conductivity detector.

3. Results

Gas chromatography has shown in our recent study on the photo-reduction of CO₂ with H₂O [3] that CH₄ was the only hydrocarbon produced in such process. It was evident from the data obtained from GC/FID previously that no other hydrocarbons could be detectable above 3 ppm. In order to analyze the formation rate of all the gases presented in the product mixture, samples of the gaseous product mixture accumulated in the reactor were determined after different durations of continuous UVC irradiation. The profiles of the product formations were obtained as shown in Fig. 2. It was observed that CO, CH₄ and H₂ were produced in this photocatalysis process. No other hydrocarbons were detected.
In the initial 6 h of irradiation, the reforming activity was not obvious. As shown in the graph, only CO was formed while the other two gases were not detected initially. The initial profiles of the product formations showed that the production yields of \( \text{H}_2 \) and \( \text{CH}_4 \) began to increase gradually after 6 h and accelerated drastically after 12 h of irradiation, whereas, the CO production rate decreased gradually after the initial 6 h. Based on the second half of the product formation profiles, the average production rate of \( \text{CH}_4 \) was approximately 0.22 micromoles per hour (\( \mu\text{mol h}^{-1} \)) while \( \text{H}_2 \) was forming at an average rate of 0.16 \( \mu\text{mol h}^{-1} \). At the end of 24 h irradiation when the 100 g of TiO\(_2\) pellets absorbed with 2.5 g of water were illuminated with UVC light, the total accumulated yields of CO, \( \text{CH}_4 \) and \( \text{H}_2 \) obtained in this experiment were 30, 70 and 40 ppm, respectively. The detection limit for CO was 5 ppm while the limits for \( \text{CH}_4 \) and \( \text{H}_2 \) were 10 ppm.

Saladin attempted photosynthesis of \( \text{CH}_4 \) using microcrystalline TiO\(_2\) in the presence of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) in the gas phase at 343 K for 25 h, and obtained a lower formation rate of 0.1 \( \mu\text{mol h}^{-1} \) for \( \text{CH}_4 \) but a higher rate of 1.4 \( \mu\text{mol h}^{-1} \) for \( \text{H}_2 \) [4]. The observation of \( \text{H}_2 \) production from the results suggested that TiO\(_2\) pellets could be also used to split water and photo-produce \( \text{H}_2 \) gas besides photo-reducing \( \text{CO}_2 \) into \( \text{CH}_4 \). Thus, such a photocatalytic process could be useful in clean energy systems if the product yields could be further improved after the reaction mechanism was fully understood and an optimal condition was obtained.

### 4. Discussion and other observation

The temperature of the catalyst pellets could not be measured directly with a thermocouple because of the different absorptivity and emissivity of the thermocouple compared with the pellets. Instead, only the gaseous reactant temperature in the reactor was determined. It was observed that the temperature increased from the initial room temperature of 293 K and stabilized at 311 K after switching on the UV lamps for about 2 h.

As the product formation seen to be continuously accelerating after 24 h of irradiation, further study on this reforming process beyond this duration would be promising for photosynthesis of \( \text{CH}_4 \) and \( \text{H}_2 \) from \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) using TiO\(_2\) pellets as catalyst. In a preliminary study on the reforming process beyond 24 h of irradiation, the maximum production yield and formation rate for \( \text{CH}_4 \) were observed as illustrated graphical in Figs. 3 and 4.

As shown in the graphs, the formation rate increased steadily up to a maximum of approximately 0.25 \( \mu\text{mol h}^{-1} \) after 24 h of irradiation. Beyond that, the rate decreased gradually and the \( \text{CH}_4 \) formation almost stabilized at a maximum yield of 8.3 \( \mu\text{mol} \) after 65 h of irradiation. Although the details for the production mechanism and the exact reasons of preventing further formation of \( \text{CH}_4 \) were not absolutely clear in this present study, the results obtained, showed good correspondence with others reports [4–7] and suggested that the process has split the water and led to photo-produce \( \text{H}_2 \) and photo-reduce \( \text{CO}_2 \) into...
CH₄. Some of the products and intermediates could have been photoadsorbed, blocked the active sites and slowed down the reformation.

It was noted that no oxygen could be detected in the gaseous production mixture. Based on the other related studies [5,8] which reported observation of O₂ in the reduction products of CO₂, it was likely that O₂ was also produced in our experiments. As we failed to detect any oxygen during the illumination, the missing oxygen could be due to the photoadsorption to the pellets, which turned violet during the irradiation. This could deduce from the colour that the catalyst might have turned itself into titanium (III) oxide during the illumination. Saladin reported the similar observation and deduced that oxygen together with some other oxygen-containing products such as CO could have been photoadsorbed and hindered the diffusion of intermediates on the surface of the catalyst [6].

5. Conclusion

Experimental study on the photocatalytic reduction of CO₂ with H₂O using TiO₂ pellets illuminated by UVC irradiation continuously for different durations has been performed. It was found that H₂ and CH₄ were formed through the photocatalytic process. The photoabsorbed products could have hindered the reaction rate. The maximum formation rate of 0.25 μmol h⁻¹ was obtained for CH₄ after 24 h of irradiation. H₂ was formed at a rate as high as 0.16 μmol h⁻¹. Should such photocatalytic process be further understood and improved, both gases could have good potential of becoming the key components of the clean energy systems in the future.

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References