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Photocatalytic reduction of carbon dioxide into gaseous hydrocarbon using TiO_2 pellets

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Abstract

It has been shown that CO_2 could be transformed into hydrocarbons when it is in contact with water vapour and catalysts under UV irradiation. This paper presents an experimental set-up to study the process employing a new approach of heterogeneous photocatalysis using pellet form of catalyst instead of immobilized catalysts on solid substrates. In the experiment, CO_2 mixed with water vapour in saturation state was discharged into a quartz reactor containing porous TiO_2 pellets and illuminated by various UV lamps of different wavelengths for 48 h continuously. The gaseous products extracted were identified using gas chromatography. The results confirmed that CO_2 could be reformed in the presence of water vapour and TiO_2 pellets into CH_4 under continuous UV irradiation at room conditions. It showed that when UVC (253.7 nm) light was used, total yield of methane was approximately 200 ppm which was a fairly good reduction yield as compared to those obtained from the processes using immobilized catalysts through thin-film technique and anchoring method. CO and H_2 were also detected. Switching from UVC to UVA (365 nm) resulted in significant decrease in the product yields. The pellet form of catalyst has been found to be attractive for use in further research on photocatalytic reduction of CO_2.

Keywords: Photocatalysis; Reduction of CO_2; Energy storage; Titanium oxide pellets

1. Introduction

Solar reforming of hydrocarbons by photocatalytic reduction of carbon dioxide has been drawing worldwide attention because of the simplicity and manageability of the system. The specificity for the formation of fuel and low cost have even made it more attractive in research studies [1]. Besides lowering carbon dioxide emission, it could also be one of the most desirable goals for storage of the solar energy if the UV band in the solar radiation is the only source used to power the reduction process [2].

The methods of reducing carbon dioxide could be electrochemical, photochemical, photocatalytic and photoelectrochemical. Pioneering studies on methods for recycling carbon dioxide into useful products, particularly using semiconductors in aqueous suspension systems, were summarized by Halmann [3,4]. Current active research studies focusing on the photocatalytic reduction of carbon dioxide in the presence of water vapour using various titanium oxide catalysts in heterogeneous systems were carried out and compiled by Anpo and Yamashita [5]. These studies provided a useful platform of fundamental information essential in pursuing research related to photoreduction of carbon dioxide through catalytic process.

Titanium oxide has been widely used as catalyst for UV irradiation and was considered the best choice among several other oxides because it has low band-gap values of approximately 3.0 and 3.2 eV for rutile and anatase, respectively [5]. Besides fulfilling the thermodynamic requirements needed for the occurrence of most of the photocatalytic reactions usually investigated, titanium oxide is reasonably cheap, photo-stable and non-toxic, making it a perfect candidate for photocatalytic process. Interested groups have been focusing on extremely small titanium oxide particles as catalysts to study the relevance of particle size to the photoactivities. The utilization of colloidal catalyst is to promote specific redox process on its surface.

Experimental studies of carbon dioxide reduction into fuel-like hydrocarbon species in saturated water vapour with the aid of

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titanium oxide film coated on copper substrates by the sol–gel and dip-coating technique has been performed in Japan [6,7]. The reduced species of methane, ethane and ethylene were detected. However, the efficiency of the reduction of carbon dioxide is still very low. Although the true reasons causing this low reduction rate are not obvious, all these investigations and studies leading to a better understanding of the fundamental mechanisms behind the reaction will be helpful for subsequent research in applying the principles for improving the efficiency and selectivity.

Another research team showed that titanium oxide highly dispersed within zeolite and mesoporous molecular sieves exhibited high photocatalytic reactivity [8]. In our preliminary study conducted recently, the results showed that the pellet form of titanium oxide catalyst could be also feasible for use in reduction of carbon dioxide although the products have not been confirmed yet [9]. In separate studies, pellet form of catalyst has been widely explored to investigate heterogeneous photocatalytic oxidation of gas-phase organics for air purification and confirmed to be a viable alternative to using thin-film catalyst [10].

In this present research, pellet form of catalyst was illuminated under UV irradiation in a quartz tube reactor attempting to reduce carbon dioxide in the presence of saturated water vapour into gaseous hydrocarbons under room conditions. The contact areas and adsorption/desorption capacity of the porous pellets are expected to be better as compared with the thin-film form of catalyst. Thus, the photocatalytic process would be enhanced between the reactants (carbon dioxide and water vapour) and catalyst (TiO_2). The effect of UV irradiation was also examined to understand how well the yields could be influenced by its wavelength.

2. Experimental

A fixed-bed photocatalytic reactor was newly designed and built in the laboratory. The detail schematic drawing of the experimental set-up is shown in Fig. 1.

The main part of the experimental rig is a cylindrical quartz tube reactor. A flat glass tray was integrated in the tube to hold the catalysts. The reactor has the size of 300 mm (length) × 74 mm (outside diameter) × 3.0 mm (thickness). It was connected to a flask containing de-ionised water and a gas cylinder supplying highly purified (99.999%) carbon dioxide gas. Above the reactor were three NEC Germicidal lamps, GL8, which were made of special glass that allowed ultraviolet rays to pass through, and were designed to radiate large amounts of UVC (253.7 nm) rays with emitting power output of 1.6 W each lamp. Due to the sensitivity of the expected results, any possible external influence on the experiment outcome was minimised by shielding the entire experimental rig away from ambient light with an opaque insulation jacket throughout the whole experiment cycle.

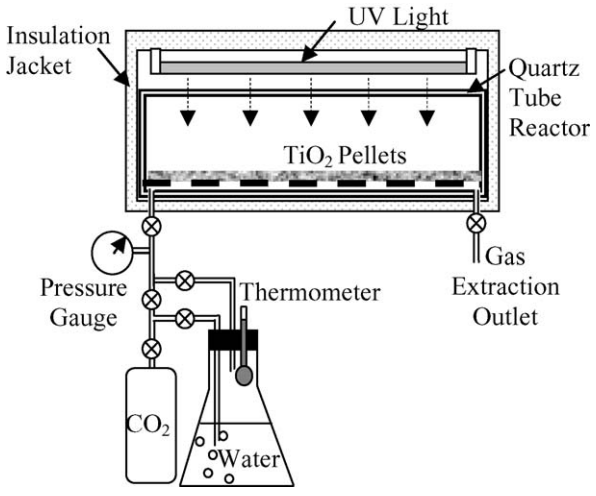

Fig. 1. Schematic drawing of experimental set-up.

The catalysts used were TiO_2 pellets, Aerolyst 7708, which were cylindrical in shape with dimension of 4 mm in both diameter and height. They were extruded from P25, Degussa's pyrogenic TiO_2, 80% anatase and 20% rutile, with particle size of 30 nm and surface area of 50 m^2/g. The catalysts were pre-treated before being used in the experiment to minimise any possible contamination in the porous pellets. After heated-up to 200 °C in oven, the TiO_2 pellets were placed in a vacuum desiccator connected to a conventional vacuum system. The desiccator containing the heated TiO_2 pellets was degassed for few hours and purged with the highly purified CO_2 gas. These degassing and purging processes were repeated for three times before the pellets were used for the experiment. One hundred grams of TiO_2 pellets were then spread out on the flat tray in the reactor.

Before the UV illumination, highly purified CO_2 gas was first flowed through the de-ionised water in the flask and purged out the air in the reactor via a fully opened valve located at the other end. The amount of moisture (water vapour) in the gas flowing through the rig could be estimated based on the temperature of the water in the flask. The rig was then isolated with a pressure of approximately 10 kPa above ambient pressure. After the whole rig is properly set-up, the rig and its contents were allowed to settle for 2 h before the first gas sample was taken to verify the mixture as the baseline and UV light was then switched on to start the experiment. The light remained on continuously for the next 48 h. At the end of the experiment, the gaseous products accumulated inside the reactor were abstracted to analyse the product yields using gas chromatography and investigate the effectiveness of this photocatalytic process.

In the second set of the experiments, TiO_2 catalysts were replaced by a new batch of pre-treated catalysts and spread out on the flat tray in the reactor. The UVC lamps were replaced by three NEC black light blue fluorescent lamps, FL8BL-B which emit ultra-violet radiation with wavelength peaking at 365 nm and have energy power output of 1.0 W for each lamp. The whole process as before was repeated. At the end of the 48 h illumination, the final product concentrations accumulated inside the reactor were again analysed to investigate the effect of the radiation wavelength on the photocatalytic reduction of CO_2.

3. Results and discussion

The data obtained from gas chromatography showed that the total CH_4 yield was about 200 ppm and lower than 100 ppm in the experiments when the pellets were irradiated for 48 h

continuously with UVC (253.7 nm) and UVA (365 nm), respectively. No other hydrocarbons were detected in the product mixture. Instead, the evolution of CO was observed and the ratio of CO/CH_4 is approximately one.

In these experiments, some hydrogen gas was also observed and the ratio of H_2/CH_4 is approximately 0.6. No oxygen could be detected in the gaseous production mixture. Saladin reported the similar observation and deduced that oxygen together with other oxygen-containing products such as CO could have been photoadsorbed, blocking the active sites and hindering the diffusion of intermediates on the surface of the catalyst [12]. Based on the other related studies [5,11] which reported observation of O_2 in the reduction products of CO_2, it is likely that O_2 was formed in our experiments and the photoadsorption prevented its detection. The production of CO and CH_4 found in our current results from these experiments have shown that CO_2 could be photo-reduced into CH_4 using pellet form of TiO_2 in the presence of water vapour. Continuous irradiation of UV light on TiO_2 catalyst pellets, Aerolyst 7708, in presence of CO_2 and water vapour mixture could have led to the following reaction, Eq. (1), under room conditions

$$2H_2O + 3CO_2 \xrightarrow[TiO_2]{} CH_4 + 2CO + 3O_2 \quad (1)$$

The observation of H_2 production in our results showed that TiO_2 pellets could be also used to split water and photo-produce hydrogen gas. Since the current conditions and other parameters have not been optimised, the product yields could be likely further improved using this present outcome as a useful baseline for subsequent studies.

3.1. Photocatalytic process using TiO_2 pellets

Illumination of these very fine semiconductor particles in the catalyst pellets by band-gap irradiation caused electron excitation from valence to the conductance band. Various sites on these particles act as reducing/oxidising centres, which will provide electrons to carbon dioxide as well as accept electrons from water vapour in the reactant mixture. The photocatalytic process involves electrons (e^-) and holes (h^+) generated at these various sites with the aid of photonic energy ($h\nu$) as shown in the schematic diagram in Fig. 2.

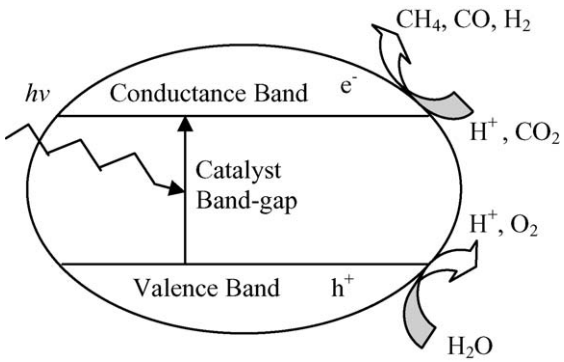

Fig. 2. Schematic of UV photo-excitation process.

The photon-generated e^- and h^+ are powerful oxidizing and reducing agents, respectively. The formation of electron–hole pairs requires sufficient photonic energy with appropriate wavelength to overcome the band-gap between valence band and conductive band. In the presence of the photonic energy provided in the experiment, the pairs of electron–hole are created in these semiconductor particles. They migrate to surface and serve as redox sources that react with absorbed reactant on the semiconductor surface. Thus, the reduction of CO_2 into CH_4 and CO compounds in the presence of H_2O took place photocatalytically at the solid–gas interface.

3.2. Proposed mechanism

Various reaction schemes for the photocatalytic reduction of CO_2 by H_2O on TiO_2 catalysts have been proposed in different studies [6,7,11,13,14]. Although the exact production mechanism of CH_4 and CO are not absolutely clear in our present study, the results obtained in the present study show good correspondence with these reports and suggest that the process would have undergone the following reforming reaction shown in Fig. 3, when the reactants and catalysts are in contact with UV irradiation.

When illuminated by UV light with sufficient photonic energy ($h\nu$) and appropriate wavelength, photon-generated electrons (e^-) and holes (h^+) are created on the surface the TiO_2 catalysts. The holes first react with water vapour adsorbed on the catalyst, resulting in producing hydroxyl radicals (·OH) and hydrogen ions (H^+). The water is further oxidized by ·OH producing oxygen and H^+. At the same time, carbon radicals (·C) are formed from CO_2 through the intermediate product of CO. The carbon radicals then react with H^+ generated from H_2O and e^- on the catalyst surface to finally produce CH_4.

The presence of CO in the gaseous product mixture presumably resulted from the incomplete reduction of CO_2. It could be due to insufficient H^+ produced from H_2O present in

$$TiO_2 + h\nu \rightarrow (h^+ + e^-)$$

$$\begin{cases} H_2O + h^+ \xrightarrow[TiO_2]{} \cdot OH + H^+ \\ \cdot OH + H_2O + 3h^+ \xrightarrow[TiO_2]{} O_2 + 3H^+ \end{cases}$$

$$2H_2O + 4h^+ \xrightarrow[TiO_2]{} O_2 + 4H^+$$

$$\begin{cases} CO_2 \xrightarrow[TiO_2]{} CO + \tfrac{1}{2}O_2 \\ CO \xrightarrow[TiO_2]{} \cdot C + \tfrac{1}{2}O_2 \end{cases}$$

$$CO_2 \xrightarrow[TiO_2]{} \cdot C + O_2$$

Resulting,

$$\cdot C + 4H^+ + 4e^- \xrightarrow[TiO_2]{} CH_4$$

$$2H^+ + 2e^- \xrightarrow[TiO_2]{} H_2$$

Fig. 3. Reaction scheme for photocatalytic reduction of CO_2 with H_2O on TiO_2 pellets.

the reactant mixture and resulted from recombination of ·C radicals and oxygen on the surface of the catalysts. Although the reactants were water saturated CO_2, the temperature of the water at the initial stage was 297 K. This implied that the absolute humility in the reactor was only less than 3%. Furthermore, some of the hydrogen ions produced from the water have combined themselves together with the electrons on the surface and produced hydrogen gas in the process. This could also contribute to the low reforming yield of CH_4.

3.3. Comparison of methane formation

Kato and Nishimura in Japan investigated various configurations of CO_2 photo-reduction with the aid of catalyst using TiO_2 thin-film coated on copper sheets. They reported that the reduction yield of CH_4 increased with an increase of UV rays irradiating duration. The concentration of CH_4 yielded as high as 17 ppm (part per million) after UV-lamp (10 W) illumination for 65 h [6]. However, such a thin-film form of coating limits the specific surface areas of the catalyst and has little adsorption capacity, which controls the photo-reduction rate.

Using pellet form of catalyst is our new approach of photocatalytic reduction of CO_2 with water vapour, instead of immobilized catalysts on solid substrates. It would have better contact areas and adsorption capacity. The yield improvement was on the order of hundreds of ppm which was very significant as compared to that obtained using thin-film coating technique although more work could be done to further improve the yields. In order to compare the data with others whose results were measured in term of μmol/g-cat, the product yield from this experiment together with others was tabulated as shown in Table 1.

In studying various types of standard TiO_2 catalysts in powder form supplied by the Catalysis Society of Japan, it was reported by Yamashita et al. that when the photocatalytic reduction of CO_2 (124 μmol) with gaseous H_2O (372 μmol) was investigated using well-characterized standard TiO_2 catalysts (JRC-TiO-4), the process led to the formation of CH_4, as well as traces of C_2H_4 and C_2H_6. The time profile for production of CH_4 with UV irradiation time indicated the yield increased steadily with time up to 4 h after which, a decrease in the reaction rate then occurred. Yield of approximately 0.68 μmol/g-cat was achieved after 6 h of irradiation [13].

In another study on effective use of various titanium oxide catalysts, Anpo et al. reported [11] that highly dispersed, anchored titanium oxide catalyst on porous Vycor glass (PVG) illuminated in the presence of a mixture of CO_2 and H_2O led to the formation of CH_4, CH_3OH and CO in gas-phase, as well as traces of C_2H_4 and C_2H_6. Approximately 0.12 μmol/g-cat of CH_4 was produced regularly after 6 h of UV irradiation on the catalyst in the presence of CO_2 (50 μmol) and H_2O (250 μmol). In these two studies, the processes were carried out in vacuum condition and using a 75 W high-pressure Hg lamp through water and colour filters, while our process was operated at room conditions and used a total power of 4.8 W only. Furthermore, only 150 mg of catalyst was used in these two processes for optimising the use of the catalyst. However, TiO_2 is not an expensive or heavy material. Achieving higher product yield in terms of ppm instead of μmol/g-cat would be of better interest from an application standpoint. By expressing all these experiment results in the measurement unit of ppm, as in Table 2 below for comparison, it shows that using the pellet form of catalyst is an attractive alternate approach for photo-reduction of CO_2 comparing to those obtained from the process using thin-film coating on copper sheet and anchoring on porous Vycor glass. In addition, although the product yields obtained using pellet (Aerolyst 7708) and powder (JRC-TiO-4) forms of catalyst have comparable results, the former form has an additional advantage that the photocatalysis process is free from filtration to recover the catalysts from the gaseous product mixture as compared to the powder form of catalysts.

Table 1
Comparison of CH_4 formation achieved with others using various forms of catalyst

Various TiO_2 catalysts		
JRC-TiO-4 (μmol/g-cat)	PVG (μmol/g-cat)	Aerolyst 7708 (μmol/g-cat)
0.68	0.12	0.10

Table 2
Comparison of CH_4 formation achieved in term of ppm

Various TiO_2 catalysts			
JRC-TiO-4	PVG	Aerolyst 7708	Thin-film
206	60	200	17

3.4. Effects of irradiation wavelengths and emission power on photo-activity

Switching from UVC (253.7 nm) to UVA (365 nm) resulted in significant decrease in methane yield from approximately 200 ppm to a range lower than 100 ppm. It showed that an increase wavelength of UV irradiation significantly decreased the product yield. Tseng et al. also observed the similar phenomena [15] in the previous study exploring the relationships between the characteristics of catalysts and the activity of the CO_2 photo-reduction by illuminating aqueous suspensions of powdered catalysts.

Besides the wavelength difference, it was noted that the total emitting power of the three UVC lamps was 4.8 W as compared to the three UVA lamps, which have the total of 3.0 W only. This could also contribute to the decrease in the photo-activity due to the less photonic energy. The reforming processes in such photocatalytic experiment could be promoted by increasing the photonic energy, depending on the absorption capacity of the catalysts. Therefore, the higher the irradiating power and the higher the absorption capacity, the better are the expected yields.

4. Summary and conclusion

CO_2 reduction into hydrocarbons by photocatalysis using TiO_2 pellets illuminated by UVC and UVA lamps has been performed. It has been established that CO_2 could be

transformed into methane gas when it is in contact with water vapour and titanium oxide pellets under the UV irradiation. The results have verified the possibility of using standard TiO_2 pellets as catalyst. The yield of the product is fairly good as compared to those obtained from the process using thin-film technique and anchoring method, but not high enough to use them as fuels. The wavelength of the UV irradiation strongly affected the product yields. There are many other parameters that could be explored, such as operating temperature, pressure, H_2O/CO_2 and irradiation duration to obtain higher yields. In conclusion, the pellet form of TiO_2 catalyst is found to be feasible and attractive for use in further investigation of CO_2 reduction for CO_2 environment management.

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