Photo reduction of CO₂ to methanol using optical-fiber photoreactor

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Abstract

Greenhouse gases such as CO₂ are the primary cause of global warming. One of the best routes to remedy CO₂ is to transform it to hydrocarbons using photo reduction. CO₂ was photocatalytically reduced to produce methanol using a Hg lamp with wavelength 365 nm in a steady-state optical-fiber photoreactor. The optical-fiber photoreactor, comprised of nearly 120 Cu/TiO₂-coated fibers, was designed and assembled to transmit and spread light uniformly inside the reactor. TiO₂ film was coated on optical fiber using a dip-coating method. Cu-loaded titania solutions were prepared by a thermal hydrolysis method. The thickness of Cu/TiO₂ film was 53 nm. The coating film consisted of very fine spherical particles with diameters of near 14 nm. The XRD spectra indicated the anatase phase for all TiO₂ and Cu/TiO₂ films. The wavelength of absorption edge on Cu/TiO₂ was near 367 nm, equivalent to a bandgap of 3.3 eV. The most active Cu species on TiO₂ surface were Cu₂O clusters, and they played an important role for the formation of methanol. The methanol yield increased with UV irradiative intensity. Maximum methanol rate was 0.45 mmole/g cat h using 1.2 wt.%-Cu/TiO₂ catalyst at 1.29 bar of CO₂, 0.026 bar of H₂O, and 5000 s mean residence time under 16 W/cm² UV irradiation. Higher than 1.2 wt.% Cu loading gave a lower rate of methanol yield because of the masking effect of Cu₂O clusters on the TiO₂ surface. The Langmuir–Hinshelwood model was established by correlating experimental data to describe the kinetic behavior. An optimum pressure ratio of H₂O/CO₂ was found in the photo reduction of CO₂ for maximum methanol yield.

Keywords: Photocatalysis; Renewable energy; Optical-fiber photoreactor; CO₂ reduction; TiO₂

1. Introduction

Greenhouse gases such as CO₂, CH₄ and CFCs are the primary causes of global warming. The atmospheric concentration of CO₂ has steadily increased owing to human activity and this accelerates the greenhouse effect. Recently, the Kyoto Protocol of the United Nations Framework Convention on Climate Change mandated a return of CO₂ emission levels to those of 1990. On the other hand, upgrading CO₂ to reusable hydrocarbons is one the best routes to overcome the energy shortage. The energy grade of CO₂ is low from a thermodynamic perspective so that any transformation of CO₂ requires energy input. Solar energy should be one of the best candidates because it is abundant and can be supplied without producing CO₂. Consequently, the photo reduction of CO₂ is highly desired. In this way, solar energy is transformed and stored as chemical energy similar to photosynthesis.

CO₂ can be photocatalytically reduced in water vapor or solvent by photocatalysts such as TiO₂ [1]. To find a highly efficient photocatalyst for the reduction of CO₂ with H₂O is one of the most challenging tasks. Eq. (1) gives an example of overall photo reduction transforming CO₂ to methanol. Methanol is the most promising product from the reduction of CO₂, because it can be easily transported, stored and can be used as gasoline-additives for automobiles. Titania-supported copper plays a crucial role for promoting the reduction of CO₂ in methanol formation [2]. The yield of photo products can be changed substantially under different experimental conditions such as UV wavelength, light intensity, additives of reaction media and reactor configuration. Other variables, such as CO₂ pressure, moisture and residence time are also important in photo reducing CO₂:

\[
\text{CO}_2 + 2\text{H}_2\text{O} \xrightarrow{hv} \text{CH}_3\text{OH} + \frac{3}{2}\text{O}_2
\]  

(1)

Practical applications of TiO₂ photocatalyst for the remediation of vapor-phase CO₂ streams often require immobilizing the photocatalyst in a packed-bed photoreactor.
A variety of heterogeneous supports have been explored, including glass surface [3,4], quartz rods [5] and monoliths [6,7]. The transmission and uniform distribution of light energy are important in designing a photoreactor, which differs completely from a traditional reactor. TiO₂-coated fiber-optical cable reactors have demonstrated some inherent advantages over packed-bed reactors in photo reactions [8,9]. Fig. 1 shows that light is transmitted into an optical fiber. The light is split to two beams when hitting the internal surface fiber, due to the difference of refraction index between the TiO₂ coating and the quartz core. Part of the light is reflected and transmitted along the fiber, while the rest penetrates and excites the titania layer at the interface. Thus the electron-hole (e⁻ and h⁺) pairs are generated; these then conduct the following photo reactions. Therefore, optical fibers can be used to radiate the light uniformly inside a photoreactor. The goal of this study is to develop a photo-reactor system in order to carry out the photo reduction of CO₂ in vapor phase. The preparation and characteristics of TiO₂ film on optical fibers are essential for the development of a photoreactor. In regard to the light source, artificial light can be used currently. However, light energy can be collected from the sun using a focus reflection dish in the future.

2. Experimental

The TiO₂ solutions were prepared using a thermal hydrolysis method for coating on optical fibers. Titanium butoxide (97%, Aldrich, USA) and polyethylene glycol (PEG, molecular weight of 20 000, Merck, Darmstadt, Germany) were added to a 0.1 M nitric acid solution. The volume ratio of titanium butoxide to HNO₃ was 1:6, and the weight of PEG was 50% of TiO₂. An appropriate amount of copper precursor, CuCl₂, was added to obtain the desired Cu loading of TiO₂. The mixed solution was heated to 80 °C for 8 h. PEG was added to prevent cracking during the drying and calcination of the film. Furthermore, PEG increased the viscosity of the solution and dispersed TiO₂ particles uniformly in the solution. The appearance of pure TiO₂ solution was transparently milky.

Optical fibers were obtained from the E-Tone Technology Company of Taiwan. The polymeric shield on the optical fiber was burned off in a furnace at 400 °C. The remaining quartz fiber had a diameter of 112 μm. Each quartz fiber was cleaned by a 5 M NaOH solution in an ultrasonic cleaner, then rinsed in de-ionized water and dried before applying dip-coating procedure. The bare fiber was immersed into the solution vertically, then pulled up at various rates by a step motor. The rates of pulling-up ranged from 5 to 50 mm/min. The TiO₂ film was dried in air at 150 °C by a rate of 1 °C/min from the ambient temperature, and maintained at 150 °C for 3 h. Then it was calcined at 500 °C for another 5 h. The same procedure of TiO₂ coatings was also applied to glass plates that were 5 cm long, 2 cm wide and 0.1 cm thick, for characterization.

The TiO₂ phase of the film was determined using the X-ray diffractometer, MAC Science M03XHF, scanning from 20 ° to 80 °. The UV–vis absorption was measured by transmission mode using a Varian Cary spectrophotometer 100, at wavelengths from 200 to 800 nm. The microstructure of the TiO₂ film on the optical fiber was inspected using a scanning electron microscope (SEM) LEO 1530 (Germany). X-ray photoelectron spectroscopy (XPS) was conducted for elemental analysis on a spectrometer of VG Microtech MT500.

An optical-fiber photoreactor (OFPR) was designed and assembled to transmit light from one side of the OFPR module to the fiber-supported TiO₂ film, as shown in Fig. 2. About 120 fibers 16 cm long were inserted into the OFPR, which had a diameter of 3.2 cm and was 16 cm long. The circular side-plates of OFPR were sealed using O-rings and the system passed the leakage test. Fig. 3 schematically illustrates the reactor system. The OFPR was irradiated through the quartz window of one side using a Hg lamp with a peak light intensity at 365 nm. The light intensity entering the quartz window could be adjusted from 1 to 16 W/cm². The whole OFPR was...
wrapped using aluminum foil to avoid the interference of indoor lamps during the reaction. Supercritical-fluid grade CO₂ was purchased from Air Products (USA) to avoid any hydrocarbon contamination. It was certified that the maximum amount of hydrocarbons was less than 20 ppb. CO₂ was bubbled through a water saturator to carry moisture. The reactor was tightly closed and maintained at 75 °C by heating tape during the reaction. The reactor was purged for one hour using helium before switching to CO₂. The flow rate of CO₂ was ~3 ml/min and this was equivalent to a residence time of 5000 s based on the reactor volume. The pressure of CO₂ was in the range of 1.05–1.4 bar, and the water pressure could be adjusted by the temperature of saturator. All reaction data was taken at steady state which could be attained in about 1 h after turning on the UV light.

Reaction products were analyzed via a sampling loop of 2.5 ml on-line by a GC equipped with FID using a 2 m long Porapak Q column. Analysis results indicated that methanol was the dominant hydrocarbon. Blank reactions were carried out to ensure that hydrocarbon production was solely from the photo reduction of CO₂. One blank was UV-irradiated without the catalyst, and another was in the dark with the catalyst under the same experimental conditions. No hydrocarbon was detected in the above blank tests.

3. Results and discussion

3.1. Characteristics of catalysts

Fig. 4 shows the SEM micrographs of bare optical fiber, cross-section of Cu/TiO₂ film and top view of TiO₂ film on top of the fibers. The bare fiber was smooth after removing polymeric shield, as shown in Fig. 4(a). The thickness of 1.2 wt.% Cu/TiO₂ films was near 53 nm on the surface of optical fiber, as shown in Fig. 4(b). Fig. 4(c) shows that the TiO₂ film consisted of very fine spherical particles with diameters of ~14 nm. The film was transparent, colorless and uniformly flat without cracks. The films of TiO₂ and other Cu-loaded-TiO₂ on fibers were also had the same thickness. The XRD spectra in Fig. 5 shows the diffraction pattern of various Cu/TiO₂ and pure TiO₂ films. Thermal treatment at 500 °C for 5 h resulted in well crystallized anatase-type TiO₂. No copper diffraction peak was observed in the XRD spectra indicating that copper was finely dispersed on TiO₂. The UV–vis absorption spectra of films are shown in Fig. 6. The absorption spectra below 300 nm decreased abruptly due to the background subtracting of the underlayer glass plate. The TiO₂ films absorbed light below a wavelength of 380 nm in the UV–vis spectra, indicating its bandgap near 3.3 eV. The UV–vis absorptions of Cu/TiO₂
catalysts were similar to those of pure titania. Fig. 7 shows the results of Cu (2p) XPS spectra on Cu/TiO2 with three different Cu loadings. According to the positions of binding energies (2p3/2, 932.8 eV; 2p1/2, 952.8 eV) and the shape of the peaks, the copper on the surface of TiO2 might exist in multiple-oxidation states, but Cu(I) would be the primary species [10].

Table 1 summaries the crystalline sizes and band gaps of prepared Cu/TiO2 films. The average crystalline sizes of all films ranged from 13.4 to 14.0 nm; these values were calculated from the Scherrer equation according to the peak broadening of XRD spectra. The crystalline sizes of Cu/TiO2 were only slightly smaller than that of TiO2. In general, the crystalline size was primarily influenced by calcined temperature, and Cu loading had negligible effect. The bandgaps ranged from 3.31 to 3.37 eV, as estimated by extrapolating the absorption edge of VU–vis spectrum to the abscissa of zero absorption, approximately at 367 nm. These values are typical TiO2 bandgaps indicating that the Cu loadings did not affect the band structure of TiO2.

Table 2 lists the molar ratios of elemental compositions of different copper-loaded-TiO2 catalysts. The bulk composition was calculated from the amount of precursors in the preparation procedure. The surface composition was estimated from the peak intensity of XPS, which usually detected ~1 nm depth of a sample. The Cu/Ti ratios of surface were higher than those of bulk, indicating that most Cu was dispersed on the surface of catalysts. The higher the Cu loading was, the higher the surface Cu ratio was. The XPS spectrum of O (1s) was de-convolved and the individual peak intensity was used to estimate the ratio of hydroxyl group (OH, 532.7 eV) and total oxygen on catalysts.

<table>
<thead>
<tr>
<th>Catalyst (wt.)</th>
<th>Cu/Ti</th>
<th>OH ratioa</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.169</td>
</tr>
<tr>
<td>0.52</td>
<td>0.012</td>
<td>0.008</td>
</tr>
<tr>
<td>1.20</td>
<td>0.029</td>
<td>0.015</td>
</tr>
<tr>
<td>2.06</td>
<td>0.077</td>
<td>0.028</td>
</tr>
</tbody>
</table>

a Estimated from the UV–vis spectra.
b Estimated from the XPS peak intensity.
c Calculated from the precursors of CuCl2 and titanium butoxide in preparation.
The results are also listed in Table 2. The OH/total oxygen ratio of Cu/TiO$_2$ was higher than that of pure TiO$_2$, and the ratio increased with increasing Cu loadings.

3.2. Photo reduction of CO$_2$

Fig. 8 shows the methanol yields versus light intensity under the partial pressures of CO$_2$ and H$_2$O at 1.29 and 0.026 bar, respectively, at 75 °C. The yield increased with light intensity in the range of 1–16 W/cm$^2$. Pure TiO$_2$ gave very little methanol yield, while Cu/TiO$_2$ significantly improved the yield. The maximum yield of methanol was 0.45 μmole/g cat h using 1.2 wt.% Cu/TiO$_2$ catalyst under a light intensity of 16 W/cm$^2$. Since the primary status of copper was Cu(I) (as shown in Fig. 7), Cu$_2$O was suggested to be the active center for methanol formation in CO$_2$ photo reduction [10,11]. Increasing Cu loading resulted in increasing photo activity, as expected. Cu$_2$O could also serve as an electron trap to reduce the recombination rate of electron-hole pairs during photo excitation of photocatalyst. Surface hydroxyls (OH) of TiO$_2$ could also promote the adsorption of the reactant, CO$_2$, so that the photo reaction was enhanced [11]. The amount of surface hydroxyl on TiO$_2$ increased with increasing Cu loading (Table 2). Thus, the overall photo activity of CO$_2$ reduction significantly increased. However, excess Cu$_2$O clusters on the surface also masked the surface of TiO$_2$ resulting in less light exposure of catalyst. Consequently the photo excitation of electron and hole pair was declined because less photo energy was absorbed. So there would be an optimum Cu loading on Cu/TiO$_2$ catalysts for maximum methanol yield. An Cu loading of 1.2 wt.% was found to give the highest yields of methanol under our experimental conditions.

The influences of CO$_2$ and water pressure were also investigated. Fig. 9 shows the methanol yields versus different CO$_2$ pressures under fixed light intensity, 13.5 W/cm$^2$ and water pressure, 0.026 bar, at 75 °C. The methanol yields increased with CO$_2$ pressure, reaching a maximum of 0.415 μmole/g cat h at 1.29 bar, then decreased with further increasing of CO$_2$ pressure on 1.20 wt.% Cu/TiO$_2$. The other two catalysts showed similar trends with lower methanol yields. Fig. 10 shows the methanol yields versus various pressure ratios of H$_2$O/CO$_2$ under fixed light intensity, 13.5 W/cm$^2$. The methanol yields also increased with H$_2$O/CO$_2$ ratios, then decreased with higher ratios. Such phenomena implied a competitive adsorption of reactants, i.e., CO$_2$ and H$_2$O, on the active sites during photo reduction. Thus there existed optimum pressures of CO$_2$ and H$_2$O in the photo reduction.

As shown in Eq. (2), a Langmuir–Hinshelwood (L–H) model was employed to correlate the experimental data of CO$_2$, water, light intensity and methanol yield. Both reactants, CO$_2$
and H2O, were assumed to be adsorbed on the same active sites of the catalyst surface. The reaction was considered to be irreversible because the partial pressures of products, methanol and oxygen, were very low. Multiple-variable non-linear regression was applied the data of 1.20 wt.% Cu/TiO2. The best fitted rate constant, k, and adsorption equilibrium constants, K1 and K2, are listed in Table 3. The value of water adsorption equilibrium constant, K1, was 51.7 bar\(^{-1}\), that was nearly three orders of magnitude higher than that of CO2, K2, 0.01 bar\(^{-1}\). The value of K2 was near zero, indicating that the adsorption of CO2 was very weak, while water was strongly adsorbed on the catalyst surface:

$$\text{Rate} = \frac{kP_H^2P_{CO_2}I^a}{(1 + K_1P_{H_2O} + K_2P_{CO_2})^3}$$ (2)

where k is the methanol rate constant (μmole/g cat bar\(^{-1}\)h), I the light intensity (W/cm\(^2\)), a the power of light intensity, K1 the adsorption equilibrium constant of H2O (bar\(^{-1}\)), K2 the adsorption equilibrium constant of CO2 (bar\(^{-1}\)).

It is well known that the surface of TiO2 becomes super-hydrophilic when irradiated by UV light. Therefore, water molecules would cover most of the surface of TiO2 catalyst during photo reduction. Our CO2 photo reduction was carried out at very low water pressure ranging from 0.0072 to 0.12 bar. At high H2O/CO2 ratio, CO2 would need to compete with H2O on the active sites in order to react with adsorbed H2O. Thus reducing H2O pressure (or raising CO2 pressure) increases the reaction rate. However, when H2O pressure is much lower than that of CO2, e.g. H2O/CO2 < 0.02, less water coverage could decrease the reaction rate. Therefore there exists an optimum CO2 pressure at a given H2O pressure, or an optimum H2O/CO2 ratio as shown in Figs. 9 and 10, respectively.

Apparent elementary steps of the CO2 photo reduction are derived in Eqs. (3)–(8) according to the results of L–H model (Eq. (2)). The rate-limiting step was assigned to be the formation of methanol (Eq. (5)). The detailed mechanism of the methanol formation could not be revealed from our present study. The adsorption of CO2 and H2O and the desorption of methanol and oxygen were not bottle necks of the photo reduction of CO2 under our experimental conditions:

$$2\text{H}_2\text{O} + \text{CO}_2 \overset{K_1}{\rightarrow} \text{CH}_3\text{OH} + \text{O}_2$$ (5)

$$\text{CH}_3\text{OH} \overset{K_2}{\rightarrow} \text{CH}_3\text{OH} + \text{S}$$ (6)

$$2\text{O} \overset{K_3}{\rightarrow} \text{O}_2 + \text{S}$$ (7)

$$\text{O}_2 \overset{K_4}{\rightarrow} \text{O}_2 + \text{S}$$ (8)

As the effect of light intensity, the power of light intensity was estimated to be ~0.2 in the methanol rate equation (Eq. (2)) within 1–16 W/cm\(^2\) UV irradiation. In general, photo activity would be directly proportional to the light intensity. However, if more light flux was supplied than the demand of photo reaction, the power of light intensity in the rate equation would gradually shift from one to less than 0.5 [12]. The light flux of our experiment was probably over-supplied. In such a case, the light flux should be decreased in order to increase quantum efficiency. On the other hand, larger reactor volume or higher CO2 flow rate can be used under the same light flux.

4. Conclusion

The catalytic reduction of CO2 has great advantages over green plants of not having to support a living system. This research has demonstrated a highly photo-efficient reactor for converting solar energy to chemical energy, such as, methanol from CO2 via photo energy. In this study, the thickness of the films was near 53 nm after calcination at 500 °C, and the average size of the nanocrystals in the TiO2 film was near 14 nm. The photo reduction of CO2 with H2O was successfully demonstrated in a photoreactor with Cu/TiO2-coated optical fibers. So far, the maximum methanol yield was 0.46 μmole/g cat h under 365 nm UV irradiation. Compared with a traditional packed-bed reactor, an optical-fiber provides a medium to transmit light throughout the reactor. Thus light energy can be spread more efficiently. In addition, a higher processing capacity is possible because the catalyst can disperse on a large external area of optical fibers in a given reactor volume. Furthermore, OFPR is a promising photoreactor that can be used in gas or aqueous phases in other photo reactions in the future.

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