Metal-doped Photocatalysts to Reduce Carbon Dioxide in Ethanolamine Solution for Methane Production

Hung-Yu Wu[1], Hsunling Bai[1*] and Jeffrey C.S. Wu[2]

[1*] National Chiao Tung University, Institute of Environmental Engineering
Hsinchu, 30010, Taiwan, hlbai@mail.nctu.edu.tw
[2] National Taiwan University, Department of Chemical Engineering
Taipei, 10617, Taiwan, cswu@ntu.edu.tw

ABSTRACT

Photocatalytic reduction of carbon dioxide (CO_2) to form valuable energy source of methane (CH_4) in the ethanolamine (MEA) solution is investigated in this study. The TiO_2 photocatalysts were prepared by doping with nano-sized metals (Fe, Zn, Mn, Ce) via the co-precipitation method. The photocatalytic reduction process was performed in the MEA solution because the MEA absorption is one of the most popular methods for CO_2 greenhouse gas capture from flue gas streams. And it is intended to integrate the CO_2 capture and utilization into one process. The tests were performed with the UV light source of 9W and 365 nm. The light intensity of 6.3 mW/cm^2 was measured at the center point between the UV light source and the outer glass of the reactor. The 5 hours test results showed the methane yield followed the order of Ce-TiO_2 > Mn-TiO_2 > Zn-TiO_2 > Fe-TiO_2. Tests were also evaluated with a solar light concentrator, and it has been proved that it is possible to produce CH_4 under solar light without the addition of any external energy source.

Keywords: carbon dioxide, photoreduction, ethanolamine, photocatalyst, methane.

1 INTRODUCTION

The global warming issue has become one of the most important environmental concerns which raised a lot of attention. The rising demand for energy is typically correlated to the increase in CO_2 emissions [1]. To reduce the CO_2 emission and mitigate the global warming effect, the CO_2 caapture, utilization and sequestration processes have been employed.

Since Fujishima and Honda (1972) have investigated that titanium dioxide (TiO_2) can be catalytic irradiated under UV light, the photocatalytic ability of the TiO_2 photocatalyst has reached widespread attention and applications [2]. Generally, metals or transition metal oxides are the main materials of photocatalysts, with TiO_2 as the most popular one due to its non-toxic, high chemical stability and appropriate band gap activation energy and range for redox reaction. Nevertheless, the TiO_2 photocatalyst has a poor utilization rate of the sunlight. In order to enhance visible light utilization, the band gap of the photocatalyst has to be reduced, and re-combination of the electron-hole pairs has to be minimized [3]. It was reported that among various transition metal ions or lanthanide group metal, e.g. copper, silver, cerium, nickel, zinc and iron etc., a suitable concentration of metal ions in TiO_2 could advance electron–hole separation [4-10].

In addition, the MEA absorption process is one of the most matured CO_2 capture processes from flue gas of fossil fuel fired power plants and other large industrial processes for mitigating the global warming effect. It could become economical if the CO_2 capture process is combined with the CO_2 photo-reduction process and producing new energy sources such as CH_4 without using an addition energy source for the CO_2 reduction process. For this reason, we explored the feasibility of this novel green method which reduce the CO_2 via photocatalytic process in an MEA solution under either UV or solar light source.

2 EXPERIMENTAL SECTION

2.1 Catalyst preparation

This study employed the co-precipitation method to prepare the metal doped photocatalysts. In a typical procedure, DI water (76 ml), TiO_2 (pure P25, 8 g) and metal precursors were mixed. Then ammonium hydroxide was added dropwise into the solution and stirred for 5 hours. The resulting mixture was washed with DI water and dried in an oven at 120^{o}C. Finally, the powder was calcined at 450^{o}C for 6 hours.

Cleantech 2012, www.ct-si.org, ISBN 978-1-4665-6277-6

2.2 Photocatalytic reduction of CO_2 into CH_4

The CO_2 reduction experiment was carried out in a batch reactor with photocatalysts illuminated by either 9W of 365 nm UV light source or under solar light concentrator. The 300 ml of ethanolamine (MEA) solution was loaded with 0.2 g photocatalyst powder. The GC/FID was used for the analysis of gas reaction products, and methane (CH_4) was detected as the main product of reaction. The schematic drawing of the experimental set-up is shown in Figure 1.

3 RESULTS AND DISCUSSION

3.1 Catalyst characterization

The feasibility of the photocatalyst is the optical absorption capacity. The UV-vis diffuse reflectance spectroscopy of the composite materials and original P25 were measured and depicted in Figure 2. The absorption edges are seen to shift to the lower-energy region in the spectra of the metal-doped TiO_2, the composite materials could noticeably enhance their optical absorption ability after metals doped on the TiO_2 (P25) photocatalyst.

The absorption edges are calculated with the method reported by Khan et al. [11] and the band-gap energy of various metal doped photocatalysts are shown in Table 1. Values of band-gap energy for metal-doped P25 (3.19-3.37 eV) are observed to be slightly decreased in comparison with that of pure P25 (3.52 eV), which indicates that the ability of visible light absorption can possibly be enhanced.

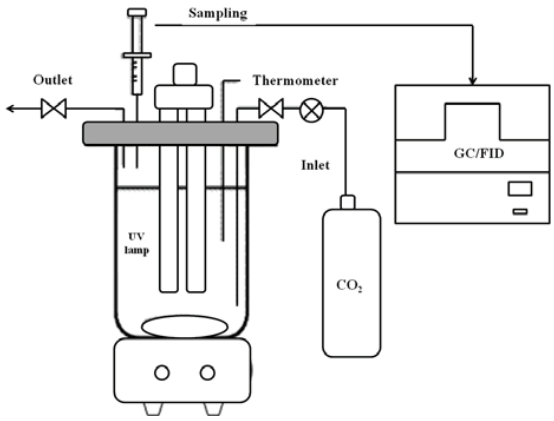

Figure 1: Schematic drawing of experimental set-up for photocatalytic reduction of CO_2 using UV lamps.

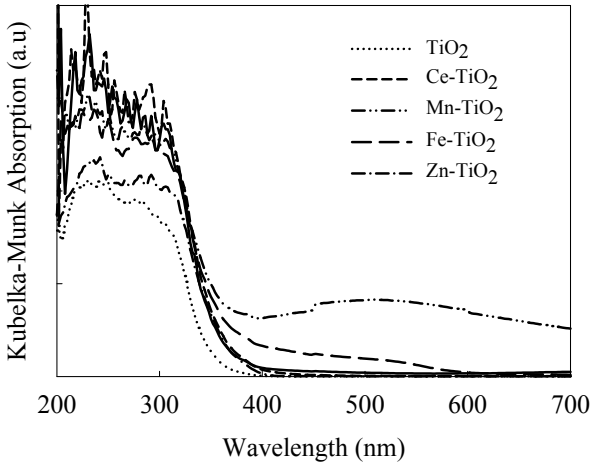

Figure 2: UV–vis spectroscopy of different photocatalysts

Catalyst	Band gap (eV)
TiO_2 (P25)	3.52
Ce-TiO_2	3.37
Mn-TiO_2	3.33
Fe-TiO_2	3.28
Zn-TiO_2	3.27

Table 1: band-gap energies of photocatalysts used in this study.

3.2 Photocatalytic activity tests

The effect of irradiation time on the CO_2 photocatalytic reduction was investigated for photocatalysts doped with several metals (Fe, Zn, Mn, Ce). In the blank experiment, only DI water and MEA (C_2H_7NO) were presented in the solution. Figure 3 shows CH_4 production rates by different metal doped TiO_2 (P25) photocatalysts under the UV irradiation. It is observed that P25 doped with metals could increase the redox ability, and the methane yields followed the order of Ce-TiO_2 > Mn-TiO_2 > Zn-TiO_2 > Fe-TiO_2. The methane yield via the Ce-TiO_2 photocatalyst appears to be the highest. Thus it was used for the following photocatalytic reduction test under the sunlight concentrator.

In order to efficiently utilize real sunlight for the photoreduction of CO_2 to CH_4, a solar concentrator was employed to transfer sunlight into the reactor.

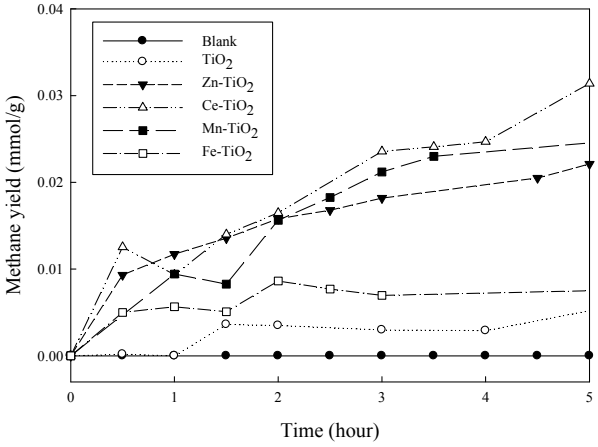

Figure 3: Time dependence of methane yield using various metal doped photocatalysts whith the UV lamp.

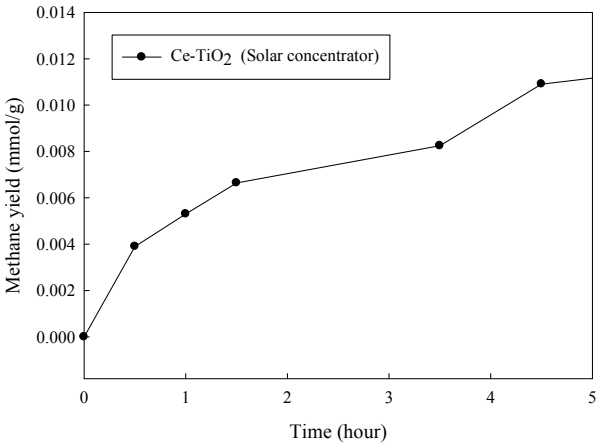

Figure 4: Time dependence of methane yield using Ce-TiO_2 photocatalyst with the solar concentrator.

The light intensity of sunlight depends on the weather of the day when the experiment was carried out, with the average intensity of natural sunlight to be 0.18 mW/cm^2 on Jan 8, 2012 from 9:00 am to 4:00 pm in Hsinchu, Taiwan. Figure 4 shows the CH_4 yield as a function of time. It is observed that the CH_4 yield continuously increases, thus it is possible to produce CH_4 under real sunlight without the addition of any external energy.

4 CONCLUSIONS

The photoreduction of CO_2 to form CH_4 was studied using MEA as the absorbent so that the CO_2 capture and utilization can be combined into one process. The photocatalytic efficiencies of different types of metals doped on the TiO_2 were investigated. It showed that the Ce-TiO_2 performed better than the other metals of Zn, Fe and Mn doped on TiO_2 under 365nm UV light source. And the Ce-TiO_2 could also be irradiated under sunlight. This reveals that real sunlight could be used for the CO_2 photoreduction into CH_4 without the addition of any external energy.

ACKNOWLEDGMENTS

Support from the National Science Council, Taiwan, through the grant number of NSC 99-2221-E- 009-037-MY3 is gratefully acknowledged.

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