Influences of Metals and Acids on the Photo Reduction of CO₂ under Catalysis of TiO₂

Endang Tri Wahyuni^{1*}, Retno Kusumaningrum², Wa ode Mulyana², and Roto Roto¹

1. Chemistry Department, Faculty of Mathematic and Natural Science, Gadjah Mada University, Yogyakarta 55281, Indonesia

2. Post Graduate Students of Chemistry Department, Faculty of Mathematic and Natural Science, Gadjah Mada University, Yogyakarta 55281, Indonesia

Abstract: Conversion of green house CO₂ into fuel gas in the presence of reducing agent sources that are Fe and Zn powder, as well as hydrogen ions supplier such as nitric and acetic acids by photo catalytic reduction with water vapor on TiO₂ has been studied. The photo reduction was carried out by batch technique, using a UV lamp with a wave length of 290-400 nm, as a photon source. The gasses produced from the photo reduction were determined by gas chromatography. The research results indicate that the photo reduction of CO₂ has successfully produced methane as a dominant product. The presence of the metals in addition to be able to improve the methane yield, it is also able to induce ethylene formation. Meanwhile the acids can considerably enhance the methane yield without formation of ethylene. Furthermore, the enhancement is observed to be controlled by mass of the metals, and the acid concentrations. It is also found that Zn and HNO₃ show stronger effect in the increasing CO₂ photo reduction.

Key words: Photo reduction, CO₂, TiO₂, Fe, Zn, methane, ethylene.

1. Introduction

The significant enhancement of the world population, vehicles number, and industry activities has gradually increased CO₂ emission. CO₂ is believed as a major contribution on the green house effect that creates further global warming. The global warming has induced the real climate change, that can treat the world sustainability. Therefore, finding an effective solution to reduce the emission of CO₂ has attracted the interest of many researchers. Recently, many efforts are made to reduce CO₂ emissions through pre- or post-combustion CO₂ capture followed by compression and geological sequestration [1]. These processes are energy intensive and thus costly.

An alternative and more preferable way is the conversion of CO₂ into useful and non-toxic compounds. The possible ways to convert CO₂ into valuable products are catalytic conversions [2-4], electrocatalytic/electrochemical process [5-7], plasma

process [8-10], enzymatic/biochemical process [11-13], and photo catalytic/photochemical process [14-20]. Among them, photo catalytic reduction seems the most intensively developed method.

Recent innovations in photo catalysis technology have made CO₂ conversion a potentially promising application. This process UV and/or visible light as the excitation source for semiconductor catalysts, and the photoexcited electrons reduce CO₂ with H₂O on the catalyst surface and form energy-bearing products such as CO (carbon monoxide), CH₄ (methane), CH₃OH (methanol), HCHO (formaldehyde), and HCOOH (formic acid). The types of the products seem to be depend on the process conditions and/or on the modification of TiO₂ photo catalyst, and are almost obtained in a mixture of two or three compounds.

Reduction of CO₂ in the presence of NaOH solution photo catalyzed by TiO₂ supported on a polymer, has been reported to produce methanol and methane, accompanied with formic acid and formaldehyde [14]. Such many products may be less favored because it will create difficulty in separation and purification.

*Corresponding author: Endang Tri Wahyuni, Ph.D., research field: environmental chemistry.

By introducing vapor water instead of water or liquid solution, only methanol and methane have been resulted from CO₂ photo reduction in the presence of various photo catalyst, including Ti-SBA [15], TiO₂ particles with various sizes [16], and Ag-TiO₂ [17]. In addition, by using TiO₂ powder, CO₂ photo reduction with water vapor has yielded methane, acetylene and ethylene as the products [18].

CO₂ photo reduction with water vapor catalyzed by TiO₂ pellet [19], as well as by modified titania, such as Cu/TiO₂-SiO₂ [20], Cu-I-TiO₂ [21], and Ag/TiO₂ [22], have been success to form CO and methane as the products.

A single product has been successfully resulted from photo reduction of CO₂ with water vapor in the presence of several titania based photo catalysts. CO gas has been resulted by using I-TiO₂ [23]. By using Cu/TiO₂ photo catalyst, methanol is obtained [24]. Methane has been produced by using Pt-TiO₂ [25] and Cu/TiO₂ [26]. The single product may be preferred, since the separation is not necessary. However only low fraction of methane was resulted [25].

Increasing methane from photo reduction of CO₂ catalyzed by TiO₂ has been performed by the addition of the electron source or reducing agent such as H₂ [27]. In addition to H₂, several metals including Fe and Zn are also known as good reducing agents [28]. Another

way to increase the methane conversion from CO₂ photo reduction is introducing hydrogen ions that can be serviced by acids. In fact the use of the metals and acids to increase CO₂ photo reduction has not been explored yet. In this paper the addition of Fe and Zn metals, and mineral and organic acids on the results of the CO₂ photo reduction are addressed.

2. Experiments

2.1 Materials and Instruments

Materials used are TiO₂, HNO₃, and CH₃COOH from E. Merck, and several gasses including CO₂, CH₄, and C₂H₄ purchased from Samator Gas Indonesia. A set of photo reduction equipment that was self designed as illustrated in Fig. 1 was employed for photo reduction. The apparatus was composed by a photo reduction glass tube having 5 L of the volume, UV lamp with the wavelength of 290-400 nm, CO₂ gas tube, and water vapor generating tube. Shimadzu Gas Chromatography was used for analyzing gasses resulted from the photo reduction.

2.2 Photo Reduction of CO₂

Photo reduction was carried out in the reactor illustrated as Fig. 1 by following optimal condition obtained previously [18]. Into the tube that has been

Fig. 1 A set of photo reduction equipment.

filled with 10 gram of TiO₂, was flown by CO₂ gas, and H₂O vapor generated from the water vapor generator. The tube then was irradiated with UV light, and during the light exposure, the tube was rotated electrically for a period of time to make effective contact among light, TiO₂, CO₂, and water vapor. When the reaction was over, the gasses produced were analyzed by gas chromatography method.

The same procedure was also performed, in which Fe and Zn powder, as well as HNO₃ and CH₃COOH were added. In addition, the mass of the metals, the concentration of the acids, and the irradiation time were varied to examine the effect of the factors on the photo reduction results.

3. Results and Discussions

3.1 The Products of CO₂ Photo Reduction

To identify the substances resulted from CO₂ photo reduction, the retention time of the peaks appear in the chromatography data of the substances were compared to the retention times of methane ($t_r = 1.596$ min) and ethylene ($t_r = 1.889$ min) standards. From the comparison it is identified that the product of CO₂ photo reduction with water vapor catalyzed by TiO₂ for 3 h period of time, is found to be methane, as a single product with low fraction. The reactions of the methane formation are written below [17]. The reaction is initiated by charge carrier that are h^+ (hole or positive radical) and electron formation (Eq. (1)) from TiO₂ during UV light exposure. The next step is reaction between the hole with water molecule to form oxygen gas and hydrogen ion (Eq. (2)), that is continued by hydrogen radical formation resulted from its reaction with the electrons (Eq. (3)). Simultaneous reaction between CO₂ with the electron into CO₂ radical is also took place (Eq. (4)). Then the CO₂ radical reacts with hydrogen radical consecutively to form methane (Eqs. (5-8)).

3.2 The Influence of Fe and Zn Metals

Fig. 2 displays the effect of the presence of Fe and Zn metals on the methane resulted. Fig. 2 exhibits that the addition of both Fe and Zn metals has improved the methane yielded.

The role of Fe and Zn metals in increasing photo reduction is by providing electron through oxidation. Both Fe and Zn can be oxidized as indicated by their standard oxidation potentials (E°) that have positive values [28], by O₂ presence in the photo reduction tube and hole (h^+) from TiO₂ during the light irradiation while releasing electron, as seen in the Eqs. (9, 10).

This oxidation is believed to enhance the amount of electrons used for CO₂ activation, and H radicals formation, that create more number of methane.

Moreover, in order to find out the better understanding the role of Fe and Zn in increasing the photo reduction, the addition of Fe and Zn with various masses in the photo reduction has also been performed. The results are presented in Fig. 3. Fig.3 generally illustrates that in addition to methane,

Fig. 2 Influence of the addition of Fe and Zn metals.

Fig. 3 Influence of masses of Fe and Zn powder.
(a) CH₄/Zn; (b) CH₄/Fe; (c) C₂H₄/Fe; (d) C₂H₄/Zn.

ethylene (C₂H₄) with lower yield is also produced with the presence of Fe and Zn in the photo reduction. The formation of C₂H₄ may follow Eq. (11), that may be simultaneous with Eq. (7):

The methane yielded proportionally depends on the metal masses up to 20 gram. Increasing the mass should enhance the number of the electron released, that provide more number of CO₂ radicals. However, when the mass is further enlarged, decreasing methane produced is observed. Very large mass of Fe and Zn may cover the surface of TiO₂ that inhibit the UV light to contact with TiO₂ surface. As a consequence the smaller number of electrons can be provided. The reduce of the methane yielded may also be caused by the formation of other gas products.

Regarding the ethylene, the increase of Fe mass from 5 gram to 30 gram (low level), also promotes higher fraction of ethylene, but further mass enlargement leads to the ethylene decreased. The explanation should be same as presented above. In contrast, for Zn, ethylene starts to form when the mass is relatively high, that is larger than 30 gram. In the low mass, the electrons from Zn, that may be in larger quantity than from Fe, are only used for photo reduction resulting in the higher methane. In such condition, the reactants have no chance to form ethylene. Furthermore, the ethylene appears to enhance with increasing Zn mass, that can be

explained as presented previously.

3.3 Influence of Acids

The results of CO₂ photo reduction with the presence of HNO₃ and CH₃COOH are illustrated as Fig. 4. It is seen in Fig. 4 that the addition of both acids can raise the methane produced, without accompanied by ethylene. Moreover, HNO₃ is seen to show stronger effect in the increasing methane formation, than CH₃COOH does. The role of the acids is by donating hydrogen ions from their ionization, as seen in Eqs. (12, 13).

As described previously, that hydrogen ions forming hydrogen radical are required for reacting with CO₂ radicals to form methane. An interesting data appears that in the presence of the acids, ethylene is not resulted from the photo reduction. With more hydrogen, more hydrogen radicals are available, but because the number of C atoms from CO₂ radicals remain the same, the ethylene (C₂H₄) cannot be obtained (Eqs. (6-8, and 13)).

Fig. 4 also demonstrates that the nitric acid has higher effect in the increasing methane produced than acetic acid. It takes to note that HNO₃ is a strong acid enabling it to reveal much more number of hydrogen

Fig. 4 Influence of acids on the methane yield.

ions compared to acetic acid, as the weak one ($K_a = 1.85 \times 10^{-5}$). The more hydrogen ions induce more effective photo reduction. It is reasonable therefore that HNO₃ promotes higher methane formation compared to acetic acid.

In order to support the role of the acids in the enhancing methane as the photo reduction product, the influence of the acid concentrations has been observed, as displayed in Fig. 5. Fig. 5 assigns the dependency of the methane resulted on the concentration of both acids. Increasing concentration of nitric and acetic acids promote more hydrogen ions and so the methane produced.

3.4 Influence of Irradiation Time

The result of CO₂ photo reduction performed in the various of period of time in the presence of Fe powder is displayed as Fig. 6 and that of Zn is illustrated by Fig. 7.

Fig. 6 demonstrates that the extension irradiation time has raised the methane and ethylene formed. The methane fraction seems to decline when the time was further expanded, that is followed by the increase of the ethylene formed.

The irradiation time determines the effectiveness of the contact among UV light, TiO₂, CO₂, H₂O, and Fe. The longer time enables the reactants to mutually contact in more effective, that give an increase in the formation of CO₂ radicals and H⁺ ions. As a result, the methane and ethylene obtained are also improved.

Interesting data is observed when the photo reduction time was further expanded, that is the methane fraction is found to reduce, while the ethylene keeps to improve. The data infers that with very long reaction time, the conversion from CO₂ radicals and H⁺ ions into methane takes place slower, but that of into ethylene proceed faster. It is important to note that the formation of methane and ethylene follows the simultaneous reactions. Accordingly, when methane formed is decreased, the ethylene conversion is raised up.

Fig. 5 Influence of the acids concentrations.

Fig. 6 Influence of photo reduction time in the presence of Fe powder.

Fig. 7 Influence of the photo reduction time with the presence of Zn powder.

Fig. 7 shows the increase of the methane and ethylene resulted from the photo reduction in the presence of Zn powder, when the photo reduction time was extended. But the gasses are observed to be constant or slightly decline as the further extension

Fig. 8 Influence of the photo reduction time with the addition of acids.

time. Increasing time can stimulate the more effective contact among the reactants that promote the CO₂ photo reduction to form higher methane and ethylene. For long time reaction, the contact among reactants may be inhibited by the gas produced, and/or makes the photo catalyst and the metal to be exhausted, leading to the slower photo reduction.

The results of the photo reduction in the presence of the acids carried out in various of time are presented as Fig. 8. It is seen in Fig. 8, the same trend as the result of the photo reduction in the presence of Zn.

In the presence of the acids, the longer of the photo reduction time can improve the releasing hydrogen ions that gives rise the CO₂ conversion into methane. For the photo reduction taking place in very long time, the ionisation of the acids may reach equilibrium condition that are not able to increase the hydrogen ions formation. This situation explains the decreasing methane conversion.

4. Conclusions

It can be concluded that the photo reduction of CO₂ with the water vapor under catalysis of TiO₂ has successfully produced methane as the fuel gas. The addition of both Fe and Zn powder, as well as HNO₃ and CH₃COOH can considerably enhance the fraction of the methane resulted. In addition to methane, photo reduction in the presence of both metals can also result in ethylene with lower fraction, that is not observed in

the presence of acids. It is implied that the ethylene formation is directed stronger by CO₂ radicals than by H⁺. Furthermore, the enhancement of methane formation is found to be controlled by mass of the metals, the concentration of the acids, and the photo reduction time. Zn and HNO₃ are observed to have stronger effect on the increasing CO₂ photo reduction.

Acknowledgements

The financial support for conduction this research from The Ministry of Higher Education and Research and Technology Republic of Indonesia, via Gadjah Mada University through the Grant No: 50/LPPM. UGM/2015 is greatly acknowledged.

References

- [1] White, C. M., Strazisar, B. R., Granite, J. S., Hoffman, E. J. and Pennline, H. W. 2003. "J. Air Waste Manage." *Assoc.* 53: 645-715.
- [2] Inui, T. 1996. "Highly Effective Conversion of Carbon Dioxide to Valuable Compounds on Composite Catalysts." *Catalysis Today* 29: 329-37.
- [3] Itkulova, S. S., Zhunsova, K. Z., and Zakumbaeva, G. D. 2005. "CO₂ Reforming of Methane over CO-Pd/Al₂O₃ Catalysts." *Bull. Korean Chem. Soc.* 26: 2017-22.
- [4] Olah, G. A., and Prakash, G. K. S. 2008. "Conversion of Carbon Dioxide to Methanol and/or Dimethyl Ether using Bi-Reforming of Methane or Natural Gas." IPC8 Class: AC07C2700F1, USPC Class: 518700.
- [5] Kaneco, S., Hiei, N., Xing, Y., Katsumata, H., Ohnishi, H., Suzuki, T., and Ohta, K. 2003. "High-efficiency Electrochemical CO₂-to-methane Reduction Method Using Aqueous KHCO₃ Media at less than 273K." *J. Solid State Electrochem* 7: 152-6.
- [6] Kaneco, S., Ueno, Y., Katsumata, H., Suzuki, T., and Ohta, K. 2006. "Electrochemical Reduction of CO₂ in Copper Particle-Suspended Methanol." *Chemical Engineering Journal* 19: 107-12.
- [7] Ogura, K., Yano, H., and Shirai, F. 2003. "Selective Conversion of CO₂ to Ethylene by the Electrocatalysis at a Three-Phases (Gas/Liquid/Solid) Interface in an Acidic Solution." *J. Solid State Electrochem* 1 (4): 554-7.
- [8] Antonius, I., Dae, R. Y., Jae-Wook, C., Hwaung, L., and Hyung, K. S. 2007. "Gliding Arc Plasma Processing of CO₂ Conversion." *Journal of Hazardous Materials* 146: 309-15.
- [9] Danhua, M., Xinbo, Z., Chunfei, W., Bryony, A., Paul, T. W., and Xin, T. 2016. "Plasma-photo Catalytic Conversion of CO₂ at Low Temperatures: Understanding

- the Synergistic Effect of Plasma-Catalysis." *Catalysis B Environmental* 182: 525-32.
- [10] Laura Frances Spencer. 2012. "The Study of CO₂ Conversion in a Microwave Plasma/Catalyst System." A Dissertation for Ph.D degree, The University of Michigan.
- [11] Jones, H. W., Donnelly, M. I., and Wolfe, R. S. 1985. "Evidence of a Common Pathway of Carbon Dioxide Reduction to Methane in Methanogens." *J. of Bacteriology* 163 (1): 126-31.
- [12] Yu, Y., Chen, B., Qi, W., Li, X., Shin, Y., Lei, C., and Liu, J. 2012. "Enzymatic Conversion of CO₂ to Bicarbonate in Functionalized Mesoporous Silica." *Microporous and Mesoporous Materials* 153: 166-70.
- [13] Chiu, S. Y., Kao, C. Y., Chen, C. H., Kuan, T. C., Ong, S. C., and Lin, C. S. 2008. "Reduction of CO₂ by High-density Culture of *Chlorella* sp. in a Semicontinuous Photobioreactor." *Bioresour Technol* 99 (9): 3389-96.
- [14] Liu, S., Zhao, Z., and Wang, Z. 2007. "Photo Catalytic Reduction of Carbon Dioxide Using Sol-gel Derived Titania." *Photochem. Photobiol. Sci.* 6: 695-700.
- [15] Hwang, J. S., Chang, J. S., Park, S. E., Ikeue, K., and Anpo, M. 2004. "High Performance Photo Catalytic Reduction of CO₂ with H₂O by TiSBA Mesoporous Material." *Stud. Surf. Sci. Cat.* 153: 299-302.
- [16] Koci, K., Obalova, L., Placa, D., Capek, L., Lacny, Z., Jirkovsky, J., and Solcova, O. 2009. "Effect of TiO₂ Particle Size on CO₂ Photo Reduction." *Applied Catalysis B: Environmental* 89: 494-502.
- [17] Koci, K., Mateju K., Obalova, L., Krejcikova, S., Lajny, Z., Placa, D., Capek, L., Hospodkova, A., and Solcova, O. 2010. "Effect of Silver Doping on TiO₂ for Catalytic Reduction of CO₂." *Applied Catalysis B: Environmental* 96: 239-44.
- [18] Wahyuni, E. T., Jumina, J., and Sugeng T. 2012. "A Study on the Photo reduction of Green House CO₂ Gas Catalyzed by TiO₂ to form Methane and Methanol." *J. Chem. Chem. Eng.* 6: 506-10.
- [19] Tan, S. S., Zou, L., and Hu, E. 2006. "Photo Catalytic Reduction of Carbon Dioxide into Gaseous Hydrocarbon Using TiO₂ pellets." *Catalysis Today* 15: 269-273.
- [20] Li, Y., Wang W. N., Zhan, Z., Woo, M. H., Wu, C. Y., and Briswas, P. 2010. "Photo Catalytic Reduction of CO₂ with H₂O on Mesoporous Silica Supported Cu/TiO₂ Catalyst." *Applied Catalysis B: Environmental* 100: 386-92.
- [21] Zhang, Q., Gao, T., Andino, J. M., and Li, Y. 2012. "Copper Iodine co Modified -TiO₂ Nanoparticles for Improved Activity of CO₂ Photo Reduction with Water Vapor." *Applied Catalysis B: Environmental* 123-4: 257-64.
- [22] Zhao, C., Krall, A., Zhao, H., Zhang, Q., and Li, Y. 2012. "Ultrasonic Spray Pyrolysis Synthesis of Ag/TiO₂ Nanocomposite Photo Catalysts for Simultaneous H₂ Production and CO₂ Reduction." *International Journal of Hydrogen Energy* 37: 9969-76.
- [23] Zhang, Q., Li, Y., Ackerman, E. A., Josifovska, M. G. and Li, H. 2011. "Visible Light Responsive Iodine Doped TiO₂ for Photo Catalytic Reduction of CO₂ to Fuels." *Applied Catalyst A: General* 400: 195-202.
- [24] Wu, J. C. S., and Lin, H. M. 2005. "Photo Reduction of CO₂ to Methanol via TiO₂ Photo Catalyst." *International Journal of Photoenergy* 7: 115-9.
- [25] Zhang, Q. H., Han, W. D., Hong, Y. J., and Yu, J. G. 2009. "Photo Catalytic Reduction of CO₂ with H₂O on Pt-Loaded TiO₂ Catalyst." *Catalysis Today* 148: 335-40.
- [26] Liu, D., Fernández, Y., Ola, O., Mackintosh, S., Maroto-Valer, M., Christopher, P. M. A., Lee, A. M., and Wu, J. C. S. 2012. "On the Impact of Cu Dispersion on CO₂ Photo Reduction over Cu/TiO₂." *Catalysis Communications* 25: 78-82.
- [27] Lo, C. C., Hung, C. H., Yuan, C. S., and Wu, J. F. 2007. "Photo Reduction of CO₂ with H₂ and H₂O on TiO₂ and ZrO₂ in Circulated Photoreactor." *Solar Energy Materials and Solar Cell* 91: 1765-74
- [28] Skoog, D. A., West, D. M., and Holler, F. J., 1990. "Analytical Chemistry: An introduction." ed. 6th. Saunders College Publishing.