Influences of Metals and Acids on the Photo Reduction of CO$_2$ under Catalysis of TiO$_2$

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Abstract: Conversion of green house CO$_2$ 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 TiO$_2$ 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 CO$_2$ 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 HNO$_3$ show stronger effect in the increasing CO$_2$ photo reduction.

Key words: Photo reduction, CO$_2$, TiO$_2$, Fe, Zn, methane, ethylene.

1. Introduction

The significant enhancement of the world population, vehicles number, and industry activities has gradually increased CO$_2$ emission. CO$_2$ 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 CO$_2$ has attracted the interest of many researchers. Recently, many efforts are made to reduce CO$_2$ emissions through pre- or post-combustion CO$_2$ 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 CO$_2$ into useful and non-toxic compounds. The possible ways to convert CO$_2$ 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 CO$_2$ conversion a potentially promising application. This process UV and/or visible light as the excitation source for semiconductor catalysts, and the photoexcited electrons reduce CO$_2$ with H$_2$O on the catalyst surface and form energy-bearing products such as CO (carbon monoxide), CH$_4$ (methane), CH$_3$OH (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 TiO$_2$ photo catalyst, and are almost obtained in a mixture of two or three compounds.

Reduction of CO$_2$ in the presence of NaOH solution photo catalyzed by TiO$_2$ 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.
By introducing vapor water instead of water or liquid solution, only methanol and methane have been resulted from CO\(_2\) photo reduction in the presence of various photo catalyst, including Ti-SBA [15], TiO\(_2\) particles with various sizes [16], and Ag-TiO\(_2\) [17]. In addition, by using TiO\(_2\) powder, CO\(_2\) photo reduction with water vapor has yielded methane, acetylene and ethylene as the products [18].

CO\(_2\) photo reduction with water vapor catalyzed by TiO\(_2\) pellet [19], as well as by modified titania, such as Cu/TiO\(_2\)-SiO\(_2\) [20], Cu-I-TiO\(_2\) [21], and Ag/TiO\(_2\) [22], have been success to form CO and methane as the products.

A single product has been successfully resulted from photo reduction of CO\(_2\) with water vapor in the presence of several titania based photo catalysts. CO gas has been resulted by using I-TiO\(_2\) [23]. By using Cu/TiO\(_2\) photo catalyst, methanol is obtained [24]. Methane has been produced by using Pt-TiO\(_2\) [25] and Cu/TiO\(_2\) [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 CO\(_2\) catalyzed by TiO\(_2\) has been performed by the addition of the electron source or reducing agent such as H\(_2\) [27]. In addition to H\(_2\), several metals including Fe and Zn are also known as good reducing agents [28]. Another way to increase the methane conversion from CO\(_2\) photo reduction is introducing hydrogen ions that can be serviced by acids. In fact the use of the metals and acids to increase CO\(_2\) 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 CO\(_2\) photo reduction are addressed.

2. Experiments

2.1 Materials and Instruments

Materials used are TiO\(_2\), HNO\(_3\), and CH\(_3\)COOH from E. Merck, and several gasses including CO\(_2\), CH\(_4\), and C\(_2\)H\(_4\) 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, CO\(_2\) 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 CO\(_2\)

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
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filled with 10 gram of TiO\textsubscript{2}, was flown by CO\textsubscript{2} gas, and H\textsubscript{2}O 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. TiO\textsubscript{2}, CO\textsubscript{2}, 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 HNO\textsubscript{3} and CH\textsubscript{3}COOH 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 CO\textsubscript{2} Photo Reduction

To identify the substances resulted from CO\textsubscript{2} 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 CO\textsubscript{2} photo reduction with water vapor catalyzed by TiO\textsubscript{2} 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 TiO\textsubscript{2} 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 CO\textsubscript{2} with the electron into CO\textsubscript{2} radical is also took place (Eq. (4)). Then the CO\textsubscript{2} radical reacts with hydrogen radical consecutively to form methane (Eqs. (5-8)).

\begin{align*}
\text{TiO}_2 + \text{light} &\rightarrow \text{TiO}_2(h^+ + e^-) \quad (1) \\
2\text{H}_2\text{O} + 4h^+ &\rightarrow \text{O}_2 + 4 \text{ H}^+ \quad (2) \\
\text{H}^+ + e^- &\rightarrow \text{H} \quad (3)
\end{align*}

\begin{align*}
\text{CO}_2 + e^- &\rightarrow \cdot \text{CO}_2 \quad (4) \\
\text{CO}_2 + \cdot \text{H} &\rightarrow \cdot \text{CH} + \text{ O}_2 \quad (5) \\
\text{CH} + \cdot \text{H} &\rightarrow \cdot \text{CH}_2 \quad (6) \\
\text{CH}_2 + \cdot \text{H} &\rightarrow \cdot \text{CH}_3 \quad (7) \\
\text{CH}_3 + \cdot \text{H} &\rightarrow \text{ CH}_4 \quad (8)
\end{align*}

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 ($E^\circ$) that have positive values [28], by O\textsubscript{2} presence in the photo reduction tube and hole ($h^+$) from TiO\textsubscript{2} during the light irradiation while releasing electron, as seen in the Eqs. (9, 10).

\begin{align*}
\text{Fe} + h^+ &\rightarrow \text{Fe}^{2+} + 2e \ E^\circ = 0.44 \text{ Volt} \quad (9) \\
\text{Zn} + h^+ &\rightarrow \text{Zn}^{2+} + 2e \ E^\circ = 0.83 \text{ Volt} \quad (10)
\end{align*}

This oxidation is believed to enhance the amount of electrons used for CO\textsubscript{2} 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,
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3.3 Influence of Acids

The results of CO$_2$ photo reduction with the presence of HNO$_3$ and CH$_3$COOH 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, HNO$_3$ is seen to show stronger effect in the increasing methane formation, than CH$_3$COOH does. The role of the acids is by donating hydrogen ions from their ionization, as seen in Eqs. (12, 13).

$$\text{HNO}_3 \rightarrow \text{H}^+ + \text{NO}_3^- \quad (12)$$

$$\text{CH}_3\text{COOH} \leftrightarrow \text{H}^+ + \text{CH}_3\text{COO}^- \quad (13)$$

As described previously, that hydrogen ions forming hydrogen radical are required for reacting with CO$_2$ 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 CO$_2$ radicals remain the same, the ethylene (C$_2$H$_4$) 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 HNO$_3$ is a strong acid enabling it to reveal much more number of hydrogen...
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ions compared to acetic acid, as the weak one (Ka = 1.85 × 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
time. Increasing time can stimulate the more effective contact among the reactants that promote the CO\textsubscript{2} 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 CO\textsubscript{2} corversion 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 CO\textsubscript{2} with the water vapor under catalysis of TiO\textsubscript{2} has successfully produced methane as the fuel gas. The addition of both Fe and Zn powder, as well as HNO\textsubscript{3} and CH\textsubscript{3}COOH 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 CO\textsubscript{2} radicals than by H\textsuperscript{+}. 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 HNO\textsubscript{3} are observed to have stronger effect on the increasing CO\textsubscript{2} photo reduction.

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