INFLUENCE OF OPERATIONAL PARAMETERS ON THE PHOTOCATALYTIC ACTIVITY OF POWDERED TiO_2 FOR THE REDUCTION OF CO_2

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ABSTRACT

In this report, the results from a study on the influence of operational parameters on TiO_2 photocatalytic activity for CO_2 reduction under an ultraviolet-visible (UV-vis) illumination are presented. The results indicated that the TiO_2 was found to be active for CO_2 reduction with CH_3OH as the major products, while other minor products (CO, CH_4, and C_2H_4) were also detected. In addition, the formation of such reduction products was obviously influenced by the operational parameters. Under this study, the optimum operational parameters for CO_2 reduction at 298 °K were determined to be: NaOH concentration 0.2 M, TiO_2 dosage 2 g/L, volume of the reaction media *75 mL, the pressure of system 800 kPa. It was also found that the increase in UV-vis illumination time have increased the yield of product formation. A possible reaction pathway for the formation of the reduction products is also discussed.*

Keywords: *titania; TiO_2; photocatalytic; reduction; carbon dioxide*

ABSTRAK

Dalam tulisan ini disajikan hasil studi tentang pengaruh parameter operasional dalam reduksi CO_2 secara fotokatalitik menggunakan TiO_2 dibawah penyinaran menggunakan lampu UV-sinar tampak. Dari hasil yang diperoleh menunjukkan bahwa TiO_2 aktif sebagai fotokatalis dalam mereduksi CO_2 dengan produk utama berupa CH_3OH, sedangkan produk lain berupa CO, CH_4, and C_2H_4 juga terdeteksi namun dalam konsentrasi rendah. Adapun terbentuknya produk-produk reduksi tersebut sangat dipengaruhi oleh parameter operasional. Di bawah kondisi eksperimen dalam penelitian ini, parameter operasional untuk mereduksi CO_2 pada suhu 298 °K adalah sebagai berikut: konsentrasi NaOH adalah 0,2 M, dosis TiO_2 sebagai fotokatalis adalah 2 g/L, volum media reaksi adalah 75 mL, dan tekanan sistem dalam reaktor adalah 800 kPa. Lebih lanjut, hasil pengamatan menunjukkan bahwa dengan bertambahnya waktu penyinaran maka jumlah produk hasil reduksi yang terbentuk semakin bertambah. Mekanisme reaksi dalam pembentukan produk hasil reduksi CO_2 juga didiskusikan.

Kata Kunci: *titania; TiO_2; fotokatalitik; reduksi; karbon dioksida*

INTRODUCTION

Attempts to solve energy and environmental issues by means of photocatalytic reaction using semiconductor titania (TiO_2) have attracted special interest [1]. It is not only due to the fact that photo reaction processes over TiO_2 catalyst can be conducted in a system under ambient conditions [2-4], but also because of its outstanding properties such as inexpensive, harmless, non-photo-corrosion, and chemically stable under photo-irradiation [5-7]. However, low photocatalytic efficiency of the TiO_2 due to either a rapid electron-hole recombination or its low light absorption capacity has become general issues in the area.

In the field of photocatalytic reduction of carbon dioxide (CO_2) for producing value added-chemicals (such as formaldehyde, formic acid, methane and methanol), the low yield of product obtained is believed due to low photocatalytic activity of TiO_2. Numerous efforts have already been made to increase the photocatalytic activity of TiO_2. Enhancement of the photocatalytic activity of TiO_2 via modification of its intrinsic properties is probably one of the most widely used strategies. The intrinsic modification of TiO_2 can be done either by doping with other metal oxides or by

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decreasing the particle size to nanometer scale. Regarding the doping with other metal oxides, the results from several works have been reported and can be found elsewhere [8-14]. Doping of TiO_2 with metal oxide is advantageous because they could shift the optical absorption of the TiO_2 to higher wavelength region (red shift) [11] and/or suppress the rate of electron hole recombination during the photocatalytic reaction [10-12]. Moreover, another approach to enhance the photocatalytic activity of TiO_2 is also introduced in term of decreasing its particle size to nanometer scale. Since nano-structured TiO_2 exhibit unusual physical and chemical properties giving a significantly different in the photocatalytic activity in comparison to the conventional bulk TiO_2 [15]. At nanometer scale in particle size, the TiO_2 is not only enhance the reduction-oxidation power of the TiO_2 but also increase the absorption affinity of the reactant onto TiO_2 surfaces, facilitating the more efficient of the photocatalytic process [16].

Although the study on the influence of intrinsic properties of the TiO_2 for CO_2 reduction have been well-reported with good achievement, however, study on the influence of extrinsic properties (i.e., reaction parameters) on the effectiveness of the TiO_2 photocatalytic process is scarce. In this study, the influence of some important operational parameters including photocatalyst dosage, volume of the reaction media, pressure in the reaction system, temperature, and illumination time are examined.

EXPERIMENTAL SECTION

Materials

The TiO_2 used in this study was taken from the same batch with the TiO_2 used in our previous study [17], and its physicochemical characteristic is provided in Table 1. Double distillate water produced from a NanoPure purification system (Millipore Corp., 17.5 MΩ·cm) was used throughout the experiments. All other chemicals along with their use were outlined elsewhere in this report.

Instrumentation

The XRD analysis was conducted on a Rigaku X-ray diffractometer operated at 40 kV and 30 mA with Cu (k = 1.5406 Å) irradiation. The Band gap energy was determined by Kubelka-Munk plot method [18], using the DR-UV-Vis data taken on a Shimadzu UV2450 spectrophotometer. The specific surface area (S_{BET}) data were calculated from a multipoint BET analysis of the nitrogen adsorption isotherm at -169 °C using a Micromeritics ASAP 2010 surface area analyzer. The transmission electron microscopic (TEM) images were recorded on aTecnai G2 F20 TEM operated at 200 kV. The oxidation state of Titanium was examined using a Thermo VG Scientific-Sigma Probe X-ray photoelectron spectroscopy (XPS) with mono-chromated Al Kα radiation and operating pressure in the sampling chamber was below 5×10^{-9} Torr. The reduction product carbon monoxide (CO) in gas phase was identified using an Agilent 7890A gas chromatography-thermal conductivity detector (GC-TCD) with a molecular sieve 5A column, while both methane (CH_4) and ethylene (C_2H_4) were identified using GC-flame ionization detector (GC-FID) with an activated-alumina column. The methanol (CH_3OH) as the product in liquid phase was determined using a Hewlett–Packard (HP) GC-FID 1530A with an HP5-MS column.

Procedure

Photocatalytic testing

The batch stainless steel type reactor (Fig. 1) was employed to conduct the photocatalytic reaction. Typically, a fresh of TiO_2 was transferred into the reactor. Prior to UV-Vis illumination with 100 W Hg lamp, ultra high purity of CO_2 99.999% was bubbled with constant flow (160 mL/min) for 60 min passing through the reaction media to obtained CO_2-saturated and air-free suspension. After bubbling, the reactor was immediately closed and photocatalytic reaction was then started by switching on the UV-vis lamp. Blank tests were also carried to ensure that a photocatalytic reduction of CO_2 is only occurred in the presence of light illumination, but not took place in the dark with TiO_2 photocatalyst or under light illumination without TiO_2.

Identification of the reduction products

The reduction products both in the liquid and gas phase were taken regularly at a series of time interval. The gaseous samples were collected using a gas-tight syringe (Hamilton, Nevada-U.S.A). The concentration of carbon monoxide (CO) in gaseous phase was analyzed using a GC-TCD instrument. Methane (CH_4) and ethylene (C_2H_4) concentrations were measured on GC-FID instrument. The GC instrument was calibrated before each analysis run using certified reference material (CRM) for gas mixture (CO, CH_4 and C_2H_4) with maximum 0.1% uncertainty level. The concentration of CH_3OH in liquid phase was measured using A GIC-FID instrument. The peak area of corresponding sample was used to estimate the CH_3OH content in liquid sample by converting the peak area to its concentration using a calibration curve. The calibration curve was obtained by plotting the peak area

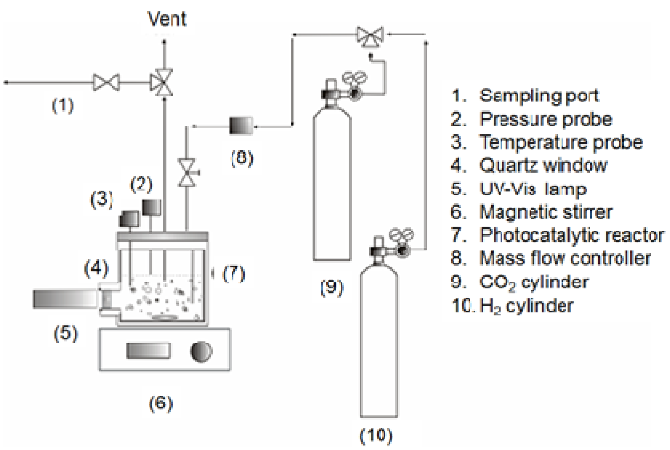

Fig 1. Schematic of experimental setup for CO_2 photocatalytic reduction

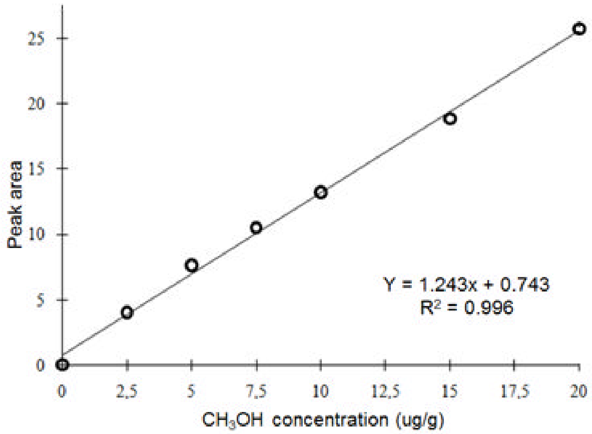

Fig 2. The calibration curve for CH_3OH in standard solutions with excellent linearity measured using GC-FID

Table 1. Physicochemical characteristic of the TiO_2

Parameter	Data (Unit)
BET surface area^a	74.33 (m^2/g)
Crysttalite phase^b	Anatase
Crysttalite size^c	22.8 (nm)
Band gap energy^d	3.30 (eV)
Oxidation state of Ti ^{e}	4^+

^{a}*Determined by BET surface area method [17]*
^{b}*Investigated by XRD and compared to the JCPDS Card No. 21-1272 [17]*
^{c}*Determined by XRD Scherrer's method [17]*
^{d}*Determined by Kubelka-Munk plotting method [17]*
^{e}*Investigated using XPS [17]*

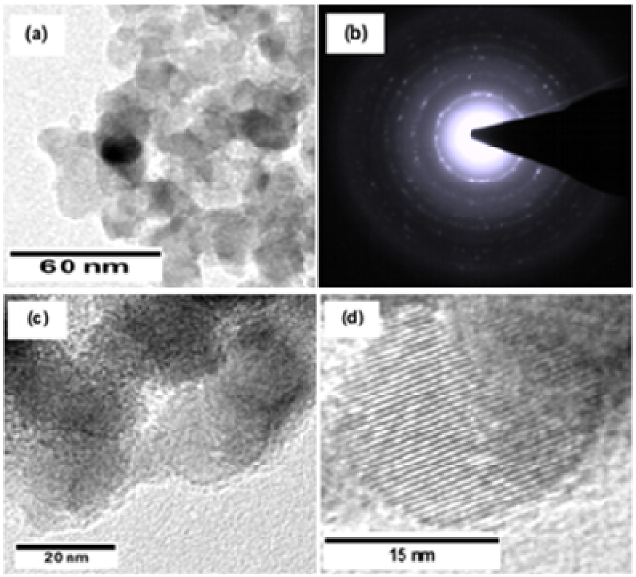

Fig 3. Typical morphology images of TiO_2: (a) bright-field-TEM, (b) Selected area electron diffraction (SAED), (c) high resolution TEM, and (d) enlarged lattice fringes

versus concentration of CH_3OH standard solutions (0-10 ug/g) as shown in Fig. 2.

RESULT AND DISCUSSION

Physicochemical Characteristic of the TiO_2

Physicochemical characteristic of the TiO_2 is listed in Table 1. In addition, Fig. 3 shows typical morphology of the TiO_2. It can be observed from the bright field image (Fig. 3a) that the particles were presence in round shaped with the average diameter of every single crystal is of about 20 nm. No shuttle-like morphology for rutile phase can be observed which indicates that the TiO_2 exists in anatase phase [19]. A selected area-electron diffraction (SAED) pattern of the TiO_2 (Fig. 3b) shows distinct concentric rings instead of sharp spots, ascribing small in size of the TiO_2 crystals [20]. In addition, Fig. 3c shows high resolution TEM of the TiO_2, where its lattice fringes images (Fig. 3d) indicates the TiO_2 is in good crystalline nature [21].

Photocatalytic Activity Evaluation

The performance of the TiO_2 was evaluated for its activity for the reduction of CO_2. In the preliminary experiment, it was found that the reduction products involved gas phase of CO and CH_4, C_2H_4, and liquid

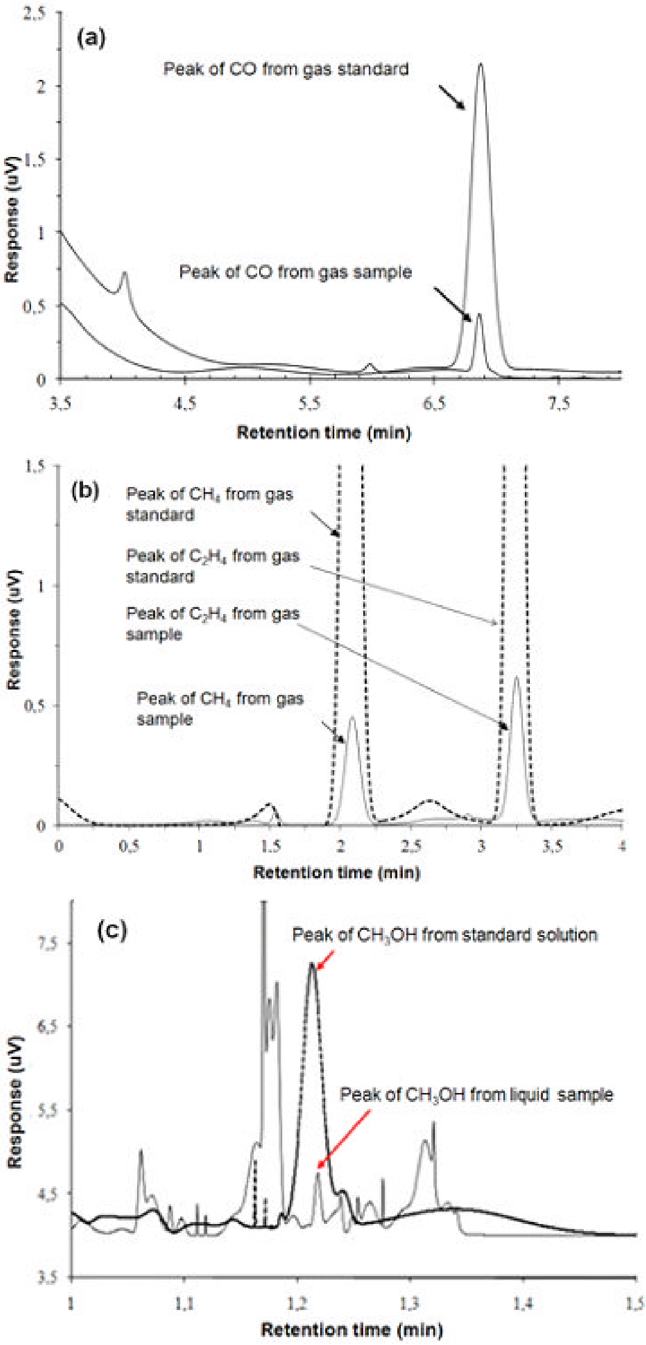

Fig 4. The typical chromatogram of the standard and detected products: (a) CO, (b) CH_4 and C_2H_4, and (c) CH_3OH

phase of CH_3OH., while other products may also be formed but the instrument used could not detect them. Blank test as a control experiment indicated no such reduction products could be detected in the absence of either photocatalyts or UV-vis illumination, implying that the CO_2 could only photocatalytically reduced by the TiO_2 under UV light illumination. Fig. 4a through 4c, show typical chromatogram of standard and detected products obtained using GC-TCD and GC-FID techniques.

For the photocatalytic reduction of CO_2 with H_2O over TiO_2-based materials, the reduction pathway generally includes the following steps, i.e., the adsorption of reactants on the catalyst, activation of the adsorbed reactants by the photo-generated charge carriers, formation of surface intermediates, and conversion of intermediates to products [22]. According to these common steps, many researchers [23-26] have proposed various reaction schemes for the photocatalytic reduction of CO_2 by H_2O over TiO_2-based photocatalyst.

Taking into account the identified product species under this study and other related literatures [23-26], the possible reaction pathway for the formation of CO, CH_4, C_2H_4, and CH_3OH during the photocatalytic CO_2 reduction with H_2O over pure-TiO_2 is suggest (Eqs. 1-15). When a photon in the form of light having energy equal or higher than the band gap energy of the TiO_2 semiconductor, the electrons jump to the conduction band (CB) leaving a positively charged hole in the valence band (VB) (Eq. 1). After the creation and excitation of the electron-hole, part of the excited electrons and holes recombined together and radiated out heat during the process (Eq. 2), this is a main limiting factor for the low efficiency of CO_2 conversion [22]. While other non-recombined photo-generated electrons-holes would take part in other reactions. A reaction between holes and H_2O adsorbed on the TiO_2 surface produces HO^- and H^+ (Eq. 3). The formed H^+ reacts with excited electron leads to the formation of hydrogen radicals (●H) (Eq.4), while reaction between OH^- and holes produced hydroxyl radical (●OH) [27] (Eq. 5).

$$TiO_2 \xrightarrow{E_{photon} \geq E_{band\ gap}} e^-_{cb}(TiO_2)+h^+_{vb}(TiO_2) \tag{1}$$
$$e^-_{cb}(TiO_2)+h^+_{vb}(TiO_2) \rightarrow \text{Heat} \tag{2}$$
$$H_2O+h^+ \rightarrow HO^- + H^+ \tag{3}$$
$$H^+ + e^- \rightarrow \bullet H \tag{4}$$
$$OH^- + h^+ \rightarrow \bullet OH \tag{5}$$
$$CO_2 + e^- \rightarrow \bullet CO_2^- \tag{6}$$
$$\bullet CO_2^- + \bullet H \rightarrow CO + OH^- \tag{7}$$
$$CO + e^- \rightarrow \bullet CO^- \tag{8}$$
$$\bullet CO^- + \bullet H \rightarrow C + OH^- \tag{9}$$
$$C + \bullet H \rightarrow \bullet CH \tag{10}$$
$$\bullet CH + \bullet H \rightarrow CH_2 \tag{11}$$
$$CH_2 + \bullet H \rightarrow \bullet CH_3 \tag{12}$$
$$\bullet CH_3 + \bullet H \rightarrow CH_4 \tag{13}$$
$$\bullet CH_3 + \bullet CH \rightarrow C_2H_4 \tag{14}$$
$$\bullet CH_3 + \bullet OH \rightarrow CH_3OH \tag{15}$$

At the same time, the excited electrons (e^-) were transferred from the CB of TiO_2 for the reduction of CO_2

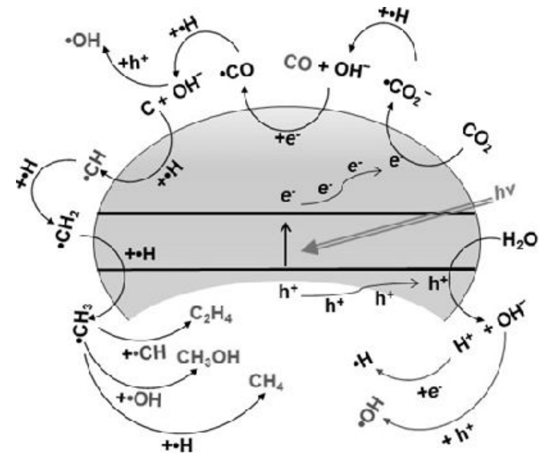

Fig 5. A reaction pathway for the product formation on TiO2 surface during the photocatalytic CO_2 reduction

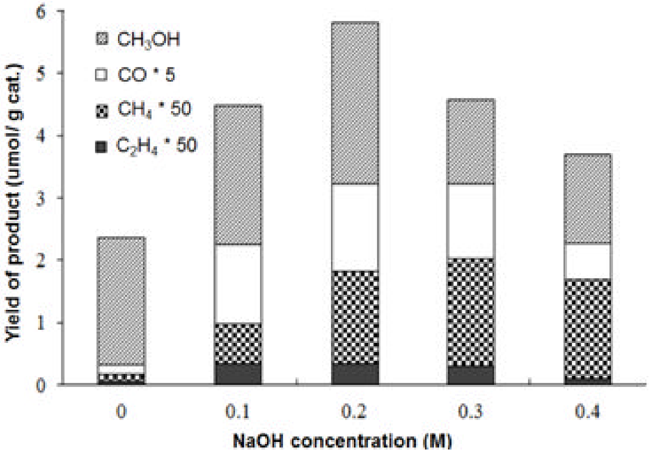

Fig 6. The influence of NaOH concentration on the yield of photocatalytic products

producing carbon dioxide radicals (●CO_2^-) (Eq. 6). The ●H generated from hydrogen reduction reacted with ●CO_2^- to produce carbon monoxide (CO) and other ion hydroxyl (OH^-) according to Eq. 7. A further reaction between CO and excited electrons generated CO radicals (●CO^-) (Eq. 8). The surficial C generated from reaction between ●CO $^-$ and ●H (Eq. 9) took part on a consecutive reaction to form intermediate ●CH_3 (Eqs. 10-12). Further reaction of intermediate radicals ●CH_3 with other species on TiO_2 surface could produce the final products CH_4, C_2H_4 and CH_3OH (Eqs. 13-15). The CH_4 was confirmed to be produced via reaction between ●CH_3 and ●H according to Eq. 13. The C_2H_4 may be produced by the reaction between ●CH_3 and ●CH according to Eq. 14. The CH_3OH was yielded by the reaction between ●CH_3 and ●OH (Eq. 15). The reaction scheme for the formation of CO, CH_4, C_2H_4 and CH_3OH using pure TiO_2 is elaborated further in Fig. 5. Similar reaction pathway through the formation of surficial carbon (C) and methyl radical (●CH_3 has been proposed earlier by Anpo et al. [23] and Kocí et al. [24] for a photocatalytic reduction on a solid-liquid reaction system involving dissolved CO_2 in aqueous solution.

Influence of NaOH concentration

In this study, sodium hydroxide (NaOH) aqueous solution was chosen as a liquid medium for the photocatalytic activity testing because the NaOH demonstrated a significant contribution on the photocatalytic process by increasing the yield of reduction products [12,24]. It has been reported that the OH^- ions in aqueous solution, which is provided by NaOH, could act either as strong hole scavenger which can inhibit the recombination of electron-hole pairs. The longer decay time of electron-hole pairs would facilitate the more effective of the photocatalytic process [28]. And also, the OH^- ions can form OH radicals (●OH). The involvement of ●OH in the photocatalytic process is explained in next section. Moreover, the NaOH could increase the solubility of CO_2 in aqueous solution [4], which contribute to increase the availability of the CO_2 as reactant in the solution. To investigate the influence of NaOH concentration on the photocatalytic reduction of CO_2, the NaOH concentration was varied from 0 to 0.4 M, while other experimental parameters were kept the same. From the results obtained, it was found that reduction products including CO, CH_4 and C_2H_4 in gas phase and CH_3OH in liquid product were obviously detected. Fig. 6 presents dependence of product yields on the NaOH concentration. As can be seen in Fig. 6, the yield of photo reduction products increased with the increased of NaOH concentration up to 0.2 M and decreased after the NaOH concentration higher than 0.2 M. This might be due to the number of hole scavenger (OH^-) formation under 0.2 M NaOH are optimum for a contribution to the inhibition of the electron-hole recombination. On the other hand, increasing the concentration of NaOH above 0.2 M demonstrates a detrimental effect because excess OH radical (•OH) formed may oxidize the species in the reactor.

Influence of photocatalyst dosage

It has been well known that photocatalytic reactions take place on TiO_2 surface active site, where the dosage of TiO_2 play a key role in the photocatalytic process. Thus, the dosage is a crucial point, which needs to be optimized. The study on the influence of photocatalyst dosage on the reduction of CO_2 was conducted ranging from 0 to 4 g/L, and the result is shown in Fig. 7. As can be seen, the yields of products were found to increase with increasing the dosage of the TiO_2 and achieved its optimum level at 2 g/L and then decrease when TiO_2 dosage exceeds 2 g/L. This

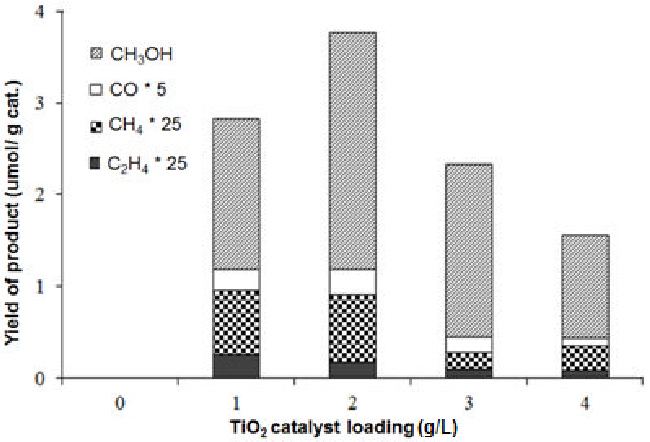

Fig 7. The influence of photocatalyst dosage on the yield of photocatalytic products

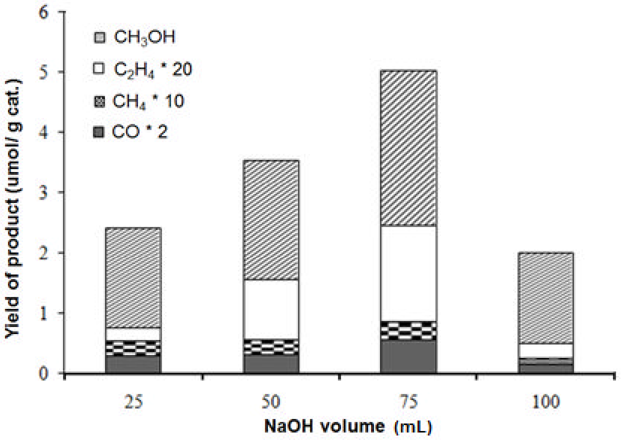

Fig 8. The influence of volume of the reaction media on the yield of photocatalytic products

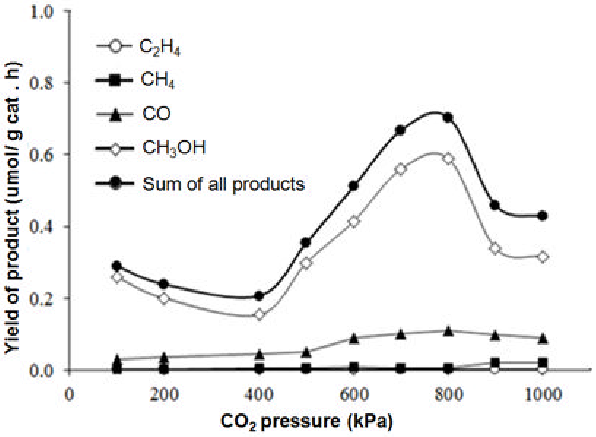

Fig 9. The influence of CO_2 pressure on the yield of photocatalytic products

may be attributed to the fact that high TiO_2 dosage can scatter the light due to opacity of the suspension, which prevents the light to reach every particle of the photocatalyst [3,12,24]. In addition, the high TiO_2 dosage may also become a favorable condition for surface agglomeration and diminishing the surface active sites, which further declined the rate of product formation [29].

Influence of volume of reaction media

In a photocatalytic process, the volume of the reaction media is an important key and it has to be optimized to obtain an appropriate volume of the reaction media for an optimum photocatalytic process because the volume can influence the effectiveness of the UV-vis light energy supply. When the energy light is not sufficiently provided, the process of the electron excitation on the TiO_2 surface may not occurred at optimum condition. When the energy light is over supplied, it will be wasted in the form of heat. One way to be done to avoid such insufficient or over supplied of the energy light during the photocatalytic process is by optimizing the volume of the reaction media because the reaction media could be used to maintenance the supply of the energy light at an adequate level. In the present study, the dependency of the product yield on volume of the reaction media (NaOH suspension) was evaluated and the result is shown in Fig. 8. As can be seen in Fig. 8, the volume of the reaction media has obviously influenced the yield of reduction products. The yields of product increase with increasing the volume of the reaction media and achieving its optimum level at 75 mL. The yield of products decreased when the volume of the reaction media was larger than 75 mL. In the present experimental study, when the volume of the reaction media is small (< 75 mL of NaOH), the UV-vis light energy is over supplied and wasted as heat, which is presumably the reason for the lower product yield. While at a large volume (> 75 mL of NaOH), insufficient mixing is suggested for the reason of the decrease in the product yield, where the TiO_2 particles cannot be maintained in uplift and the TiO_2 particles tend to fall down and located at the bottom part of the reactor, resulting in non uniform of the particle distribution [30]. The non-uniformity in particle distribution at a large of volume of the reaction media since the particle might be agglomerated which reduce the number of active site at the TiO_2 surface active, thus decrease the TiO_2 activity. In addition, the higher volume of NaOH used (100 mL for example), it corresponds to a situation where the quartz glass window for light transmission from the light source to the TiO_2 particles is covered by the suspension. Under this condition, the light cannot be well-transmitted to entire suspension in the reactor so that hinder the light to reach every particle of the photocatalyst.

Influence of pressure in reactor

The concentration of CO_2 in water at ambient

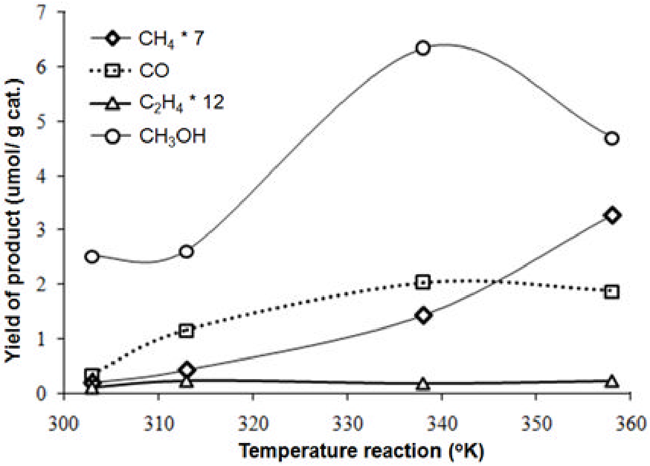

Fig 10. The influence of temperature on the yield of photocatalytic products

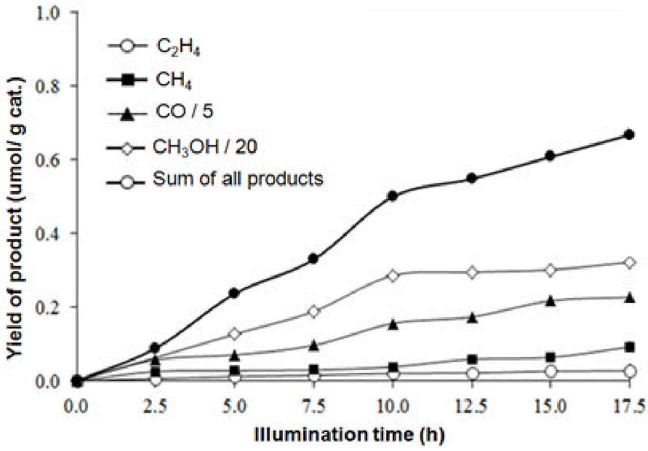

Fig 11. Illumination time dependence of the yield of photocatalytic products

pressure is very small because of its low solubility property. One can be done to increase the solubility of the CO_2 in water is by elevating its pressure in a gas-water interface [31-32]. To investigate the influence of CO_2 pressure on the photocatalytic reduction of CO_2, the pressure was varied from 100 kPa to 1000 kPa and the results are presented in Fig. 9. As can be seen from Fig. 9, a small decreased in the yield of reduction product was observed with increasing the pressure up to 400 kPa, although the reason for this is not completely clear. Moreover, the yield of reduction product has significanlty increased with increasing the pressure up to 800 kPa. The accumulation of reduction product at 800 kPa was found to be 5.89, 0.52, 0.02, and 0.011 µmol/g cat., for CH_3OH, CO, CH_4 and C_2H_4, respectively. The yield increase of those reduction products was probably due to the following two reasons: Firstly, elevating the CO_2 pressure consequently increased the solubility of CO_2 in the reaction media and thus increase the number of TiO_2 surface-contacted CO_2 molecules which further converts to important incipient CO_2^- radicals ($\bullet CO_2$) for the product formation. The possible involvement of the $\bullet CO_2$ during the photocatalytic reaction is schematically illustrated in Fig. 5. Secondly, in the present study, the photocatalytic was conducted in alkaline solution (NaOH). At concentration optimum (0.2M) of NaOH used, the estimated pH value >12. Saturating the solution with CO_2 brought the pH of the solution to value of about 7-9. Based on the carbonate equilibrium system [25], the carbonate species in the reaction system was dominated by bicarbonate ion (HCO_3^-). The presence of this HCO_3^- in the OH^--CO_2 saturated system may accelerate the photocatalytic reduction process [28]. Moreover, the yield of products gradually decreased by increasing the CO_2 pressure over 800 kPa. Tseng et al. [12] and Mizuno et al. [32] suggested that conversion of lower hydrocarbon to higher molecular weight under high pressure condition could probably be the reason for decreasing the yield of the reduction product. However, the higher molecular weight than all indentified products could not be detected under instrument conditions of the present study.

Influence of temperature

In a TiO_2 photocatalytic process at under ambient temperature, photon radiation is the primary source of energy for the formation of electron-hole pair because the band gap energy of TiO_2 is relatively high for thermal excitation to overcome [33]. On the other hands, thermal energy supply in the form of temperature heat to increase the rate of photo reaction is required because the thermal energy could induce the collision frequency of molecule in solution [34]. Fig. 10 presents a temperature dependence of the reduction products. As can be seen in Fig. 10, the product yield was a little increased with small variation of the reaction temperature (from 303 °K to 313 °K). Fox and Dulay [35] reported that the majority of the photocatalytic reaction is not sensitive to small temperature variations. However, further significant increase of the yield of product can be observed at large temperature variations (from 313 to 338 °K). For example, the yield of CH_3OH increased significantly by increasing the temperature up to 338 °K and then decreased. In case of C_2H_4, no significant change was found for the yield during the course of reaction. Moreover, the yield of CO decreased while CH_4 increased when the temperature increase above 338 °K. Kohno, et al. [36] reported that a drastic decrease in the CO formation followed by increasing the yield of CH_4 occurred at temperature reaction above 523 °K. They assumed that the increase of the yield CH_4 might be due to the photocatalyst used was present at the reduced state at higher temperature condition, leading to shift the product selectivity from CO to CH_4. A similar phenomenon was observed in the present study, where the yield of CH_4 was found to increase while the yield of CO decreased at higher temperature process. Thus, we suggested that the reaction temperature has shifted the product selectivity in a similar manner.

Influence of illumination time

The study on the influence of illumination time on the product formation was conducted for a period of 0-17.5 h, and the result is presented in Fig. 11. From Fig. 11, it can be seen that the yield of CH_3OH increased rapidly with illumination time at first 10 h, because more photo-electron are generated with increasing the illumination time [28]. Small increase in the yield of the CH_3OH was observed after 10 h illumination. The change in the rate of product formation after certain period of illumination can be attributed to increasing the chance for photocatalyst particles to aggregate, lesser strength of the surface adsorption power of photocatalysts and increasing in the number of active sites occupied by intermediate products, which are supposed to be a constructive condition for weakening the photocatalytic performance [3]. In addition, a small increased of the yield of CO, CH_4 and C_2H_4 can only be observed along with illumination time.

CONCLUSION

In summary, it was found that the CO_2 could be reduced through photocatalytic reaction over TiO_2 under UV-vis illumination. The reduction products including CH_3OH, CO, CH_4, and C_2H_4 were detected. The operational parameters employed have remarkably influenced the rate of product formation, implying that optimization of reaction condition is important. Optimization of the operational parameters would offer an efficient of the photocatalytic process.

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