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CARBON DIOXIDE PHOTOCONVERSION. THE EFFECT OF TITANIUM DIOXIDE IMMOBILIZATION CONDITIONS AND PHOTOCATALYST TYPE

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Abstract. Carbon dioxide and water vapor were effectively photoconverted to methane using either pure or modified-TiO_2 and UV-Vis irradiation. The process of photoconversion in the gas phase was carried out in a tubular reactor equipped with a perforated TiO_2-coated support. The effect of selected parameters of TiO_2 immobilization procedure, such as the time and temperature of drying step and the photocatalyst amount, on photocatalytic efficiency was investigated. The effect of TiO_2 loading with Ag/Au nanoparticles on CO_2 photoconversion efficiency was also studied. CH_4 was found to be the major photoreduction product. The highest methane production was observed after irradiation of CO_2+H_2O mixture over Au-TiO_2 photocatalyst. After one hour of UV-Vis irradiation 503 ppm of methane was formed.

keywords: TiO_2, photoreduction, CO_2 photoconversion, titanium dioxide

1. Introduction

The reduction of carbon dioxide has recently been regarded as an important research area in chemical technology, not only for solving the problems resulting from environmental pollution, but also for finding ways to maintain carbon resources, which are being depleted by burning fossil fuels. Photocatalytic CO_2 conversion offers a promising way for clean, low cost and environmentally friendly production of fuels by solar energy. Photocatalytic reduction of CO_2 could be carried out in CO_2-saturated aqueous solution containing suspended TiO_2 (Li et al., 2010; Dey et al., 2004) liquid CO_2 (Kaneco et al., 1997), high pressure CO_2 system with TiO_2 powders suspended in isopropyl alcohol (Kaneco et al., 1998) and in the gas phase - CO_2 with H_2O vapor irradiated over TiO_2 (Tan et al., 2008; Xia et al., 2007; Nguyen et al., 2008; Tan et al., 2006). The UV-irradiated TiO_2 surface can generate electrons to reduce the CO_2 molecules present in aqueous and gaseous streams at ambient temperature and pressure conditions. Photogenerated electron-hole pairs migrate to the surface and in the presence of H_2O molecules lead to the reduction of CO_2 in CH_4 and compounds such as C_2H_2, CH_3OH, C_2H_5OH at the solid-gas interface (Usubharatana et al., 2006; Varghese et al., 2009).

Photocatalytic reactions could be carried out in the presence of pure and modified TiO_2 (Fujishima et al., 2006; Chatterjee et al. 2005; Zaleska, 2008). Zhang et al. (2011) studied the effect of calcination temperature (375, 450, 550°C) and dopant concentration of iodine (I_2) (5, 10, 15 wt.%) on the efficiency of photoconversion. A fixed amount of powder catalyst (200 mg) was dispersed on a glass-fiber filter and placed at the bottom of the cylindrical photoreactor. The photocatalytic activities of the I-TiO_2 powders were investigated by photocatalytic reduction of CO_2 with H_2O under visible light (>400 nm) and also under UV-visible illumination. CO was found to be the major photoreduction product. A high efficiency of CO_2 reduction was observed for 10 wt.% I-TiO_2 photocatalysts (the highest CO yield equivalent to 2.4 $\mu mol \cdot g^{-1} \cdot h^{-1}$) under visible light. The highest activity in the presence of UV-Vis light showed 5 wt.% I-TiO_2, calcined at 375^{o}C (600 ppm after 90 minutes), and the increase in calcination temperature decreased the efficiency of the process of photoreduction. Too high iodine doping level may result in recombination centers and thus lower the photocatalytic activity (Zhang et al., 2011). Photocatalytic reduction of CO_2 with H_2O in the gaseous phase was studied by Chen et al. (2009) using thin films P-25 (prepared by reactive magnetron sputtering) under UV irradiation (100 W). The main product of the reaction of methane was also detected in the form of trace amounts of other hydrocarbons such as methanol. The highest concentration of the products was observed for pure anatase, and the lowest for pure rutile. Chen et al. (2009) have shown that there is synergy between CO_2 concentration and the temperature of the process. The highest methane yields were produced under the optimal combination of high CO_2 concentration (approximate 45% volume) and elevated temperature (approximately 80°C). Under these conditions, after 4 h of irradiation 200 nmol of methane were received. It was also noted that conditions of TiO_2 film synthesis at the surface of boro-silicate glass (e.g. deposition angle during current magnetron sputtering) affected the effectiveness of the process (Chen et al., 2009). The results obtained by Tan et al. (2006) confirmed that CO_2 could be reformed in the presence of water vapor and TiO_2-P 25 pellets into CH_4 under continuous UV irradiation at ambient conditions. Total CH_4 yield was 200 ppm and lower than 100 ppm after 48 h of irradiation with UVC (253.7 nm) and UVA (365 nm), respectively (Tan et al., 2006). Li et al. (2010) studied a photoconversion process using Cu/TiO_2-SiO_2. Glass wool was placed in the reactor as the support for the glass fiber filter loaded with a thick film of powder catalysts. The glass wool support was also moisturized with 3.0 g deionized water to maintain saturated water vapor in the reactor. Irradiation source was a Xenon lamp (irradiation intensity 2.4 mW/cm^2). The measured production rate of the products increased with the irradiation time and reached a peak value at around 4 h. The methane production rate was 13.2 $\mu mol/(g \cdot h)$. It was found that a photocatalyst after regeneration can be used again for photoconversion process but its activity is already significantly lower (Li et al., 2010).

Photocatalytic reduction of CO_2 with H_2O in the gaseous phase was studied by Nguyen et al. (2008) using Cu-Fe/TiO_2 catalyst coated on optical fibers under UVA and UVC irradiation. Methane and ethylene were observed as the main products to evolve from this photoreactor. The presence of Fe as a co-dopant in Cu/TiO_2 photocatalyst was found to synergistically reduce CO_2 with H_2O to ethylene at the quantum yield and total energy efficiency of 0.024% and 0.016%, respectively. This phenomenon could be explained by an efficient charge transfer mechanism between TiO_2 as a support and Cu as well as Fe as co-dopants. Methane was formed more favorably than ethylene on Cu/TiO_2. Meanwhile, Fe as a co-dopant on Cu/TiO_2 photocatalyst was found to depress methane formation. The highest ethylene production rate was observed for TiO_2 doped with 0.25 wt.% of Cu and 0.25 wt.% of Fe and it was 0.53 $\mu mol(g \cdot h)^{-1}$ (Nguyen et al., 2008). Thus, the efficiency of currently available TiO_2-based photocatalysts is still not sufficient for practical use. Therefore, the development of new ones and optimization of existing photocatalysts exhibiting activity upon visible light with surface characteristics of improved performance and of high chemical and physical stability are crucial for broader scale utilization of photocatalytic systems in commercial applications. To avoid the above listed problems and to improve solar photocatalytic CO_2-to-light hydrocarbons conversion two main approaches are proposed: (1) TiO_2 modification to increase the spectral sensitivity of TiO_2-based photocatalysts to visible light and to compete with electron-hole recombination (by metal and non-metal co-doping), and (2) enhancement of interface surface area by photoreactor design.

Apart from photocatalyst properties, the activity is also affected by the method and parameters of a photocatalyst immobilization procedure. In our investigation, TiO_2-based photocatalyst was deposited on the surface of a flat perforated steel tray, easily removable from the reactor. The photoreactor was equipped with a parabolic, aluminum mirror to concentrate light. Thus, the aim of this study was to investigate the effect of selected parameters of immobilization step, such as the time and temperature of drying and the photocatalyst amount, on photocatalytic efficiency.

2. Experimental

2.1. Materials

TiO_2 P-25 having mixed anatase and rutile structure 4:1 (particle size 40 nm, $S_{BET} = 50 m^2/g$), was obtained from Evonik, Germany. Titanium isopropoxide (pure p.a.; TIP) was purchased from Aldrich and used as titanium source for the preparation of TiO_2 nanoparticles. Hydrogen tetrachloroaurate(III) tetrahydrate (99.9%) and silver nitrate were provided by POCh and used as starting materials for the preparation of gold/silver nanoparticles. Sodium borohydride and ascorbic acid (99%) were purchased from Aldrich and used as reducing agents. Cyclohexane was used as continuous oil phase, sodium bis-(2-ethylhexyl) sulfosuccinate (AOT) purchased from

Aldrich as surfactants, 2-propanol as a cosurfactant and aqueous solution as the dispersed phase.

2.2. Photocatalytic conversion of carbon dioxide

Compressed CO_2 from a cylinder was led to the photoreactor via a gas flow meter, a safety tank equipped with a manometer and an absorber with demineralized water. The reactor chamber was purged with CO_2 gas for 30 min with 80 $dm^3 \cdot h^{-1}$gas flow rate. The reaction system was maintained at 4903 Pa positive pressure. After 30 min purging, the reaction chamber was closed and irradiated using 1000 W Xenon lamp (Oriel), which emits both UV and visible light. The optical path included a 10 cm thick water filter to cut off IR. A schematic illustration of the batch reactor system for the CO_2 photoreduction test is shown in Fig. 1.

The photocatalytic reduction CO_2 was tested in a bench-scale photocatalytic reactor (V=314 cm^3) with a perforated TiO_2-cover tray. The reactor chamber was made of a cylindrical quartz tube (i.d. 50 mm, length 160 mm) and equipped with inlet and outlet valves, as shown in Fig. 2.

Perforated removable trays were placed in the quartz tube, which served as a reaction chamber and was positioned over aluminum parabolic mirror with 188.4 cm^2 collecting area. Thus, the in-going gas phase passed through the perforated barrier and was irradiated from the top by incident radiation, and from the bottom by reflected light.

The TiO_2 suspension was prepared by addition of an appropriate amount of water to 0.5 g of the photocatalyst. Both sides of the internal element of the photoreactor were coated with TiO_2-based suspension by painting procedure. The obtained TiO_2-coated support was dried from 5 to 35 hours at different temperatures (80, 120 or 160°C). A steel or plastic support was used to check the impact of such a support on the effectiveness of the process.

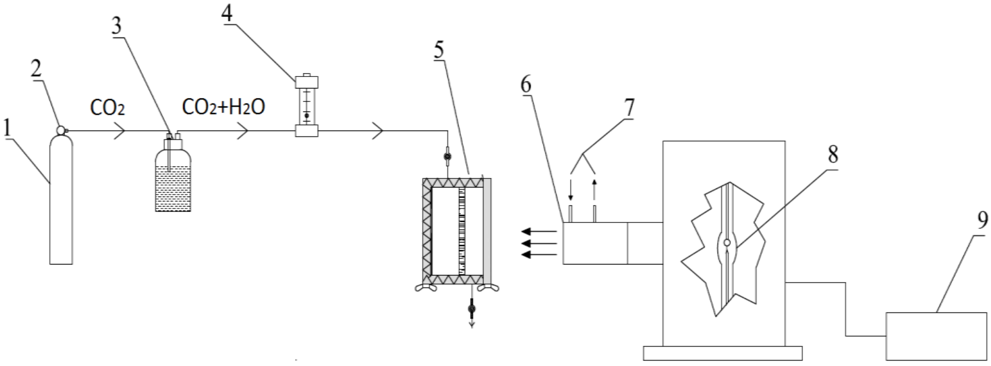

Fig. 1. Schematic illustration of the batch reactor system for the CO_2 photoreduction test: 1) cylinder of CO_2; 2) gas cylinder valve; 3) water bubbler; 4) gas flow meter; 5) photoreactor equipped with a quartz window; 6) water filter; 7) inlet and outlet cooling water; 8) xenon lamp; 9) feeder

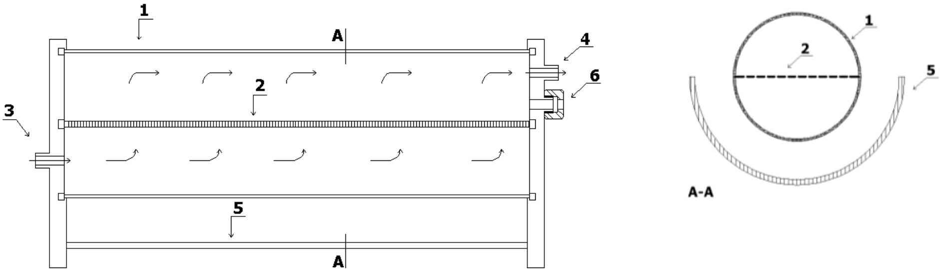

Fig. 2. Schematic diagram of the photoreactor: 1) quartz tube; 2) perforated TiO_2-covered tray; 3) gas inlet; 4) gas outlet; 5) parabolic mirror; 6) sampling port

2.3. Gas chromatographic analysis

A Perkin-Elmer model Clarus 500 gas chromatograph was used together with a porapak-Q 100-120 mesh column (2 m x 2.1 mm i.d.) equipped with a flame ionization detector. In each case a 0.200 cm^3 of gaseous sample were injected in a splitless mode. The operating conditions were as follows: the initial GC column temperature 105°C. The injector temperature was 150°C and the detector temperature was 220°C. The carrier gas used was nitrogen. The flow was kept at a constant 17 cm^3/min. The gas phase from the reaction chamber was sampled by the gas-tight membrane. The gas samples were analyzed in a duplicate at given periods of time. The retention time for methane, ethene and ethane was respectively 0.74, 1.31 and 1.58 minutes.

3. Results and discussion

For studying the photocatalytic conversion of CO_2 into light hydrocarbon with the TiO_2, it was necessary to investigate the influence of the selected parameters affecting the step of photocatalyst immobilization (e.g. the drying temperature and time, the type of support and TiO_2 amount). The efficiency of CO_2 photoconversion was estimated as methane concentration after 1 h irradiation of CO_2+H_2O mixture over TiO_2 supported on the surface of a flat perforated steel tray. The TiO_2 P-25/UV-Vis system was chosen as a reference generating methane as the main product of CO_2 photoconversion. Commercially available TiO_2 P25 was chosen for this investigation as a standard used in heterogeneous photocatalysis. The effect of these parameters was achieved in separate experiments and is presented in Tables 1-3. Table 1 shows the efficiency of methane generation in the presence of P-25 dried in different temperatures after a coating process. It was found that the increase of drying temperature from 80 to 120°C resulted in the increase of methane concentration from 36 to 66 ppm, respectively. However, as the drying temperature increased up to 160°C, CH_4 concentration decreased, reaching the lowest value equal to 4.7 ppm (see Table 1).

The effect of the drying time of TiO_2 suspension deposited on the surface of a flat perforated steel tray on CO_2 photoconversion efficiency is presented in Table 2. The obtained data suggested, that the increase in drying time from 5 to 20 h resulted in the increase of methane concentration from 24 to 90 ppm. However, time elongation to 35 h caused only slight increase in methane concentration. After 60 min. irradiation of CO_2+H_2O mixture over TiO_2 dried in 35 h, methane concentration was 99 ppm. Thus, a 20-hour drying time was chosen for further investigations to save energy during the preparation procedure.

Table 1. The effect of drying temperature TiO_2 on CO_2 photoconversion efficiency (drying time: 20 h, photocatalyst: P-25, average photocatalyst amount: 0.37 g)

Drying temperature [^{o}C]	Methane concentration after 1h exposure for UV-Vis irradiation [ppm]
80	36
120	66
160	4.7

Table 2. The effect of drying time TiO_2 on CO_2 photoconversion efficiency (drying temperature: 120°C, photocatalyst: P-25, average photocatalyst amount: 0.37 g))

Drying time [h]	Methane concentration after 1h exposure for UV-Vis irradiation [ppm]
5	24
20	90
35	99

The influence of TiO_2 amount applied to the surface during coating procedure on CO_2 photoconversion was also investigated and is presented in Table 3. The enhancement in the photocatalytic efficiency for higher amount of P-25 deposited on the porous steel tray was observed. It is expected that introducing a higher amount of TiO_2 can extend the surface area of the available photocatalyst and raise efficiency of CO_2 photoconversion. Methane concentration will amount to 39, 90 and 135 ppm for TiO_2 mass equal to 0.2541, 0.3642 and 0.4825 g, respectively. Further increase in TiO_2 amount resulted in mechanical instability of the obtained TiO_2 thin film. It was noticed that for a higher amount of the photocatalyst, TiO_2 layer suffered cracking and TiO_2 partly fell away during the photoconversion process.

Steel and plastic trays were tested as TiO_2 support materials. Both trays had the same size and perforation pattern. The same coating procedure resulted in a much lower amount deposited on the surface of the plastic tray due to weaker adhesive properties. The amount of the photocatalyst deposited on the surface of the steel and plastic plates was equal to 0.37 and 0.08 g of TiO_2, respectively. Thus, the application of a plastic support caused the decrease in methane concentration to 34 ppm after 1 h of irradiation (see Table 4).

Table 3. The effect of TiO_2 amount on CO_2 photoconversion efficiency (drying temperature 120°C, drying time 20 h, photocatalyst P-25)

Mass of the photocatalyst deposited on the surface of a perforated steel tray [g]	Methane concentration after 1h exposure for UV-Vis irradiation [ppm]
0.2541	39
0.3642	90
0.4825	135

Table 4. The effect of the type of support on CO_2 photoconversion efficiency (drying temperature 120 °C, drying time 20 h, photocatalyst P-25)

Type of support	Methane concentration after 1h exposure for UV-Vis irradiation [ppm]
steel	90
plastic	34

After selecting conditions of the photocatalyst immobilization step, TiO_2 modified with noble metals was used for CO_2 photoconversion. TiO_2 modified with monometallic nanoparticles (Ag or Au) and TiO_2 modified with bimetallic nanoparticles (Ag/Au) were prepared using a microemulsion system (water/AOT/cyclohexane) according to the procedure described by Zielinska-Jurek et al. (2011). The efficiency of methane generation, after a 1 h exposure of CO_2+H_2O mixture to UV-Vis irradiation over noble metal modified TiO_2, are presented in Table 5.

Table 5. The efficiency of CO_2 photoconversion in the presence of TiO_2 modified with noble metal nanoparticles (immobilization conditions: drying temperature 120°C, drying time 20 h, a steel perforated tray)

Type of dopant	Metal precursor used during preparation	Amount of metal precursors used during preparation [mol. %]		TiO_2 source[1]	Methane concentration after 1h exposure to UV-Vis irradiation [ppm]	Mass of the photocatalyst [g]
		Au	Ag			
Ag	$AgNO_3$	-	6.5	TIP	493	0.4002
Au	$HAuCl_4$	1.5	-	TIP	503	0.4165
Ag/Au	$AgNO_3$ and $HAuCl_4$	0.5	2.5	TIP	164	0.4636

[1] TIP – TiO_2 obtained by hydrolysis of titanium(IV) isopropoxide in the microemulsion system

Higher efficiency of CO_2 photoconversion was observed for TiO_2 modified with gold nanoparticles. 503 ppm of methane were obtained in the presence of the sample 1.5% Au/TiO_2 after one hour of exposure to UV-Vis irradiation. Photoconversion efficiency for the modified photocatalyst bimetal nanoparticles Ag-Au/TiO_2 after a 1 h exposure to UV-Vis irradiation was 164 ppm. The obtained results suggested that the deposition of gold or silver nanoparticles on the surface of TiO_2 resulted in the enhancement of CO_2 photoconversion efficiency. Noble metals deposited or doped with TiO_2 have high Schottky barriers among the metals and thus act as electron traps, facilitating electron–hole separation and promoting the interfacial electron transfer process (Li et al., 2010; Dey et al., 2004). Additionally, noble-metal nanoparticles have often been used to extend the absorption properties from the ultraviolet to visible region and to enhance the photocatalytic activity of titanium(IV) oxide (Kaneco et al., 1997; Tan et al., 2008; Xia et al., 2007; Nguyen et al., 2008). Silver and gold nanoparticles possess the ability to absorb visible light, due to localized surface plasmon resonance (LSPR).

4. Conclusions

Selected parameters of TiO_2 immobilization on the surface of inert support in the CO_2 photoconversion were investigated. It was found that drying temperature and time, the type of support, as well as the amount of used TiO_2 significantly affected the efficiency of the CO_2 photoreduction process. The highest methane concentration was observed since TiO_2 was deposited on the surface of a perforated steel tray and dried at 120°C for 20 h. It has been found that with the increase of the mass of TiO_2 the efficiency of the process increases. Up to five-fold higher methane concentration was observed after 1 h irradiation in the presence of TiO_2 modified with noble metal nanoparticles than that of pure TiO_2.

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