

## A NEW GAS PHASE PHOTOCATALYTIC REACTOR FOR CO<sub>2</sub> CONVERSION: OPTIMAL PHOTOREDUCTION CONDITIONS WITH TiO<sub>2</sub> P25 PHOTOCATALYST

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### Abstract

In this work, a new gas phase photocatalytic reduction system was designed to convert CO<sub>2</sub> into fuels. The optimal conditions (such as humidity, initial concentration of CO<sub>2</sub> and the placement of powder photocatalyst in the reactor) for CO<sub>2</sub> photocatalytic reduction were systematically investigated with the commercial photocatalyst TiO<sub>2</sub> Evonik P25 in the homemade gas phase reactor. Methane (CH<sub>4</sub>) and hydrogen (H<sub>2</sub>) were the main products. Also carbon monoxide (CO) was detected. The photocatalytic reduction rate was decreasing with increasing dilution of CO<sub>2</sub> by Helium. The humidity is the key role for the CO<sub>2</sub> photocatalytic reduction as the source of needed H<sup>+</sup> and hydroxyl radicals, the best value of relative humidity was experimentally set to 51.8% leading to the highest yields of all products (CH<sub>4</sub>, H<sub>2</sub> and CO). In addition, the photocatalytic conversion was also influenced by the different placement of photocatalyst, the perfectly spread sample which possessed more effective gas-solid contact showed higher conversion than that of piled one.

**Keywords:** CO<sub>2</sub> reduction, Photocatalysis, TiO<sub>2</sub>

### 1. INTRODUCTION

CO<sub>2</sub>, as one of the important carbon sources which is low cost and abundant at the atmosphere and also one of the greenhouse gases causing the global warming, is more and more attracting the interest of many researchers. Especially, it is used to transform into the useful fuels and other chemicals, which was widely studied in recent years. However, it is well known that CO<sub>2</sub> is very stable and inert molecule, thus, it is very hard to transform CO<sub>2</sub> from the thermodynamic point of view. Many efforts were devoted to high conversion efficiency of CO<sub>2</sub>, such as catalytic hydrogenation, electrocatalysis, photocatalysis, thermolysis, biocatalysis, etc [1,2]. Recently, photocatalytic conversion has become the hot research topic because of its similarity with the natural photosynthesis, which belongs among environmental friendly, mild and easy to control reactions. Therefore, many photocatalysts were designed for the use for the conversion of CO<sub>2</sub>, such as oxide and sulfide semiconductor, carbon-based materials, etc. [3-5]. And along with the intensive study of carbon dioxide conversion, the new photocatalysts are being found and used to improve the efficiency. However, the photoreactors are also another crucial factor for limited conversion efficiency of CO<sub>2</sub>. Many researchers designed different photocatalytic reactors for conversion of CO<sub>2</sub>, such as monolith reactor, optical fiber reactor, fixed bed reactor, annular batch reactor, etc. [6,7]. Wu et al. [8] used the optical fiber reactor to transform CO<sub>2</sub> to methanol, and the highest conversion rate reached with NiO/InTaO<sub>4</sub> photocatalyst. Muhammad Tahir and NorAishah Saidina Amin [9] adopted the monolith photoreactor to photoreduction of CO<sub>2</sub>, and the major product was CO with the Cu/In co-doped TiO<sub>2</sub> photocatalyst and H<sub>2</sub> as reductant. The photoreduction results showed the monolith photoreactor for CO production was 12-times higher than the

cell-type photoreactor. Yuan et al. [10] transformed CO<sub>2</sub> into fuels using the optical fiber monolith reactor; the new reactor effectively improved the conversion of CO<sub>2</sub> to methanol. Cheng et al. [11] built a novel twin reactor and used it for conversion of CO<sub>2</sub> to CH<sub>3</sub>OH with mixture of CO and CO<sub>2</sub> as the feed, the result showed remarkably increased conversion of carbon dioxide. Our group designed various stirred batch annular reactors, which were used for photocatalytic reduction of CO<sub>2</sub> towards possible fuels such as CH<sub>4</sub>, CO, CH<sub>3</sub>OH, etc. [12-16].

Although there were many investigations focused on CO<sub>2</sub> conversion with different photocatalysts, most of the reactors contain both liquid and gas phase, or only liquid, or gas with sacrificial agent. In this work, we designed a pure gas phase photocatalytic reactor for CO<sub>2</sub> conversion to fuels, and the optimal conditions for the CO<sub>2</sub> conversion were investigated in the presence of commercial catalyst TiO<sub>2</sub> P25 which is considered as the standard photocatalyst and it is also well known photocatalyst for degradation of pollutants.

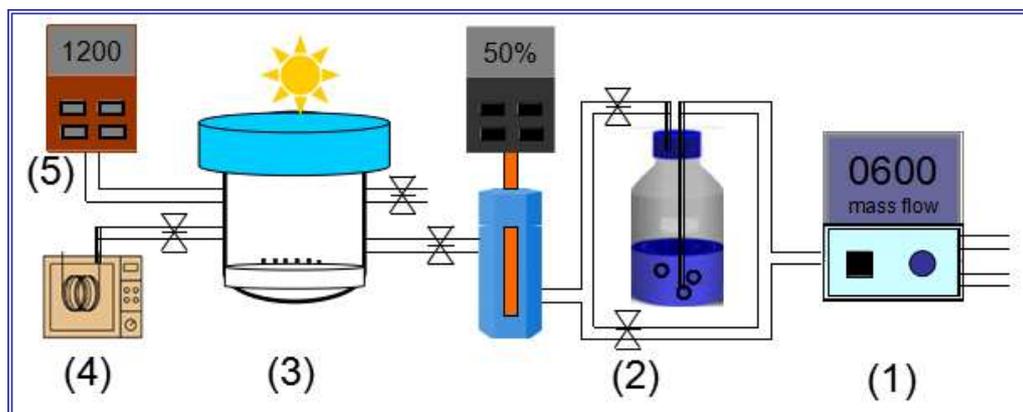
## 2. EXPERIMENTAL

### 2.1. Materials

TiO<sub>2</sub> P25 was purchased from Sigma-Aldrich (Prague, Czech Republic); A supercritical fluid-grade CO<sub>2</sub> was obtained from SIAD Technical Gases, CZ.

### 2.2. Photocatalytic reduction of CO<sub>2</sub>

The scheme of the photocatalytic reduction system is depicted on Fig.1, and it mainly contains five parts:(1) the mass flow controller; (2) humidity adjustment; (3)photoreactor; (4)GC analysis; (5)pressure test. The photocatalytic reduction processes of CO<sub>2</sub> can be described as follows: first, the flow of CO<sub>2</sub> gas and/or carrier gas (such as He) was controlled by the Sierra mass flow controllers which allows us to obtain different concentration of CO<sub>2</sub> in the reactor; second the CO<sub>2</sub> or the mixed gas is being saturated by water vapor by passing through the deionized water which could adjust the humidity of the gas in the reactor; 100 mg of TiO<sub>2</sub> P25 was spread on the glass at the bottom of reactor, the outlet valve of reactor was adjusted to control the gas flow so all the air was removed from the reactor; after 20 minutes the reactor was sealed and pressurized to above 1.3 atm. The photocatalytic reduction of CO<sub>2</sub> started by turning on the UV lamp and the reaction time was 24 hours. Gas samples were discontinuously taken and immediately analyzed on GC/BID. Among the detected products was CH<sub>4</sub>, H<sub>2</sub> and CO.



**Fig. 1** The schematic description of gas phase photocatalytic reduction of CO<sub>2</sub>.

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization of TiO<sub>2</sub> photocatalyst

According to information from producer, specific surface area of TiO<sub>2</sub> Evonik P25 photocatalyst was 50 m<sup>2</sup> g<sup>-1</sup>, band gap energy was 3.38 eV, sample contained 80 wt.% anatase and 20 wt.% rutile with crystallite size of 25 and 54 nm, respectively.

#### 3.2. The influence of different concentration of CO<sub>2</sub> on photocatalytic reduction

The production of one reaction is greatly limited by the initial concentration of reactant, thus the influence of different initial concentration of CO<sub>2</sub> (different concentration of CO<sub>2</sub> was obtained by diluting by helium) on products yields was investigated, the results are showed in Fig.2. According to the results, it can be clearly found that the yield of H<sub>2</sub> is the higher than those of CH<sub>4</sub> and CO in every photocatalytic reduction process. Also it possesses highest yield of all products (CH<sub>4</sub>, H<sub>2</sub> and CO) at 100% initial concentration of CO<sub>2</sub> in the gas phase reactor. The results are in agreement with the report from Lo et al. [17] who investigated photocatalytic reduction different concentration of CO<sub>2</sub> (diluted with N<sub>2</sub>) with acidic photocatalyst (TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>), and the yields of CO and CH<sub>4</sub> were enhanced with increasing the initial concentration of CO<sub>2</sub>, but the H<sub>2</sub> was used as reductant in this photocatalytic reduction process. Moreover, it can be seen that the yield of CH<sub>4</sub> is also high when the initial concentration of CO<sub>2</sub> is around 31% or 20%, but the H<sub>2</sub> is much lower compared to initial concentration 100% of CO<sub>2</sub>. This result is corresponding with the work published by Akhter et al. who has chosen the concentration 20% of CO<sub>2</sub> as initial concentration for the reaction [18]. Based on experimental data pure carbon dioxide was used for further experiments.

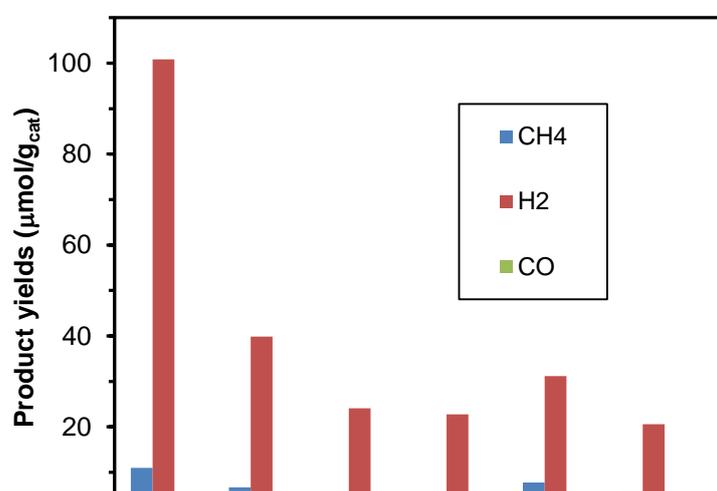
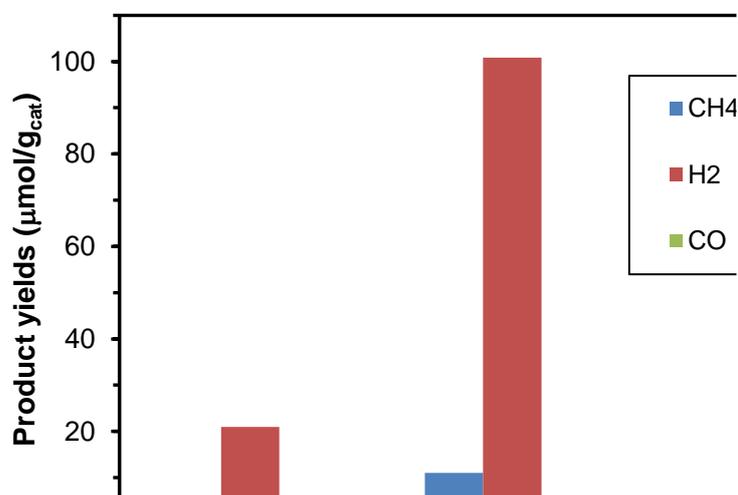


Fig.2 The influence of different CO<sub>2</sub> concentration on photocatalytic reduction.

#### 3.3. The influence of different humidity on the photocatalytic reduction of CO<sub>2</sub>

It is well known that the CO<sub>2</sub> can be transformed into the organic compounds and O<sub>2</sub> molecules via the natural photosynthesis. Therefore the artificial photocatalytic reduction CO<sub>2</sub> must meet the similar requirements and only after that CO<sub>2</sub> can be transformed into the so much desired fuels. Especially, the humidity, which offers the necessary reductant, is seriously important for the conversion of CO<sub>2</sub> under the light irradiation, thus the influence of different humidity in the reactor for CO<sub>2</sub> conversion was investigated. The results are shown in Fig.3. It can be clearly found that the conversion rate of CO<sub>2</sub> was critically limited by

the humidity. Apparently, the order of all the products yield ( $H_2$ ,  $CH_4$  and  $CO$ ) is decreasing in order of humidity as follows  $\sim 51.8\% > \sim 69.7\% > \sim 29.2\%$ . The reason may be due to that the low humidity possesses small amount of  $H_2O$  molecules which could not offer enough reductant for photocatalytic reduction of  $CO_2$ ; the high humidity contains more  $H_2O$  molecule, but the  $H_2O$  molecule is the polar molecule which could be adsorbed on the surface of  $TiO_2$  and inhibit the proceeding of photocatalytic reduction  $CO_2$ , thus the  $CO_2$  conversion efficiency was decreased at high humidity. Specially, the conversion of  $CO_2$  with the humidity at 51.8% is obviously higher than that of  $\sim 69.7\%$  and  $\sim 29.2\%$ , indicating that the humidity around  $\sim 51.8\%$  is the best one for the  $CO_2$  conversion in our home-made photocatalytic reduction reactor. The results are well in agreement with the paper published by Rani et al. They have tested various amounts of relative humidity ranging from 0 to 100% for the photocatalytic reduction of carbon dioxide with co-catalyst (Cu, Pt) sensitized  $TiO_2$ . The highest yields of both products, methane and hydrogen, were obtained in the presence of 55% of relative humidity [19].

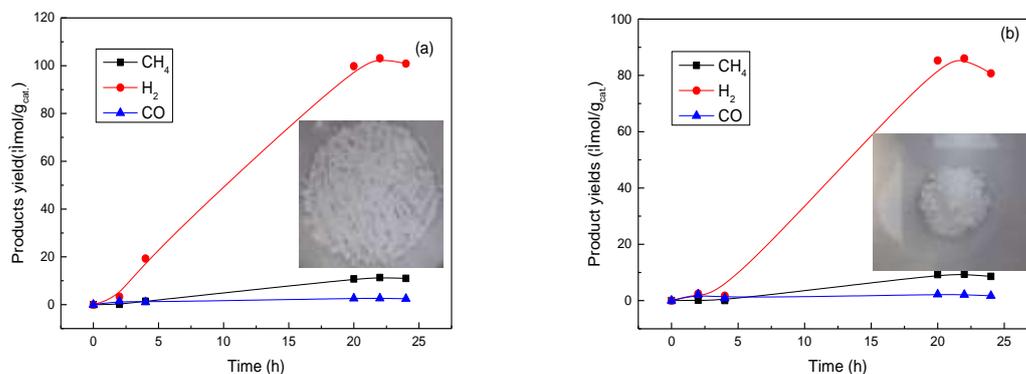


**Fig.3** The influence of different humidity for photocatalytic reduction of  $CO_2$ .

### 3.4. The influence of $TiO_2$ P25 placement on photocatalytic reduction of $CO_2$

The catalytic efficiency of gas-solid phase reaction is mainly relied on the gas-solid contact [20], which mean the shape and/or placement of catalysts is important to gas-solid reaction under the same conditions, the effective gas-solid contact could possess better adsorption of reactant. Actually, the different shapes and/or placement of the catalysts could obtain different surface properties (such as surface area, different surface groups, etc.) which limited the surface reaction sites of catalysts for gas-solid phase reaction, thus the effective gas-solid contact can offer more reaction sites and the catalytic rate will be enhanced. In terms of this reason, the different placements of P25 for photocatalytic reaction of  $CO_2$  were investigated. The results are shown in Fig.4. Fig.4 (a and b) shows that P25 was dispersed and piled onto the glass, respectively. It was experimentally confirmed that the products yield in the presence of dispersed P25 were higher than in presence of the piled P25 under the same conditions. The reason could be attributed to more effective gas-solid contact of the dispersed sample between  $CO_2$  and P25, therefore there were more active, easily reached reaction sites and also higher photons absorption. Therefore the yields of  $CH_4$ ,  $H_2$  and  $CO$  were  $11.0 \mu\text{mol/g}_{\text{cat}}$ ,  $100.9 \mu\text{mol/g}_{\text{cat}}$ . and  $2.5 \mu\text{mol/g}_{\text{cat}}$ . after 24 h of irradiation, respectively. And the yields in the presence of piled sample were lower because the piled P25 photocatalysts possesses smaller gas-solid contact between  $CO_2$  and P25 and of course lower ability to absorb photons, resulting in lower amount of active sites available for the photocatalytic reduction process itself. Even though specific surface area is not the most decisive property for the rate of photocatalytic reduction of  $CO_2$  if two different photocatalysts are

being compared, but in case of the same material higher specific surface area leads toward higher reaction rate. This was for example confirmed by, Zhang et al. who reported various nanoporous polymer monolith-supported Degussa P25 photocatalysts with different specific surface area and compared to powder P25. All the photocatalysts were tested for the photocatalytic degradation of Rhodamine B and the results confirmed that the reaction rate is increasing with increasing specific surface area [21].



**Fig.4** The influence of different P25 placements for conversion CO<sub>2</sub>

#### 4. CONCLUSION

In summary, we successfully built a gas phase reactor for the photocatalytic reduction of CO<sub>2</sub>. The influencing factors were investigated in order to find optimal reaction conditions. It was found out the photocatalytic reduction rate was decreasing with increasing dilution of CO<sub>2</sub> by Helium. Also the humidity strongly influences the CO<sub>2</sub> photocatalytic reduction. Based on the experimental data the best value of humidity was set to 51.8% which exhibited highest conversion rate under the same conditions. In addition, different placements of photocatalyst and its influence on the photocatalytic reduction of CO<sub>2</sub> was investigated. The highly dispersed sample showed much higher conversion rate than the piled one. Finding the optimal conditions for a new reactor is a beginning for further work focused on better understanding the reaction mechanism of the photocatalytic reduction of carbon dioxide.

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