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Communications

Photocatalytic conversion of CO_2 into hydrocarbon fuels with standard titania (Degussa P25) using newly installed experimental setup

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ABSTRACT : Photoreduction of CO_2 into hydrocarbon fuels on the surface of photocatalyst is one of the breakthroughs in the field of photocatalysis. At present various approaches have been investigated with the aim of increasing the CO_2 conversion efficiency. The reactor for photoconversion of CO_2 plays a vital role in experimental setup. In this work an attempt was made to testify a newly designed the photoreactor for conversion of CO_2 into useful products. The photoreactor was specifically designed for simple operation bearing features of temperature and pressure control. The reactor has been tested successively with the standard titania, Degussa P25 yielding methane with moderate production rate of 30.8 $ppm \cdot g^{-1} \cdot h^{-1}$ under UV lamp with 365 nm wavelength. The methane yield obtained is comparable to the values reported in literature. Thus we anticipate that this experimental setup equipped with newly designed photoreactor can yield competitive amounts of fuels from CO_2 photoredcution via 365 nm UV light illumination on various photocatalysts.

Energy is the "fuel of life." It exists all around us in various forms such as heat, light and electricity. Living organisms must acquire energy in the form of minerals, proteins, carbohydrates etc. to survive on this earth. Most of the energy is generated from non-renewable resources like coal, fossil fuel oils, natural gas and nuclear resources (radioactive elements). Currently a large portion of energy in terms of heat and electricity arrives from oil and gas reserves. One of the key pollutants generated by the consumption of fossil fuels is CO_2.[1] Utilization of fossil fuels and various industrial processes emit CO_2 leading to a rise in the level of atmospheric CO_2. Such emissions causes the serious issues of global warming and environmental pollution.[1-2] Various approaches have been investigated for reducing the concentration of atmospheric CO_2 to a normal level by following two key research streams[3-4]: (1) CO_2 capturing and (2) its transformation into useful products. The later research stream employs two main processes, thermochemical and photochemical for conversion of CO_2 into useable products. The thermochemical process is less preferred for the reasons of energetically intensive and costly. While, the photochemical conversion is a cost effective and preferred process for the photoreduction of CO_2 into useful liquid fuels like methanol, formaldehyde, and methane gas.[5-8] Unfortunately, the yield of photochemical conversion product is much less. Thus requires gigantic efforts for improving the CO_2 photoreduction efficiency. Therefore, the photochemical reduction of CO_2 has the dual advantage of reducing atmospheric CO_2 concentration and producing useful products. However, the conversion efficiency still very low. An extensive amounts of research are being carried out to enhance the performance and productivity in this research area. In this work, the photoreduction of CO_2 was carried out using standard titania photocatalyst, Degussa P25. The experiment was performed using a newly designed photoreactor. The reactor assembly composes of a stainless steel platform, a circular photoreactor (Volume of the photoreactor = 15.4 cm^3) bearing an inlet and outlet valves. The photoreactor has two side openings covered with rubber septum for sampling purposes and a thermocouple to measure inside temperature of the photoreactor. The schematic diagram of the experimental setup is shown in Figure 1.

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The design of the photoreactor assembly is shown in Figure 2. The experimental setup consists of the following components:

1. CO_2 gas cylinder providing 99.999% CO_2 to the photoreactor.
2. Mass flow controller (MFC) installed in the inlet line before the reactor and a vacuum pump at the last preceding the outlet line.
3. Gas bubbler containing deionized water providing a mixture of CO_2 and H_2O to the photoreactor.

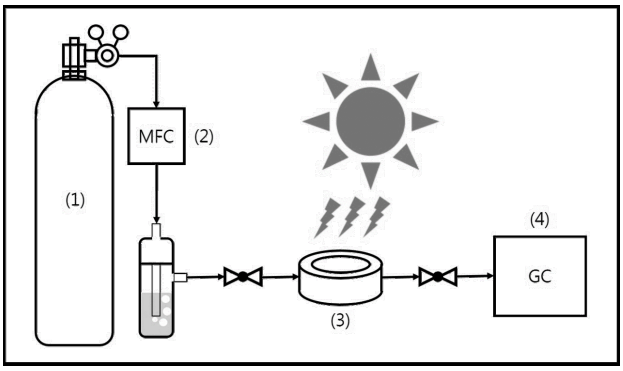

Figure 1. The schematic representation of the experimental setup for CO_2 photoreduction comprising of (1) CO_2 gas Cylinder, (2) Mass Flow Controller, (3) Photoreactor for conversion of CO_2, (4) Gas Chromatography unit

The complete experimental procedure from start to the final product involved various steps. The experimental procedure begins with the purging of the photoreactor using a vacuum pump. Both the photoreactor lines and the photoreactor are needed to be evacuated in order to remove any reactive gases or air in the reactor setup. Before the purging of the photoreactor, the line from CO_2 cylinder to the photoreactor was flushed with CO_2 for a long time to remove any air in the line if present. The inlet valve of the photoreactor was then closed to saturate the inlet line with CO_2 gas. Meanwhile, the photoreactor was purged by opening the outlet valve and purging was continued till the vacuum reaches a value of 2.0×10^{-2} Torr. Upon reaching the desired vacuum value the outlet valve of the photoreactor was closed gently while the inlet valve was opened to pass CO_2 gas into it. Before the photocatalyst loading, the reactor was purged with CO_2 gas for 5 times in order to remove any air or other impurities present in the system.

The CO_2 gas flow rate was controlled by a mass flow controller (MFC) installed in the feed line prior to the photoreactor as shown in Figure 1. The CO_2 was passed through the MFC and a water bubbler to generate a mixture of CO_2 and H_2O. The flow range of the MFC was adjusted at 0-10 cm^3/min. Just after opening the valve of CO_2 cylinder, the MFC displayed a flow rate of 10 cm^3/min. As the CO_2 gas continues to flow, the flow rate was decrease and eventually reached to 0 cm^3/min. This value was achieved for the reason of achieving zero pressure difference within the system (the photoreactor and the lines). At this point it was considered that the photoreactor and inlet line was saturated with a mixture of CO_2 and H_2O. The GC analysis of mixture gas (CO_2 and H_2O) in the photoreactor was conducted as a background test. The test shows no carbon containing compounds in the GC analysis and therefore used as reference data in further calculations.

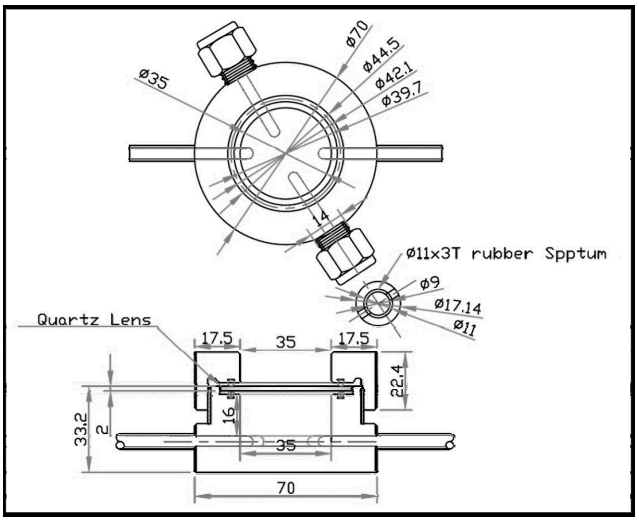

Figure 2. Design of the photoreactor for conversion of CO_2.

Afterwards the photoreactor was loaded with 50 mg of Degussa P25, the standard titania photocatalyst. The purging using high purity CO_2 gas was repeated with titania, Degussa P25 loaded the photoreactor for at least five times before illumination. The CO_2 gas from the cylinder was opened and CO_2 flows to the photoreactor through the water bubbler. The photoreactor is considered to be saturated with CO_2 and H_2O mixture when MFC displays 0 cm^3/min flow rate, indicating no further flow of CO_2 gas from CO_2 cylinder into system. At this stage the inlet valve of the photoreactor was closed and was subjected to illumination for photoreduction of CO_2 into valuable products. The illumination was carried for three hours using light from a UV lamp with 365 nm wavelength (UVP, UVGL-58, light intensity: 1200 μWcm^{-2}). The

increase in the temperature of the photoreactor under illumination and relative humidity was also measured (80 %). After one hour illumination, the final temperature of the photoreactor was found to be 35°C. This increase in temperature was considered to have negligible effect on the photocatalytic activity of P25.[9] The products measurement was controlled using gas chromatograph (Shimadzu GC-2014) equipped with flame ionization (FID) and thermal (TCD) detectors.
The sample of the products was taken from the photoreactor by using a syringe (500 μL). The syringe was inserted in the photoreactor through side opening enclosed with a rubber septum. The sample was then injected to the GC for product analysis. The GC analysis of the product sample shows a dominant yield of methane with minor yields of other hydrocarbons such as ethane, propane, and butane. The standard titania, Degussa P25 yield methane at a production rate of 30.8 ppm g^{-1} h^{-1}.

The possible photocatalytic reactions involved in photoreduction of CO_2 into CH_4 can be explained on the basis of commonly accepted two electron scheme.[10] Upon illumination, TiO_2 absorbs light and generate pairs of photoexicted electrons (e^-) and holes (h^+) which can be trapped by appropriate TiO_2 sites (Eq. (1)). Meanwhile, holes reacts with water giving rise to oxygen and protons (Eq. (2)). CO_2 molecules can then interact with the electrons and protons to give methane or other useful products (Eq. (3)).

$$TiO_2 + h\nu \rightarrow e^-_{CB}+h^+_{VB} \quad (1)$$

$$2H_2O + 4h^+ \rightarrow 4H^+ + O_2 \quad (2)$$

$$CO_2+8H^+ + 8e^- \rightarrow CH_4+2H_2O \quad (3)$$

Conclusively we have demonstrated operation of a distinct CO_2 photoreactor with simple mechanical design captivating the features of temperature and pressure control. The moderate yield of CH_4 as a main product advocates the reliability and efficient operation of newly installed experimental setup. Despite of significant progresses in the field of CO_2 photoreduction, it exhibits a challenging issue of diverse products ranging from CO to CH_4. One of the effective strategies to quick fix this dilemma is the development of hybrid photocatalysts leading to produce favorable hydrocarbon fuels. Our research group is actively involved in the development of such photocatalytic materials useful for converting CO_2 to hydrocarbon fulels by employing the newly designed experimental setup.

KEYWORDS : Photoreactor, Photocatalyst, CO_2 conversion, Hydrocarbon fuels, P25 TiO_2.

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