Novel plasma photocatalysis process for syngas generation via dry reforming of methane

Wei-Chieh Chung[a], I-Yu Tsao[b], Moo-Been Chang[a],*

[a] Graduate Institute of Environmental Engineering, National Central University, No. 300, Zhongda Road, Zhongli District, Taoyuan City 32001, Taiwan
[b] Institute of Materials Science and Engineering, National Central University, No. 300, Zhongda Road, Zhongli District, Taoyuan City 32001, Taiwan

ABSTRACT

How to effectively reduce anthropogenic greenhouse gases emission to alleviate global warming has been a public concern since 20th century. Hence, development of effective CO_2 and CH_4 reduction technique is a common objective worldwide. Simultaneous conversion of CO_2 and CH_4 into syngas can be a candidate to achieve the objective. Among several conversion techniques, plasma and photocatalysis are two promising techniques possessing good potentials. In this work, a spark discharge reactor and a series of perovskite-type photocatalysts are developed and combined to form hybrid plasma photocatalysis systems to evaluate the effectiveness for converting CO_2 and CH_4 to form syngas. Experimental results indicate that the spark discharge reactor packed with LFO600 photocatalyst increases the syngas generation rate from 13.0 to 18.5 mol per kilowatt-hour, corresponding to 42% of enhancement. Furthermore, characterizations of photocatalysts reveal that plasma can promote the surface structure of photocatalyst to increase the lifetime of electron-hole pairs which possibly leads to higher syngas generation rate. Additionally, the hybrid plasma photocatalysis system developed has been demonstrated with good potential to improve plasma and photocatalysis performances.

1. Introduction

Anthropogenic greenhouse gases (GHGs) emission is increasing year by year and the global CO_2-eq emission yielded 47.6 Gt in 2012. Hence, development for effective CO_2 and CH_4 abatement technologies is urgent. Currently, some techniques are available to reduce CO_2 emission, i.e. capturing, utilizing and storing CO_2, known as carbon capture, utilization and storage (CCUS). CO_2 can be captured via several approaches, i.e. post-combustion capture, pre-combustion capture and oxyfuel combustion/capture [1–3]. Captured CO_2 can be further stored into minerals (carbon storage or carbon sequestration) [4,5] or converted into other products (carbon utilization). Carbon utilization provides another way to reduce CO_2 emission with lower impact to the environment, including direct utilization, e.g. solvent and refrigerant [6], and indirect utilization, i.e. using CO_2 as one of reactants to generate methanol, urea or syngas [7,8].

Syngas generation from CO_2 and CH_4, known as dry reforming of methane (DRM), can be viable for carbon utilization because of its capability to convert the two most important GHGs simultaneously [9–11]. Furthermore, the product of DRM, syngas, can be utilized as an energy carrier or feedstock of Fischer-Tropsch process for hydrocarbon generation [12,13]. From the viewpoint of thermodynamics, DRM is an

endothermic reaction with $\Delta H^0_{298\,K}$ of 247 kJ/mol. As a result, activation of DRM requires a high energy input and a high operating temperature is needed. Catalytic reforming is an efficient method to activate DRM at a comparatively lower temperature, and various types of catalysts have been investigated to enhance CO_2/CH_4 conversions and syngas generation. Among various transition metals investigated, nickel-based catalysts have good catalytic activities to generate syngas, but the obstacles including high energy consumption and catalyst deactivation limit their applications [14–17]. Besides, noble metal-based catalysts possess even better catalytic activities and longer lifetime, i.e. higher coke resistivity [18–21]. However, noble metal-based catalysts are expensive and limit their applicabilities [22].

Direct conversion of CO_2/CH_4 via photocatalysis is investigated because of its advantages of solar energy utilization and mild and safe operation [23–25]. Photocatalytic conversion of CO_2/CH_4 can be operated at room temperature and there is no external energy demand since the driving force of photocatalysis is solar energy. Metal oxide semiconductors are applied to convert CO_2 into valuable products including acetic acid, formaldehyde, methanol and carbon monoxide in the presence or absence of CH_4 [26,27]. However, some shortcomings restrict its value, including low solar energy utilization rate and low reaction rate due to high band gap and high reduction potential of CO_2

[28,29].

Non-thermal plasma is another promising technique to conduct DRM. In non-thermal plasma, electrons are accelerated to have kinetic energy of several eV and further to collide with molecules to induce electron impact vibrational excitation, electron excitation, dissociation and ionization to convert CH_4 and CO_2. So far, various types of non-thermal plasma reactors have been investigated for DRM, including corona discharge [30,31], dielectric barrier discharge (DBD) [32–34], arc discharge [35,36], spark discharge [37,38] and microwave [39,40]. GHGs conversion and syngas generation efficiencies are dependent on gas temperature, electron density, electron energy distribution, lifetimes of free electrons and reactive species and geometry of reactor [41]. Fridman proposed that vibrational excitation of CO_2 is the most important channel for electron impact dissociation, thus, how to generate abundant vibrationally excited CO_2 becomes an objective of non-thermal plasma reforming [42]. Compared to catalysis, non-thermal plasma reforming can generate syngas at a lower temperature (from several tens of Celsius to several hundreds of Celsius), however, non-thermal plasma reforming has a lower GHGs conversion and syngas selectivity if compared to catalytic reforming and these remain the major obstacles of non-thermal plasma reforming [40].

To solve the shortcomings of catalysis, photocatalysis and non-thermal plasma reforming, combining them can be a good choice to enhance syngas generation and to improve the sustainability of the process [42–44]. Generally, there are two methods to combine non-thermal plasma and catalyst: the one is to pack catalyst behind the discharge region and the other one is to pack catalyst into the discharge region [45,46]. Several studies have been conducted to discover and discuss the interactions between non-thermal plasma and catalyst, including the former system (post-plasma catalysis, PPC) and the latter system (in-plasma catalysis, IPC). Non-thermal plasma influences the properties of catalyst, e.g., specific surface area, pore size and cluster size. Meanwhile, catalyst also affects the characteristics of plasma, e.g., electron energy distribution, electron density and local discharge [46–51]. Generally speaking, the synergies between non-thermal plasma and catalyst are complicated. To date, several plasma catalysis systems have been applied for DRM and the performance can be enhanced via appropriate combination [8,12]. However, interactions are still vague and require more detailed investigations to elucidate the mechanism.

Packing photocatalyst into a plasma reactor also induces synergies between plasma and photocatalyst. Li et al. packed TiO_2 photocatalyst into a DBD reactor to remove 2,4-dichlorinated phenol (2,4-DCP) from wastewater. With the concentration of 2,4-DCP of 50 mg/L, discharge voltage of 75 V and pH of 5.32, 2,4-DCP removal efficiencies achieved with plasma and plasma photocatalysis reactor are 76.1 and 83.7%, respectively. They also found that packing TiO_2 into plasma reactor enhances hydroxyl radical formation to further increase the removal rate of 2,4-DCP [52]. Assadi et al. prepared SiO_2-TiO_2 photocatalyst which was coated on glass fiber tissue (GFT) and combined with DBD to remove isovaleraldehyde (ISOVAL). As the relative humidity, specific energy (when DBD is applied) and flow rate are controlled at 60%, 9 J/L and $2\,m^2$/h, respectively, ISOVAL removal increases from 70.0, 64.0 mg/h for photocatalysis, DBD system to 148.7 mg/h for DBD photocatalysis system. They proposed that DBD photocatalysis system has a higher removal capacity than DBD and photocatalysis system due to several reasons. The first one is that plasma generates reactive species including free electrons, O radical, OH radical and ozone and these plasma-generated species can react with ISOVAL. The second one is that plasma enhances desorption of byproducts to accelerate conversion and mineralization of ISOVAL. The third one is that plasma creates electron-hole pairs via ion bombardment [53].

Perovskite-type photocatalysts, with the formula of ABX_3, have several advantages if compared with traditional photocatalysts, i.e., (1) perovskites are easily modified by substituting metals in A or B sites or substituting anions in X, (2) perovskites have good thermal stability and

photocorrosion resistivity, (3) their valency, stoichiometry and vacancy can be varied widely, and (4) perovskites possess various electromagnetic properties, i.e., piezoelectricity, ferroelectricity, paramagnetic, ferromagnetic, antimagnetic and multiferroicity [54–56]. Electromagnetic properties also influence the photocatalytic activity of perovskites and their interactions with plasma. However, detailed investigation is needed to elucidate the phenomenon.

More importantly, previous studies seldom discuss how plasma influences catalyst and photocatalyst. It should be pointed out that the physicochemical properties of catalyst/photocatalyst influence the performance of plasma catalysis system as well. Also, study on packing perovskite-type photocatalyst into plasma is lacking and the interactions between plasma and photocatalyst is unclear. Hence, this work aims to provide the information on how plasma influences photocatalyst, and how the physicochemical properties of photocatalyst influence the performance of plasma photocatalysis process. In this study, perovskite-type catalysts including $NiTiO_3$, $LaFeO_3$ and $AgNbO_3$ are prepared since they possess bandgap smaller than 3.1 eV (corresponding to visible light) and good photocatalytic activities toward hydrogen generation. Furthermore, physicochemical properties of the photocatalysts prepared in this work are quite different. Hence, a number of plasma and plasma photocatalysis processes are applied to investigate the CH_4/CO_2 conversion capacity and energy utilization efficiency. Besides, plasma-photocatalyst interactions are also investigated and discussed via photocatalyst and plasma characterizations.

2. Experimental section

2.1. Preparation of photocatalysts

Photocatalysts including $NiTiO_3$, $LaFeO_3$ and $AgNbO_3$ are prepared via citric acid method and the procedure is described as following [57–59]: 6.30 g of citric acid (HOC(COOH)(CH$_2$COOH)$_2$·H$_2$O, 99.5%, SHOWA) is firstly added into 92 mL of deionized water. Next, 0.01 mol of precursors containing A-site metal (nickel acetate (Ni(CH$_3$COO)$_2$·4H$_2$O, 98.0%, SHOWA), lanthanum nitrate (La(NO$_3$)$_3$·6H$_2$O, 97.0%, SHOWA) or silver nitrate (Fe(NO$_3$)$_3$·9H$_2$O, 99.0%, SHOWA)) and B-site metal (titanium isopropoxide (Ti(C$_3$H$_7$O)$_4$, 95.0%, ACROS), iron nitrate (Fe(NO$_3$)$_3$·9H$_2$O, 99.0%, SHOWA) or niobium chloride (NbCl$_5$, 98.0%, STREM)) are added into the solution, respectively, and the mixed solution is stirred at 80 °C for 1 h. The solution is then added with 68.4 mL of ethyl glycol (HOCH$_2$CH$_2$OH, 99.5%, SHOWA) and stirred at 85 °C until the gel is formed. The next step is to place the solution into an oven and dry at 120 °C to remove moisture. Dried solid is removed and placed into a crucible and calcined at 600, 800 and 1000 °C, respectively, for 2 h and the ramping rate of calcination is 5 °C/min. It is noted that at a temperature lower than 500 °C, perovskite phase cannot be formed especially $NiTiO_3$ [60]. Calcined solids are further ground and sieved between 70 and 100 meshes. The average size of powder is about 150–200 μm. $NiTiO_3$, $LaFeO_3$ and $AgNbO_3$ prepared are denoted as NiTOt, LFOt and ANOt, respectively, t herein stands for calcination temperature, i.e. NiTO600, NiTO800 and NiTO1000. To distinguish the photocatalysts prior to and after reforming reaction, photocatalyst after reforming reaction is denoted as ABOt-U, U represents the catalyst is used, i.e. NiTO600-U, LFO600-U and ANO600-U, respectively.

2.2. Characterization of photocatalysts

NiTO, LFO and ANO are characterized by the followings techniques: X-ray diffraction (XRD) is applied to analyze the crystalline structure of photocatalyst. Scanning electron microscopy (SEM) is conducted to examine the surface structure of photocatalyst. Transmission electron microscopy (TEM) is applied to analyze the microstructure of photocatalyst. N_2 adsorption and desorption is conducted to measure the