Energy Conversion and Management 124 (2016) 305–314

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Dry reforming of methane by combined spark discharge with a ferroelectric

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ARTICLE INFO

Article history:
Received 16 March 2016
Received in revised form 8 July 2016
Accepted 9 July 2016
Available online 18 July 2016

Keywords:
CCUS
Dry reforming of methane
Syngas
Plasma catalysis
Ferroelectric

ABSTRACT

The increasing anthropogenic emission of greenhouse gases (GHGs) is causing global warming which is a matter of deep public concern. Dry reforming of methane (DRM) is an attractive means of reducing the emission of GHGs, because it can convert CO_2 and CH_4 into syngas. Non-thermal plasma has been investigated for use in DRM and the results demonstrate that plasma can convert CO_2 and CH_4 into syngas at a lower temperature than catalysis, but the specific energy is relatively high. Combining a catalyst with non-thermal plasma in hybrid system can produce various synergistic effects that reduce specific energy. In this work, $BaZr_{0.05}Ti_{0.95}O_3$ (BZT) with a perovskite structure and ferroelectric property is packed into the plasma reactor to form a hybrid system. The syngas generation efficiency of BZT with a spark discharge reactor is investigated. The spark discharge reactor yields 49.4% conversion of CO_2 and 52.5% conversion of CH_4 and the BZT packed bed reactor yields 79.0% conversion of CO_2 and 84.2% conversion of CH_4. With respect to energy utilization, the BZT packed bed reactor has an specific energy of 0.218 MJ/mol, which is 18.7% lower than that of the spark discharge reactor without a ferroelectric (0.268 MJ/mol). Characterization of BZT reveals that the presence of BZT increases the charge density in the plasma reactor, favoring CO_2 and CH_4 dissociation. Also, SEM and XPS results show that BZT is modified with plasma, resulting in a positive synergy between the plasma and the ferroelectric.

1. Introduction

Global warming has been a public concern since the late 20th century and various techniques for reducing anthropogenic emission of greenhouse gases (GHGs) have been developed [1]. Among them, carbon capture, utilization and storage (CCUS) may be effective. Carbon utilization is a set of techniques that convert CO_2 into useful chemicals, including urea, salicyclic acid and syngas [2–4]. Reforming CH_4 with CO_2, which is called the dry reforming of methane (DRM, Reaction (1)), is a technique that can potentially reduce CH_4 and CO_2 emissions simultaneously because it converts CH_4 and CO_2 into syngas (H_2 + CO) which can be a feedstock for the Fischer-Tropsch process for synthesizing straight-chain hydrocarbons (Reaction (2)) [5–8]. Additionally, syngas is a good fuel which can be combusted to generate electricity [9].

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO \quad \Delta H^{\circ}_{298K} = 247\ \text{kJ/mol} \tag{1}$$

$$(2n+1)H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O \tag{2}$$

Dry reforming techniques, including catalysis and plasma reforming, have been investigated for converting GHGs and generating syngas. In catalytic reforming, noble metals and Ni-based catalysts are commonly used. Noble metal catalysts exhibit good activity and durability, but their high cost limits their range of application [10–13]. Ni-based catalysts have comparable activity and lower cost, but their shorter lifetime compared to noble metal catalysts, caused by coke deposition, inhibits their commercialization [14–18].

Plasma reforming is another technique that has been extensively studied. Various plasma reactors including corona discharge, dielectric barrier discharge, arc discharge, atmospheric-pressure glow discharge, spark discharge, microwave and thermal plasma have been investigated for DRM to generate syngas [19–25]. Thermal plasmas have a larger treating capacity and a higher energy consumption than non-thermal plasmas. Non-thermal plasmas have a lower energy consumption, but they generate less syngas, which is a major disadvantage. Therefore, increasing syngas generation efficiency using non-thermal plasma is a critical challenge.

Combining plasma with a catalyst to form a hybrid plasma-catalysis reactor has the potential to enhance DRM performance. Currently, the two ways to combine plasma and catalyst are: to place a catalyst process after the plasma process, as in post-

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http://dx.doi.org/10.1016/j.enconman.2016.07.023
0196-8904/

plasma catalysis (PPC) and the other is to place the catalyst inside the plasma reactor, as in in-plasma catalysis (IPC) [26,27]. In PPC, the catalyst may strongly react with the intermediate species that are generated by the plasma, enhancing catalytic performance [28]. In IPC, the synergistic effects of plasma and catalyst are complex and DRM efficiency is expected to be improved [29–32]. Many catalysts have been used in hybrid systems including PPC and IPC and possible synergistic effects have been identified. However, such hybrid system for DRM faces several challenges, such as insufficient operating time, limited lifetime of the catalyst and low energy utilization [7,31].

A ferroelectric has the unique characteristic of spontaneous electric polarization. It can be polarized by applying an external electric field, so it has a higher dielectric constant than an insulator. The polarization of a ferroelectric remains at a certain strength when the external electric field is removed, and this feature can be exploited in many electric products, such as random access memory (RAM) and radio-frequency identification (RFID). The polarization of a ferroelectric generates surface charge which can interact with free electrons in plasma, increasing the energy density in the plasma reactor [33,34]. Previous studies have demonstrated that syngas generation efficiency can be enhanced by introducing a ferroelectric into plasma reactor [7,35]. In this work, ferroelectric powder ($BaZr_{0.05}Ti_{0.95}O_3$) that is prepared by the sol-gel method and utilized in a spark discharge reactor to determine the DRM efficiency. The characteristics of the ferroelectric are discussed and possible synergistic effects between ferroelectric and plasma are suggested.

2. Experimental section

2.1. Preparation of ferroelectrics

A ferroelectric is prepared by the sol-gel method as followings [36]. 0.04 mole of barium nitrate ($Ba(NO_3)_2$) and 0.04 mole of citric acid were dissolved in 40 mL of deionized water, and 0.002 mole of zirconium ethoxide ($Zr(C_3H_7O)_4$) and 0.038 mole of titanium butoxide ($Ti(C_4H_9O)_4$) were dissolved in 40 mL of *n*-propanol. The two solutions were mixed and stirred for 1 h at 80 °C. Next, 0.04 mole of ethyl glycol was dissolved in 40 mL of deionized water and the solution was added to the above mixture with stirring for 4 h at 90 °C. Then, the mixture was stirred at 85 °C until the gel was formed. The gel-like mixture was dried overnight at 120 °C and then calcined at 1150 °C for 2 h at a ramping rate of 5 °C/min to obtain nanocrystalline $BaZr_{0.05}Ti_{0.95}O_3$. The powder was then crushed and sieved into two groups of pellets of different sizes: one was 40–70 mesh and the other was 120–140 mesh, corresponding to sizes of 210–420 and 105–125 μm, respectively. The pellets were calcined again using the same procedure as above to stabilize the crystals. The forms of BZT are denoted as C-BZT (coarse BZT particles of size of 210–420 μm) and F-BZT (fine BZT particles of size of 105–125 μm), respectively. To elucidate the influence of plasma on BZT, the C-BZT powder after plasma catalysis test was further characterized and is designated as C-BZT-P (coarse BZT particles used for plasma catalysis) for the comparison with unused C-BZT powder.

2.2. Characterization of ferroelectrics

C-BZT and C-BZT-P were characterized by X-ray diffraction (XRD). The XRD patterns were obtained with a D8AXRD diffractometer using Cu Kα monochromatic X-rays and operated at 40 kV and 40 mA over scattering angles 2θ from 20° to 100° in steps of 0.05°/s. The nitrogen adsorption and desorption isotherms of the ferroelectric were obtained at 77 K using a Micromeritics ASAP–2010 Analyzer while the specific surface areas and average pore diameters were calculated by the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) method using the nitrogen adsorption/desorption data within the 0.05–1 P/P_0 range. X-ray photoelectron spectroscopy (XPS, Thermo VG-Scientific Sigma Probe) was used to analyze the oxidation state and chemical bonding of C-BZT and C-BZT-P powder. Finally, the morphologies of the ferroelectric were studied by scanning electron microscopy (SEM, FEI Nova NanoSEM 230), and an INCA X-sight energy dispersive X-ray microanalysis (EDS) system was then used to verify semi-quantitatively the composition of the supported phases.

2.3. Experimental setup

Fig. 1 presents the experimental setup. The spark discharge reactor comprises one glass tube, one stainless steel tube and one stainless steel rod. The glass tube has an outer diameter of 24 mm and a length of 360 mm. One stainless steel tube with an outer diameter of 6 mm and an inner diameter of 3 mm is connected to a DC pulse power supply as the cathode. Another solid stainless steel with an outer diameter of 8 mm is connected to ground and serves as the ground electrode. The DC pulse power supply provides DC pulse voltages of up to 20 kV and a discharge frequency of up to 20,000 Hz. In this work, the discharge frequency is fixed at 20,000 Hz. The feeding rates of gaseous reactants including CH_4 (99.99%) and CO_2 (99.99%) are controlled by mass flow

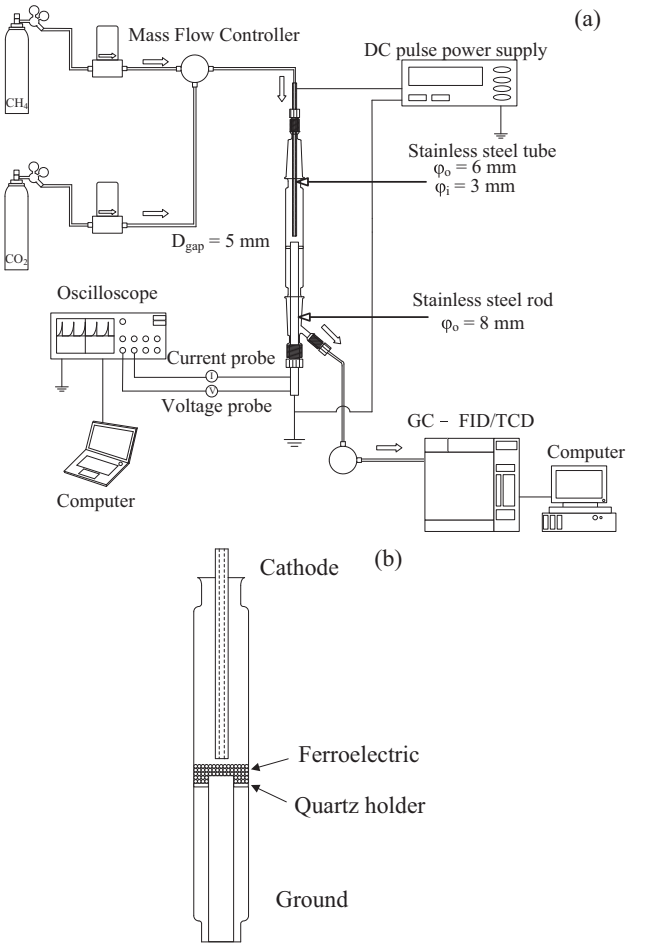

Fig. 1. Experimental setup of (a) reforming system and (b) discharge reactor with ferroelectric packed bed.