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Dry reforming of methane using different dielectric materials and DBD plasma reactor configurations

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ABSTRACT

The effect of quartz and alumina dielectric materials on the efficiency of dielectric barrier discharge (DBD) cold plasma reactor using different configurations for dry reforming of methane (DRM) has been investigated. The performance of dielectric materials was analysed at different feed ratios, gas hourly space velocity (GHSV, h^{-1}) and specific input energy (SIE, kJ L^{-1}). In both reactors, the main products detected were CO and H_2 with considerable amounts of C_2H_6. Alumina reactor prevailed in performance and the maximum conversion achieved was 74% and 68% for CH_4 and CO_2, respectively at GHSV (92 h^{-1}) feed ratio (1:1), SIE (370 J ml^{-1}) and discharge volume (V_D = 15.7 cm^3). The CO/H_2 ratio and yields were also higher in alumina than the quartz reactor under the same experimental conditions. Furthermore, different reactor configurations displayed a significant impact in the performance of DBD plasma. Increasing discharge volume (V_D) enhanced the conversion and selectivity for both dielectrics. The energy efficiency (EE) was of 0.085 and 0.078 mmol kJ^{-1} for alumina and quartz, respectively. The high EE in alumina reactor was evidently due to higher dielectric constant, which exhibited enhancement in power dissipation, discharge energy and reactor temperature. Stability test conferred alumina DBD plasma reactor performed better than the quartz.

1. Introduction

The two major concerns over fossil fuels utilization are energy insecurity and greenhouse gases (GHGs) emissions. GHGs such as methane (CH_4) and carbon dioxide (CO_2) have distinct threat to climate change [1]. In 2016, the main contributors of GHGs are CH_4 and CO_2, with 16% and 76% share in total emissions, respectively [2]. As the demand for energy increases, it is imperative to convert surplus entities like GHGs, into valuable fuels. Many approaches have been developed for conversion of low value GHGs towards mitigating global warming and sustainable development. Among the available technologies dry reforming, steam reforming and partial oxidation of methane are considered attractive [3–5]. Dry reforming of methane (DRM) is one of the promising techniques to convert both CH_4 and CO_2 for the production of syngas (H_2, CO) (Eq. (1)) [6–8]. Syngas can be used as feedstocks for Fischer-Tropsch (FT) synthesis to produce straight chain hydrocarbons.

Recently, plasma technology is gaining interest as an effective technology for processing of GHGs to value-added chemicals. DRM to syngas by plasma reactor can be conducted using thermal and non-thermal process. Since thermal plasma requires high input energy and installation cost, thus, considered less economical [9,10]. Non-thermal plasma through dielectric barrier discharge (DBD) is the better choice for DRM due to its lower energy consumption, high electron density, simple design, easy to scale up and low installation cost [11,12]. DBD generates high energetic electron discharges, radicals and ions that excite, ionize and dissociate CH_4 and CO_2 to final products [6]. However, DBD plasma has lower energy efficiency (EE) (mmol kJ^{-1}) compared to gliding arc and microwave plasma. This provides an opportunity to work on EE of DBD plasma to improve the performance [13]. Numerous studies are conducted to test DRM using DBD plasma under various experimental conditions [14–16]. The performance of DBD plasma is entirely dependent on feed flow rate, feed molar ratio, input power, catalyst loading and temperature [17,18].

Although DBD plasma has been successfully investigated for DRM application with appreciable amount of desired products, the foremost concern is the carbon deposition, due to methane cracking and Boudouard reaction as described in Eqs. (2) and (3).

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$$CH_4 + CO_2 \Longleftrightarrow 2CO + 2H_2 \Delta H^{\circ}_{25^{\circ}C} = 247\ \text{kJ mol}^{-1}\ \text{(DRM)} \quad (1)$$

$$CH_4 \Longleftrightarrow C + H_2 \Delta H^{\circ}_{25^{\circ}C} = 75\ \text{kJ mol}^{-1}\ \text{(Methane cracking)} \quad (2)$$

$$2CO \Longleftrightarrow C + CO_2 \Delta H^{\circ}_{25^{\circ}C} = -172\ \text{kJ mol}^{-1}\ \text{(Boudouard reaction)} \quad (3)$$

There are many attempts to minimize coke formation in DRM including using catalyst, diluent gases and presence of packing materials in the discharge zone [19]. Previous studies advocated that dielectric material has a substantial effect on the plasma chemistry [20] and affected its activity in plasma based DRM process [21]. Dielectric materials may also have influence on the coke deposition due to different discharge behaviour and internal reactor temperature [22]. Therefore, it is imperative to investigate the characteristics of dielectric materials and its influence on DRM performance in DBD plasma [23]. Most of the studies have been conducted using quartz, which is moderately expensive and fragile [24,25] as a dielectric material. Effect of the electrical parameters i.e. input power, discharge characteristics and frequency, studied by Sazal et al. [22], using quartz as dielectrics, recorded the conversion of CH_4 as 52%. Furthermore, specific input energy (SIE) is considered one of the key parameters in evaluating plasma reactor as it characterize the energy density of the DBD plasma [19]. SIE affects the conversion efficiency of reactant gases while taking flow rate constant and varying input power [26,27]. Higher SIE reflects higher utilization of energy culminating to lower energy efficiency (EE) [28,29]. Recently, the use of ceramic as the dielectric material and influence of input power and frequency have been discussed by Ozkan et al. [20], in DBD plasma for CO_2 conversion to CO and O_2. The parameters that directly account for EE are conversion of reactant gases and SIE. The conversion efficiency and selectivity has been investigated to evaluate the EE of the DBD plasma reactor [28]. Meanwhile, the CH_4 and CO_2 conversion efficiency was improved by increasing SIE, however, the EE of the DBD plasma reactor decreased since the selectivity of the product gases were not much affected by applying high SIE [29]. The materials having high dielectric constant are considered more suitable for a DBD reactor as they can partially suppress coke formation. This is because higher dielectric constant possesses high reactor temperature due to strong electric field. Furthermore, coke can react with reactive oxygen to form CO_2 at elevated temperature [30]. The properties of dielectric material i.e. dielectric constant (permittivity), morphology, and temperature tolerance are the key parameters to increase the EE of DBD plasma reactor.

High dielectric constant of a material could increase the electric discharge capacity and reactivity of DBD plasma to achieve the desired performance [31,32]. The relative permittivity, described as electric field, is produced per unit charge in that medium or known as electric susceptibility [33]. The generated electric field depends on the nature of dielectric material while discharge behaviour depends upon dielectric capacitance and gas gap capacitance. The reactor configuration also plays a key role in the discharge characteristics of DBD plasma [22].

DBD reactor can be fabricated in various configurations, but planar and cylindrical geometries are frequently used. Reactor configuration consists of discharge gap, discharge length, and discharge volume, size, catalyst position and all these variables are directly related to GHSV (h^{-1}). Montoro et al. [28], studied the effect of dielectric material packing placed in the discharge zone and concluded that the morphology of packing dielectric material is an important factor in reactor performance. To the best of our knowledge, reactor configuration has never been considered exclusively in previous reports. Recently, Tu et al. [34], and Chung and Chang [10] suggested that the reactor configuration (geometry) in DBD plasma can contribute to reactor efficiency and products selectivity. Therefore, it is appropriate to investigate reactor configuration to enhance the performance of a DBD plasma reactor for DRM.

In this study, dielectric materials namely quartz and alumina were investigated as a DBD plasma reactor to evaluate the performance and stability in DRM. The operating parameters investigated were GHSV (h^{-1}), feed ratio and SIE. The characterization of alumina tube before and after DRM activity was conducted to analyse the morphology. Furthermore, the performance of the reactor with different configurations such as discharge gap, length and volume was evaluated for both dielectric materials. EE was determined for both dielectrics materials at the optimum process parameters and reactor configuration.

2. Experimental

2.1. Experimental setup

The schematic diagram of the DBD plasma reactor experimental set-up is shown in Fig. 1. The plasma system consisted of a power supply (CTP-2000K Nanjing Suman Electronics Corp. China), which was integrated with an AC voltage regulator and used to generate plasma for DRM activity. Tektronix TDS2012B two-channel digital oscilloscope with high voltage probe Tek P6015A was used to assess the input voltage and current. The reactor consisted of a cylindrical dielectric tube (quartz or alumina) having length 40 cm with 10 mm and 12 mm inner and outer diameters, respectively. The dielectric materials were purchased from Toho Ceramic Technology Co. Ltd (China) and Jinzhou Jingdian quartz glass Co. Ltd (China) and its physical properties are listed in Table 1. Stainless steel rods of different diameters were used as the main electrode, while aluminium mesh with different lengths was employed as the ground electrode. The reactor temperature was measured by Infrared (IR) thermal imager (Fluke Ti400) and the thermal images were analysed by Fluke SmartView® software to obtain the temperature profile in the reactor. Feed gases CH_4 (99.9%) and CO_2 (99.9%) were regulated by mass flow controllers (ALICAT Scientific 200 SCCM). The reactor outlet gas flow rate was measured by bubble flow meter as it is being considered as reliable in previous studies [12].

The feed and product gases were analysed by an online Gas Chromatograph (GC) (Agilent 6890N) equipped with thermal conductivity detector (TCD) and flame ionization detector (FID). A HP-PlotQ capillary column (Agilent, 40 m × 0.53 mm ID, 40 μm) for detecting air and CO_2, one unit of Molsieve capillary column (Agilent, 30 m × 0.530 mm ID, 25 μm) for separating H_2, O_2, N_2, CH_4 and CO were connected to TCD detector. In addition, one unit of HayeSep Q-Supelco, 6 ft × 1/8 in. ID × 2.1 mm OD, 80/100 mesh) for back flushing C_2 to C_6 was connected to the TCD. To separate C_1 to C_6 hydrocarbons, a unit of GS-GasPro (Agilent, 60 m × 0.32 mm ID) capillary column was connected to the FID detector.

2.2. Material characterization

The morphology of the material was examined before and after the reaction by field emission scanning electron microscopy (FE-SEM), Energy-dispersive X-ray spectroscopy (EDX) and Raman analysis. FE-SEM and EDX were conducted in Hitachi SU8020 integrated with the beam of X-Max^N by OXFORD instrument optics and full control of probe current from 1pA to more than 5nA. Raman analysis was performed in HORIBA LABRAM HR EVOLUTION (France) with the wavelength for ultra-violet: 325 nm = He Cd and in the range of 0–4000 nm.