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Carbon dioxide dissociation to carbon monoxide by non-thermal plasma

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ABSTRACT

The decomposition of carbon dioxide was investigated in a non-thermal plasma dielectric barrier discharge reactor filled with glass balls. The CO_2 conversion was maximum by using a sinusoidal excitation compared to pulsed excitation. The CO_2 conversion and the CO selectivity are increased in the presence of helium, particularly with the AC power supply, but with a decrease in energy efficiency. The formation of solid materials composed of carbon but also of silica was highlighted for the first time, proving that carbon was incorporated into the silica network along with CO_2 dissociation under non-thermal plasma conditions. The temperature control of the reactor wall has shown that the CO selectivity is favored by a low temperature wall, whereas the CO_2 conversion remained constant, suggesting that the carbon balance default is due to the CO decomposition on the reactor wall.

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1. Introduction

The International Energy Agency states that the concentration of CO_2, the main greenhouse gas (GHG), has been increasing significantly in the atmosphere over the past century, while the impact of GHG on climate change is now admitted [1]. For this reason, the remediation of CO_2 has received considerable attention in the recent years. High energy processes are required to overcome the high thermodynamic stability of CO_2. However the changing paradigm in the use of perennial energy sources such as solar, wind and geothermal energy makes possible the development of reactions requiring intensive energy [2].

Among the possible technologies to valorize CO_2, the Boudouard reaction in which CO_2 reacts with carbon to produce carbon monoxide [3] and the dry reforming of hydrocarbons by thermal catalysis have been largely studied [4]. As an alternative to conventional catalytic dry reforming reaction, non-thermal plasma appears as an interesting technology since highly energetic electrons generated by plasma at room temperature are able to initiate chemical processes. Dielectric barrier discharge (DBD) plasma was used for many applications such as ozone generation [5], VOC removal [6], surface treatment [7] and also reforming reactions [8–10]. The nature of the dielectric barrier material is one of the key parameter for the performances of the DBD plasma. The most frequently material used are quartz, alumina or silica glass due to their high dielectric constant [11]. Moreover, introduction of a dielectric material as balls or pellets into the plasma reactor leads to an increase of the electric field which increases then the electron energy leading to an expected higher CO_2 conversion [12].

The reforming reaction of CH_4 by CO_2 to produce syngas by DBD plasma was investigated by many researchers in various experimental conditions at different input power, total flow rate, CH_4/CO_2 ratio, and distance between electrodes. The results reported in literature showed that the production of syngas from CH_4 and CO_2 is always accompanied by C2–C6 hydrocarbons formation, the main products being ethane and propane, whatever the CH_4/CO_2 ratio used to perform the reaction [13–15]. Many reactions are proposed to occur under non-thermal plasma. The most commonly proposed mechanism for the first step is the dissociation of methane and carbon dioxide induced by highly energetic electrons with energy between 1 and 10 eV in microdischarges (Eqs. (1) and (2)) [16]:

$$CH_4 + e^- \rightarrow CH_3 + H + e^- \quad (1)$$

$$CO_2 + e^- \rightarrow CO + O + e^- \quad (2)$$

Successive removing of hydrogen from CH_3 is possible by electron impact (Eqs. (3)–(5)), leading to the formation of carbon black [17]:

$$CH_3 + e^- \rightarrow CH_2 + H + e^- \quad (3)$$

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$$CH_2 + e^- \rightarrow CH + H + e^- \quad (4)$$

$$CH + e^- \rightarrow C + H + e^- \quad (5)$$

The formation of solid carbon can also result from carbon monoxide or carbon dioxide dissociation (Eqs. (6) and (7)):

$$CO + e^- \rightarrow C + O + e^- \quad (6)$$

$$CO_2 + e^- \rightarrow C + O_2 + e^- \quad (7)$$

Apart from reforming reactions, the direct decomposition of carbon dioxide to carbon monoxide could be an interesting way to valorize CO_2 and to limit the formation of side products from hydrocarbons [18]. Non-thermal plasma can promote the highly endothermic reaction (Eq. (8)) [19–21]:

$$CO_2 \rightarrow CO + 1/2\,O_2 \ (\Delta H = 280\ \text{kJ/mol}) \quad (8)$$

In the present work, we have investigated the carbon dioxide dissociation (CO_2 splitting) with or without helium as diluent with a particular attention to the CO selectivity (the carbon balance) and to the characterization of carbonaceous species deposit which to our knowledge, has never been characterized. This last point is rarely studied, authors generally focused only on CO formation. Moreover the influence of the plasma source (pulsed or AC power supply) was also investigated. The dielectric material was the Pyrex® glass wall of the reactor tube which was filled with glass balls.

2. Experimental

The reactor is a classical coaxial packed-bed type filled with glass balls of 1.8–2.0 mm diameter. The role of glass balls in the plasma zone is to obtain a more homogeneously repartition of plasma than for an empty reactor [22]. The reactor tube (16 mm o.d and 14 mm i.d.) is made of Pyrex®. The inner electrode is a stainless steel rod (6.2 mm o.d.) and the outer electrode is a copper foil (80 mm length) wrapped on the external reactor wall. The reactor is equipped with a double walled into which cold air circulates in order to control the temperature (Fig. 1b). A thermocouple is located on the outer electrode to record the external temperature of the reactor.

The high voltage is applied to the inner electrode whereas the outer electrode is grounded (Fig. 1b). The reaction was performed by flowing carbon dioxide alone or mixed with helium in the Pyrex® tube reactor.

The plasma discharges were generated using two different power supplies: a monopolar pulsed electric generator (A2E

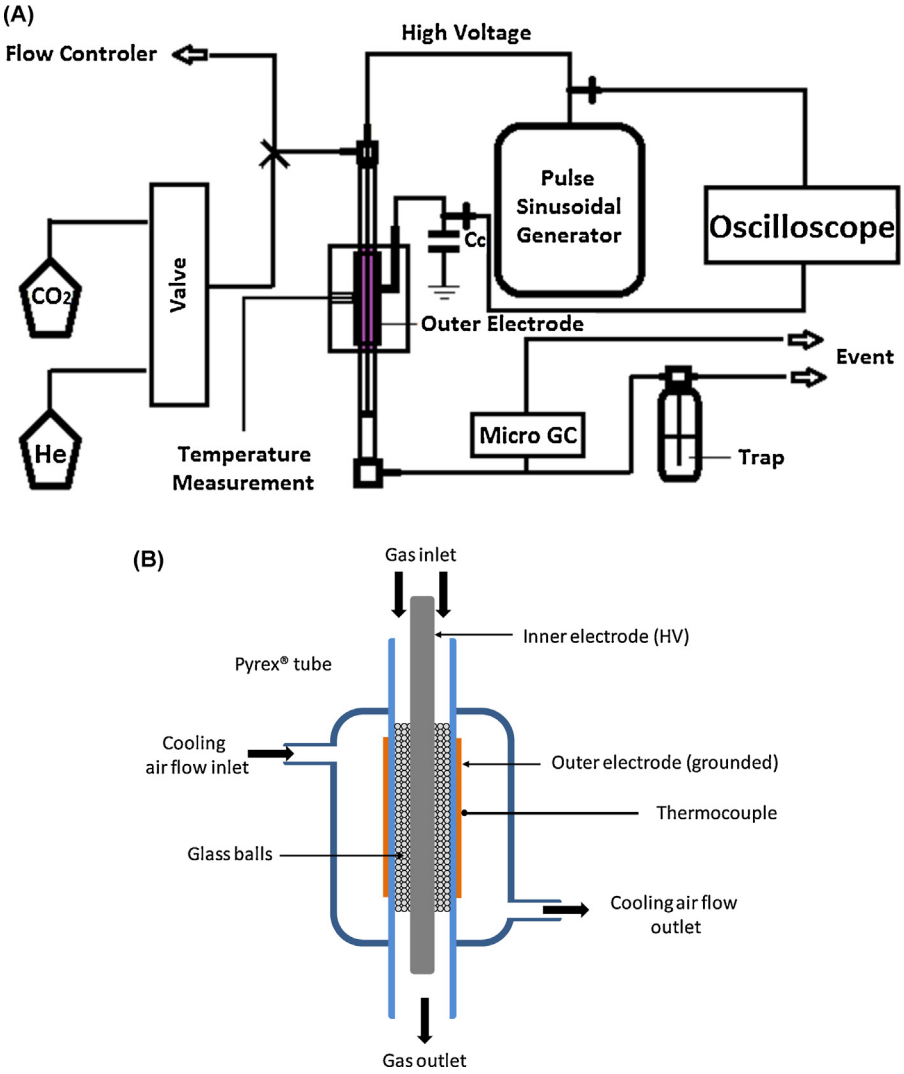

Fig. 1. (a) Experimental setup; (b) reactor scheme.

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