



Pulsed dry methane reforming in plasma-enhanced catalytic reaction



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ABSTRACT

Pulsed dry methane reforming (DMR) in dielectric barrier discharge (DBD) and 12 wt.% Ni/Al₂O₃ catalyst hybrid reaction was investigated, aiming for efficient conversion of greenhouse gas (CH₄, CO₂) into syngas (H₂, CO) at low temperature. CO₂ was continuously supplied, while CH₄ was introduced intermittently for 1 min at constant interval of 3 min. Although solid carbon was deposited during the reforming reaction, carbon was almost fully removed by turning off CH₄ flow and applying CO₂-fed DBD. Pulsed transient analysis revealed that CH₄ dehydrogenation and subsequent reverse water–gas–shift reaction is sufficiently fast with and without DBD, producing syngas with the H₂/CO ratio of 0.8–0.9. In contrast, carbon removal reaction, i.e. Boudouard reaction, is promoted clearly by DBD hybridization. Radical injection is primarily important step. Besides, selective surface heating by DBD such as charge recombination on the catalysts is anticipated to promote carbon diffusion through Ni catalyst particles and subsequent oxidation by adsorbed CO₂. DBD and catalyst hybrid reaction enabled higher CH₄ and CO₂ conversion without having serious coking problem.

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1. Introduction

Carbon capture and storage (CCS) is one of the most powerful solutions that minimizes CO₂ emission into atmosphere. However, from economic point of view, even the mature CCS technology has not been used worldwide [1] because CO₂ does not produce value-added products, and is separated permanently with additional energy and cost. Moreover, the concern about environment and health impact in case of unexpected leakage of CO₂ demands further risk assessment of the technology, causing significant delay of CCS installation. By now, enhanced oil recovery (EOR) in the remote area is the most successful example of CCS. Inevitably, CO₂ conversion into useful chemicals is highly desired as next generation greenhouse gas control technology [2–4]. Establishing a new carbon circulation pathway is critically important.

In recent year, power-to-gas conversion is highlighted where water electrolysis driven by renewable electricity is combined with catalytic conversion of CO₂ [5]. CO₂ is converted into CH₄ with the renewable H₂, then distributed through existing natural gas grid for widespread use. Based on the similar concept, we propose CH₄ conversion with CO₂ using non-thermal plasma enhanced catalytic reaction. This technology is known as dry methane reforming (DMR) and a mixture of CO and H₂ (syngas) is synthesized.

Analogous to electrolysis of water splitting, renewable electricity is converted into chemical energy via non-thermal plasma assisted endothermic reactions. Syngas is converted preferably into carbon containing liquid fuels such as gasoline and methanol whose energy density is 10–100 times greater than that of solid state secondary batteries. Transport and storage capability of renewable energy is greatly improved and CO₂ utilization is realized simultaneously. Currently, electrochemical reaction is dominantly studied for electrical-to-chemical energy conversion [4,5]. Besides, non-thermal plasma provides additional energy and material conversion pathways, contributing to an extended carbon recycling network and fuel flexibility [2,4,6,7].

In this study, pulsed dry methane reforming (DMR; CH₄ + CO₂ = 2CO + 2H₂) in 12 wt.% Ni/Al₂O₃ catalysts and dielectric barrier discharge (DBD) hybrid reaction was investigated. CH₄ was temporarily injected for reforming reaction, while CO₂ plasma was generated alternately to remove solid carbon precipitated onto the catalysts. By examining time-dependent consumption of CH₄ and CO₂ and the evolution of CO and H₂ profiles, rate-controlling step and related kinetics are evaluated. Optical emission spectroscopy, catalyst bed temperature analysis, and time dependent changes of those quantities are also investigated for better understanding of reaction enhancement mechanisms. We found that hybrid reforming enables better carbon deposition control, allowing continuous operation without serious coke deposition. Moreover, unique non-equilibrium reaction feature was brought by pulsed CH₄ injection: H₂ was produced rather selectively at the moment

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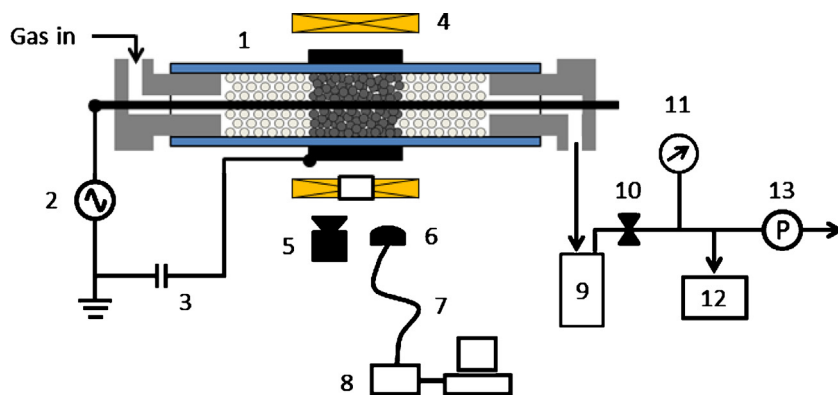


Fig. 1. Schematic diagram of experimental setup: (1) Packed-bed DBD reactor; (2) High voltage power source; (3) Capacitor (0.036 μF); (4) Furnace; (5) Thermography; (6) Optical lens system; (7) Optical fiber; (8) Spectrometer and computer; (9) Cold trap (-40°C); (10) Metering valve; (11) Pressure gauge; (12) Quadruple mass spectrometer; (13) Vacuum pump.

of CH_4 injection, whereas gas phase CO conversion via vibrationally excited CO was enhanced when Boudouard reaction is initiated by turning off CH_4 flow. Reforming kinetics, coke formation mechanisms and synergistic effect brought by DBD are comprehensively discussed.

2. CO_2 and CH_4 reforming by non-thermal plasma

Dry methane reforming has drawn keen attention as viable CO_2 utilization technology because it may have one of the greatest commercial potentials [3,8]. Various catalysts have been developed and reaction kinetics are well understood [9]. However, a commercial installation of DMR is still difficult because coke formation and catalyst deactivation problem has not been solved yet. Moreover, DMR is highly endothermic reaction: Efficient supply of high temperature heat is necessary, whereas heat transport property of a fixed bed reactor is generally poor. Therefore excessively high temperature operation is required that increases energy penalty and deteriorates materials used for reactor as well as catalysts. Increasing demand of DMR is therefore pursuing a new technology and potential use of thermal and non-thermal plasma is highlighted [10–14].

Dielectric barrier discharges (DBDs) is one of the most successful atmospheric pressure non-thermal plasma sources in industry applications [15]. Fundamental physics and chemistry in DBDs is well understood in relation to ozone synthesis and gas cleaning. More recently, DBDs and their combination with solid catalysts are recognized as viable material conversion technology at low temperature, and investigated in steam reforming [16–21], partial oxidation [22–27], and dry reforming [28–36] of hydrocarbon fuels. As for non-thermal plasma assisted dry reforming, carbon deposition and deactivation of catalysts cause serious problem. Although CH_4 conversion and product selectivity is enhanced by DBD hybridization, coke formation is not avoidable and overall reforming performance is deteriorated in almost all applications. In contrast, non-catalytic direct CO_2 activation by plasma has been investigated [37,38]. Fridman and co-workers demonstrated that energy conversion efficiency of CO_2 dissociation in supersonic microwave (MW) plasma was greater than 80% [39]. First, CO_2 is vibrationally excited by electron impact, and then vibration-to-vibration (V–V) energy transfer leads to dissociation of CO_2 into CO and O_2 efficiently. Bogaerts and co-workers have investigated non-catalytic CO_2 dissociation numerically in DBD [40,41] and MW plasma [41]. They concluded that MW plasma is more efficient than DBD. The V–V energy transfer becomes important elementary step in MW plasma and energy efficiency improved from <5%

(DBD) to 23% (MW plasma). However, as CO_2 conversion increases, energy fed into products (CO and O_2) leads to increased energy penalty and 80% energy efficiency, i.e. ref 39, was not demonstrated numerically.

Comprehensive analysis of CH_4 conversion efficiency in DBD is presented in ref 11. CH_4 conversion efficiency of 10% was estimated by simplified one-dimensional numerical analysis of streamer type discharge produced in pure CH_4 . It was also studied by the experiments, showing energy efficiency of less than 1% was obtainable: More than 90% of energy fed into DBD was converted into heat and removed by water-cooled electrodes [42]. Another 9–10% was used for gas heating. However, energy efficiency was greater than 50% when DBD was combined with solid catalysts [43]. The importance of vibrational excitation of CH_4 and their interaction with solid catalysts was pointed out in steam methane reforming in DBD/catalysts hybrid reaction [16,17]. Nozaki et al. performed detailed kinetic analysis of plasma-catalyst hybrid reaction in terms of overall methane steam reforming reaction [43]. Reaction order for overall reaction and pre-exponential factor of Arrhenius equation were clearly enhanced by DBD hybridization, implying that dissociative chemisorption of CH_4 on catalysts is enhanced by vibrational excitation. In that case, activation energy of CH_4 dissociation is expected to decrease [44–46]; however, overall activation energy was kept unchanged by DBD, showing the same value as thermochemical reaction system ($E_a = 100 \text{ kJ/mol}$). Such discrepancy between molecular scale and macroscopic analysis is commonly observed [47]. Deep understanding of complicated interaction between plasma and catalytically functionalized surface is needed to maximize the synergistic effect of plasma hybrid reaction.

3. Experimental

Experimental setup is schematically shown in Fig. 1. Detailed reactor configuration and electrode geometry are provided previously [48]. Briefly, a quartz tube with 20 mm inner diameter was used for the packed-bed DBD reactor. Catalyst pellets (ISOP, 12 wt.% Ni/ Al_2O_3 and ϕ 3 mm; Süd-Chemie Catalysts Japan, Inc.) were packed over 20 mm length and both sides were supported by non-catalytic Al_2O_3 pellets (ϕ 3 mm). Catalysts were reduced for 90 min in $\text{H}_2/\text{N}_2 = 50/450 \text{ cm}^3/\text{min}$ at 600°C prior to the experiment. Stainless steel rod with 3 mm diameter was inserted into the center of the quartz tube as a high voltage electrode. Ground electrode has a slit (10 mm width, see Fig. 2) and the temperature distribution of the catalyst bed was measured by thermography (TH5140; NEC San-ei Instruments Ltd.). A high voltage power source was used to generate DBD (Logy Electric LHV-13AC). It features compactness

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