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Review of catalysis and plasma performance on dry reforming of CH_4 and possible synergistic effects

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ABSTRACT

Global warming has received much public concern and carbon dioxide utilization has been considered as one of viable approaches to reduce the CO_2 emissions and alleviate global warming. Dry reforming of methane (DRM) is regarded as potential technique to reduce anthropogenic (greenhouse gases) GHGs emissions. Both catalysis and plasma technologies have been applied for DRM to investigate the CO_2 and CH_4 conversion as well as syngas generation efficiency. For catalysis, noble metal catalysts exhibit good activity but the cost is too high. Ni-based catalysts are usually investigated and several methods of modifying are postulated to enhance their DRM performance including better metal-support interaction, basicity of catalyst and smaller metal cluster size. However, catalysis needs to be operated at a high temperature which results in high energy consumption. Moreover, coke deposition leads to deactivation of catalyst which also limits the lifetime of catalyst. Plasma reforming which can be operated at a wide range of temperature (from room temperature to over 1000 °C) is another technique for DRM. Both non-thermal plasma and thermal plasma are proved to effectively convert CO_2 and CH_4 into syngas. However, the energy utilization efficiency is still low and relatively low syngas selectivity results in low syngas generation efficiency. Thus, combination of catalysis and plasma can be an alternative to integrate the advantages of catalysis and plasma. Plasma catalysis is proved to have synergistic effects to improve the syngas generation efficiency, since catalysis and plasma can improve the performance of each other. Plasma can enhance catalysis activity and durability, while the existence of catalyst promotes electron density in plasma and energy utilizing efficiency is expected to improve. In this study, the mechanisms of catalysis promotion are described, the synergistic effects between catalyst and plasma are elucidated, and possible approaches to optimize DRM are proposed.

Contents

Abbreviations: GHGs, greenhouse gases; CCUS, carbon capture, utilization and storage; SRM, steam reforming of methane; F–T process, Fischer–Tropsch process; POM, partial oxidation of methane; DRM, dry reforming of methane; ATR, auto-thermal reforming of methane; DBD, dielectric barrier discharge; APGD, atmospheric-pressure glow discharge; APPJ, atmospheric-pressure plasma jet; RF, radio frequency discharge; PPC, post-plasma catalysis; IPC, in-plasma catalysis; E-R, Eley-Rideal; L–H, Langmuir–Hinshelwood; RWGS, reverse water gas shift; TPD, temperature programmed desorption; XPS, x-ray photoelectron spectroscopy; SPS, smaller particle size; SMSI, stronger metal-support interaction; MABS, more active basic sites; HOA, higher oxygen affinity; SEI, specific energy input; EE, energy efficiency; DAP, direct current arc plasma; SMC, smaller metal clusters; RAS, reduction of active sites; OV, oxygen vacancy; PSV, pore structure variation; EPOC, electrochemical promotion of catalysis

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1. Introduction

Global warming caused by the increasing greenhouse gases (GHGs) emission is an emerging issue which has caused much public concern. Carbon dioxide and methane are two dominating GHGs due to their high emissions and concentrations in atmosphere. In 2010, CO_2 accounts for 76% of 50.1 Gt global CO_2-equivalent emission while CH_4 accounts for 16% [1]. For the purpose of reducing GHGs emission, carbon capture, utilization and storage (CCUS) which combines several techniques is currently under development [2–6]. Among them, carbon dioxide utilization is a promising technology. CO_2 is mainly utilized in two ways: one is to apply CO_2 directly as refrigerant [7,8], cleaning and extracting agent [9] or solvents [10,11]. Another way is to use CO_2 as one of the reactants to produce valuable chemicals [12–15]. The products may include urea [16,17], polycarbonate [18,19], salicyclic acid [20], cyclic carbonate [21], polypropylene carbonate [21], acetylsalicylic acid [22], methanol [23,24] and syngas [25,26]. Among them, syngas generation is not currently commercialized. However, it has received much attention because it can be operated at atmospheric pressure and a wide range of operating temperature. Syngas is composed of hydrogen and carbon monoxide which can be utilized as fuel or feedstock of Fischer–Tropsch process to produce hydrocarbons, e.g., acetic acid, dimethyl ether and nonadecane [27].

Various techniques including steam reforming of methane (SRM, reaction (1)), partial oxidation of methane (POM, reaction (2)) and dry reforming of methane (DRM, reaction (3)) can be applied to convert methane into syngas to reduce GHG emissions:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H^{o}_{298\ K} = 206\ \text{kJ/mol} \tag{1}$$

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \quad \Delta H^{o}_{298\ K} = -36\ \text{kJ/mol} \tag{2}$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H^{o}_{298\ K} = 247\ \text{kJ/mol} \tag{3}$$

SRM is a commercialized technique to generate syngas or H_2, however, the endothermic reaction needs a high temperature (usually higher than 700 °C) to activate the reforming reaction [28–33]. Comparatively, POM is an exothermic reaction which is favorable to be operated at a lower temperature (300–500 °C), leading to lower energy consumption. Unfortunately, the ratio of O_2/CH_4 needs to be controlled precisely, otherwise full oxidation would happen to generate CO_2 and overheat the reaction bed [33–36]. If SRM and POM are combined as a hybrid system, the net entropy can be zero and the process is called auto-thermal reforming of methane (ATR). The energy utilizing efficiency of ATR is higher since the heat released during POM can be used to activate SRM. However, ATR operation needs to be well-controlled to prevent overheating [37–39]. DRM was invented by Fischer and Tropsch in 1928 to convert CH_4 and CO_2 simultaneously [40]. It is noted that Fisher and Tropsch also invented F–T process in 1925 [27]. DRM has received much attention since the reactants of DRM are two most important GHGs [41–47].

Because DRM is highly endothermic, catalyst is needed to reduce the operating temperature. Noble metals including Pd, Pt, Rh, Ru and Ir have been investigated as catalyst for DRM and the results show good activities [48–57]. Pawelec et al. [58] prepared Pt-Ni/ZSM-5 catalyst via impregnation for DRM and the results show that Pt-Ni/ZSM-5 can convert 53.8% of CH_4 and 98.5% of CO_2 at 600 °C [58]. It is noted that the theoretical conversions of CH_4 and CO_2 at 600 °C without catalyst are 41% and 55%, respectively [59]. Both CH_4 and CO_2 conversions achieved with Pt-Ni/ZSM-5 catalyst are higher than the theoretical values, indicating that noble metal catalysts are of excellent activities for DRM. However, noble metals are expensive. Alternatively, transition metals including Fe [60], Co [61–63], Zr [64] and Ni [65–69] catalysts are investigated for DRM. Among them, Ni-based catalysts are demonstrated with good activity toward DRM. However, catalyst deactivation remains a serious obstacle for scaling up the catalytic reforming system. Specifically, carbon deposited on catalyst would block the pores of catalyst to inhibit the catalytic reactions [70–74]. Carbon deposition inevitably takes place during DRM, and can be of different forms (in regular arrangement or randomly distributed) [75–77]. Durability of catalyst may be improved by transforming inactive carbon species into active species, e.g., carbon whiskers, to reduce carbon deposition [69,77].

Plasma is another promising technique to be scaled up and commercialized for DRM [78–80]. Plasma is the fourth state of matter, containing charged particles (electrons, cations and anions) and electrically neutral particles (atoms, molecules and radicals). In fact, the plasma system is complex to have much more species to induce chemical reactions, e. g., electron impact ionization and radical recombination. Plasma can be generally divided into two types according to the average gas temperature. In thermal plasma, average temperature of electrons and gas molecules are close to each other (10^4–10^5 °C for electrons and 10^3–10^4 °C for gas molecules, respectively) and is also called equilibrium plasma [81]. Since all particles including charged particles and neutral gas molecules are of high inertial energy, CH_4 and CO_2 dissociation could take place spontaneously. Thermal plasmas have been applied for DRM and the results show that GHGs conversions achieved with thermal plasma can reach over 80% and carbon deposition is suppressed [82,83]. Although thermal plasmas have excellent GHGs conversion and syngas generation, the operation requires massive heat energy to maintain the high operating temperature. On the other hand, non-thermal plasma is operated at a lower temperature, i.e., room temperature to hundreds of °C. In non-thermal plasma, the average temperature of electrons is much higher than that of gas molecules (10^4–10^5°C and 10^2–10^3 °C, respectively) and is also called non-equilibrium plasma [81]. Non-thermal plasmas including corona discharge, gliding arc, dielectric barrier discharge (DBD), atmospheric-pressure glow discharge (APGD), microwave discharge and spark discharge have been investigated to generate syngas. Generally, CH_4 and CO_2 conversions achieved with non-thermal plasmas are lower than that of catalysis and thermal plasma, resulting in lower energy utilization. Moreover, by-products including coke, ethane, acetylene and C_{6+} are inevitably formed during discharges and limit its application.