



Reaction phenomena of catalytic partial oxidation of methane under the impact of carbon dioxide addition and heat recirculation



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ABSTRACT

The reaction phenomena of CPOM (catalytic partial oxidation of methane) in a Swiss-roll reactor are studied numerically where a rhodium-based catalyst bed is embedded at the center of the reactor. CO₂ is added into the feed gas and excess enthalpy recovery is performed to evaluate their influences on CPOM performance. In the study, the mole ratio of O₂ to CH₄ (O₂/CH₄ ratio) is fixed at 0.5 and the mole ratio of CO₂ to O₂ (CO₂/O₂ ratio) is in the range of 0–2. The results reveal that CO₂ addition into the influent has a slight effect on methane combustion, but significantly enhances dry reforming and suppresses steam reforming. The reaction extents of steam reforming and dry reforming in CPOM without heat recovery and CO₂ addition are in a comparable state. Once CO₂ is added into the feed gas, the dry reforming is enhanced, thereby dominating CH₄ consumption. Compared to the reactor without excess enthalpy recovery, heat recirculation drastically increases the maximum reaction temperature and CH₄ conversion in the catalyst bed; it also intensifies the H₂ selectivity, H₂ yield, CO₂ conversion, and syngas production rate. The predictions indicate that the heat recirculation is able to improve the syngas formation up to 45%.

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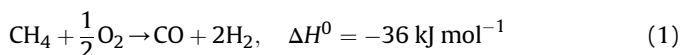
1. Introduction

Hydrogen is likely to become an important energy carrier in the foreseeable future, especially for its applications in fuel cell vehicles. This is attributed to its portable, environmentally friendly, and high energy density characteristics [1]. Hydrogen can be produced through non-fossil fuel processing routes, such as water electrolysis, photocatalytic water splitting, and biological photosynthesis and fermentation [2–5]. However, the efficiencies of the aforementioned methods are too low to be competitive for commercial production. In contrast, the thermochemical methods are the most feasible and practical means to produce hydrogen so far.

Methane or natural gas is the most commonly employed feedstock for commercial hydrogen production. In recent years, shale gas, due to the breakthrough of hydraulic fracturing, also plays an important role in supplying methane, thereby significantly extending the reserves of natural gas [6,7]. This makes hydrogen production from natural gas become more attractive for the development of prospective hydrogen economy. Hydrogen can be

extracted from methane through a number of thermochemical techniques, such as SR (steam reforming) [8], ATR (autothermal reforming) [9,10], POX (partial oxidation) [11,12], and TCD (thermocatalytic decomposition) [13].

When POX of methane is triggered in a catalyst bed, the reaction is referred to as the catalytic partial oxidation of methane (CPOM), and its direct mechanism is expressed as



The gas mixture of H₂ and CO is named synthesis gas or syngas. Unlike SR and TCD, CPOM is an exothermic reaction and can be achieved in a very short time, with the syngas yield close to the thermodynamic equilibrium [14]. To date, SR is the most important route to produce hydrogen and syngas. Nevertheless, by virtue of the high reaction rate and exothermicity of CPOM, its reactors can be much smaller than steam reformers and operated adiabatically [15]. In contrast to the direct mechanism simply expressed in Eq. (1), CPOM intrinsically involves MC (methane combustion), SR (steam reforming), and DR (dry reforming) [16,17], and heat liberated from MC is used to trigger the endothermic reactions of SR and DR. When the three reactions are simultaneously considered, they

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Nomenclature		Greek letter	
D_i	diffusion coefficient of species i ($\text{m}^2 \text{s}^{-1}$)	ϕ	viscous dissipation
E	total energy (J)	γ	porosity
E_a	activation energy (kJ mol^{-1})	μ	viscosity (Pa s)
F_i	mole fraction	ρ	fluid density (kg m^{-3})
h_i	specific enthalpy of species i (J kg^{-1})	$\vec{\tau}$	shear stress (Pa)
h_i^0	standard-state enthalpy of species i (J kg^{-1})	<i>Subscript</i>	
ΔH^0	change of total enthalpy on standard state (kJ mol^{-1})	atm	atmosphere
J_i	diffusion flux of species i ($\text{kg m}^{-2} \text{s}^{-1}$)	CH ₄	methane
k	thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)	CO	carbon monoxide
k_{eff}	effective thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)	CO ₂	carbon dioxide
K_{eq}	equilibrium constant	DR	dry reforming
N	number of species	f	fluid
p	pressure (Pa)	H ₂ O	water
r	radial coordinate (m)	i	species i
R	universal gas constant ($=8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$)	ic	inlet channel
R_i	reaction rate of species i ($\text{kmol m}^{-3} \text{ s}^{-1}$)	in	inlet
ΔS^0	change of total entropy on standard state (kJ mol^{-1})	j	reaction j ($j = \text{MC, SR, or DR}$)
T	temperature (K)	MC	methane combustion
V	velocity (m s^{-1})	oc	outlet channel
W_i	molecular weight of species i (kg kmol^{-1})	out	outlet
Y_i	mass fraction of species i	ow	the most outer wall
		SR	steam reforming

are spoken of as the indirect mechanism. Details of the indirect mechanism are given in Table 1.

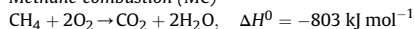
In addition to the development of alternative fuels, another important issue for sustainable environment is the reduction of anthropogenic carbon dioxide emissions and the mitigation of atmospheric greenhouse effect. CCS (carbon dioxide capture and storage) is currently the most noticeable method to mitigate the atmospheric greenhouse effect. Furthermore, a great deal of effort has been made for CO₂ utilization to produce fuels and chemicals [18]. In fuel processing, CO₂ reforming, also called dry reforming, is a promising technique to convert CH₄ and CO₂ into syngas. For example, Choudhary and Mondal [11] studied the reactions of methane with O₂ and CO₂ over a CoO/MgO/SA-5205 catalyst. Their results suggested that the CH₄ conversion and H₂ selectivity at the thermoneutral conditions were 95% and 97%, respectively, and the H₂/CO ratio in the product gas was 1.8. Foo et al. [19] investigated the methane reaction over a CO–Ni catalyst, and found that the H₂/CO ratio in the product gas increased from 0.9 for pure CO₂ reforming to 1.73 when the O₂ partial pressure increased to an equimolar level in the feed gas.

As described earlier, CPOM is an exothermic reaction in nature. When CO₂ is added into the feed gas for CPOM, DR will be intensified so as to enhance the endothermic reaction. MC is an irreversible reaction and an increase in the temperatures of the

Table 1

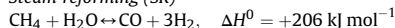
A list of indirect mechanism and kinetics of catalytic partial oxidation of methane.

Methane combustion (MC)



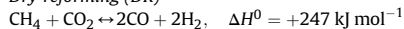
$$R_{\text{MC}} = 2.119 \times 10^{10} \exp\left(-\frac{80}{RT}\right) p_{\text{CH}_4} p_{\text{O}_2}$$

Steam reforming (SR)



$$R_{\text{SR}} = 1.0 \times 10^{-9} T^5 \exp\left(-\frac{47.3}{RT}\right) \left(p_{\text{CH}_4} p_{\text{H}_2\text{O}} - K_{\text{eq,SR}}^{-1} p_{\text{CO}} p_{\text{H}_2}^3\right)$$

Dry reforming (DR)



$$R_{\text{DR}} = 7.0 \times 10^{-7} T^4 \exp\left(-\frac{32.0}{RT}\right) \left(p_{\text{CH}_4} p_{\text{CO}_2} - K_{\text{eq,DR}}^{-1} p_{\text{CO}}^2 p_{\text{H}_2}^2\right)$$

reactants is conducive to the combustion reaction [20]. On the other hand, both SR and DR are reversible and endothermic reactions, and an increase in their reaction temperatures will facilitate the forward reaction [21], thereby advantaging syngas production. It is known that the Swiss-roll reactor is an excess enthalpy reactor where the waste heat in flue gas can be recirculated to heat the feed gas. Compared to reactors without excess enthalpy recovery, Swiss-roll reactors can achieve a higher performance of fuel combustion and increase flame stability. For instance, Shih and Huang [22] explored the effectiveness and pressure loss of a Swiss-roll recuperator in a micro gas turbine, and found that recovering exhaust heat drastically increased the effectiveness of the recuperator. Zhong and Wang [20] experimentally studied the combustion stability and extinction limits of premixed methane/air mixtures in three types of Swiss-roll combustor. Their results indicated that the Swiss-roll combustors greatly enhanced combustion stability and extended the extinction limits.

Inspired from the past studies concerning CPOM, DR with CO₂ utilization, and heat recirculation in Swiss-roll reactors, the present study is intended to investigate syngas production from methane and CO₂ in a Swiss-roll reactor. Particular emphasis is placed on the influences of CO₂/O₂ ratio and heat recovery on the performance of CPOM. To the authors' knowledge, very little research has been performed on syngas production under the interaction of CPOM, CO₂ addition, and heat recovery. Consequently, the obtained results are able to provide useful insight into the operation of CPOM and the design of reactors for syngas production in association with CO₂ utilization. These are conducive to abating anthropogenic CO₂ emissions into the atmosphere and mitigating global warming.

2. Methodology

2.1. Physical description

When the number of turns of the Swiss-roll reactor is increased, more waste heat from the product gas can be recovered in the reactor. In a previous study [17], it was found that the enthalpy

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