Full Length Article

Chemical looping partial oxidation of methane with CO_2 utilization on the ceria-enhanced mesoporous Fe_2O_3 oxygen carrier

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GRAPHICAL ABSTRACT
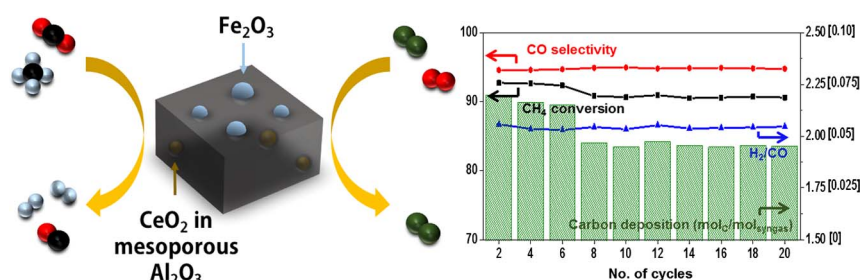
ARTICLE INFO

ABSTRACT

The high-purity syngas production with a molar ratio of H_2 to CO equal to 2 was achieved through a chemical looping process with a CH_4-CO_2 feed mixture on a ceria-enhanced mesoporous Fe_2O_3/Al_2O_3 oxygen carrier. The presence of CO_2 in the mixture feed enables the H_2/CO ratio to be maintained as 2 desirable for the syngas-to-liquid hydrocarbon process by suppressing the methane decomposition even when the amount of reducible oxygen carrier was sufficiently small. By incorporating a small amount of CeO_2 (molar Ce/Fe ratio = 0.15) to the iron oxide mesoporous oxygen carrier by the sol-gel method, the syngas selectivity also increased although the amount of reducible oxygen was large enough to cause the total combustion. Due to the co-feeding of CO_2 with CH_4 and the textural property of the ceria-enhanced Fe_2O_3/Al_2O_3 mesoporous oxygen carrier, the enhanced redox activity for the chemical looping process was demonstrated under the CO_2/CH_4 feed ratio of 0.28 with the redox performance of CH_4 conversion = 93.11%, CO selectivity = 93.23%, average carbon deposit = 0.048 mol_C/mol_{syngas}, and average H_2/CO ratio = 2.04. The fluctuation of the H_2/CO ratio with the reaction time was minimized by adjusting the real-time CO_2/CH_4 feed ratio and then, the consistent syngas production was realized even in the fixed bed chemical looping process.

1. Introduction

Although the conversion technology of methane (CH_4) into synthesis gas (syngas) has been matured by steam reforming of methane, the heat requirement for the steam generation and endothermic reforming reaction ($\Delta H_{298K}^0 = 206 \, kJ \, mol^{-1}$) has been a main obstacle to the

energy-efficient process [1–3]. Moreover, the produced hydrogen (H_2) to carbon monoxide (CO) ratio (H_2/CO) of 3 is higher than the required value for the Fischer–Tropsch synthesis which prefers the H_2/CO ratio of about 2 [4]. Contrarily, partial oxidation of methane can lead to the stoichiometric H_2/CO ratio of 2 favorable to the gas-to-liquid (GTL) process and its exothermic heat ($\Delta H_{298K}^0 = -36 \, kJ \, mol^{-1}$) makes the
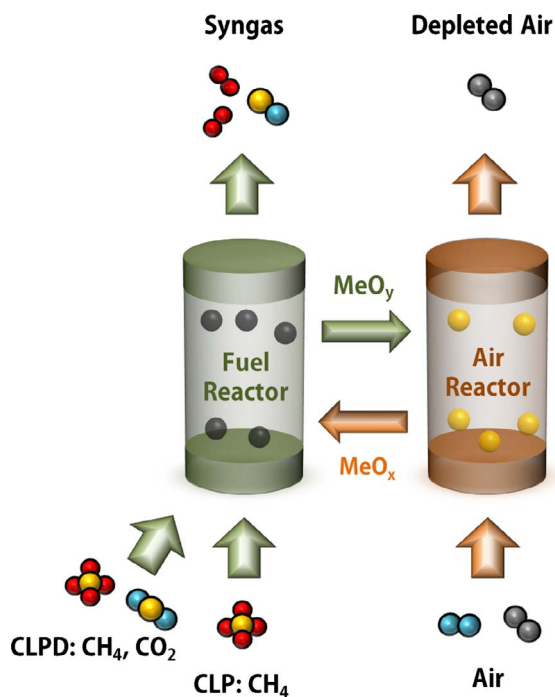
Fig. 1. Schematic representation of chemical looping process.

auto-thermal reforming feasible. However, a hot spot formation from explosive reactant mixtures has been a challenge to scaling up the process [5,6]. It also requires an energy-intensive air separation unit to supply high-purity oxygen (O_2) [7].

The chemical looping process has been recently combined to partial oxidation of methane to overcome its obstacles and therefore, a chemical looping partial oxidation of methane (CLP) was proposed. In CLP, the reduction and oxidation reactions are spatially separated into two different fuel and air reactors by transferring oxygen from a transition metal oxide [8–10]. Therefore, the direct contact of explosive mixtures is intrinsically eliminated and the nitrogen (N_2) dilution in the product stream is avoided even without an air separation unit [11]. The produced H_2/CO ratio of CLP can also approach 2 required for the GTL process. To be specific, CH_4 is partially oxidized by the transition metal oxide with the syngas production in the fuel reactor. Then, the reduced metal oxide is re-oxidized by air with the production of heat in the air reactor (Fig. 1). The re-oxidized metal oxide is recycled to the fuel reactor, suggesting that the cyclic use of the metal oxide plays an important role in CLP [12,13].

The product compositions of CLP are highly dependent on redox properties of metal oxides, referred to here as the oxygen carrier. While CeO_2 prefers the partial oxidation and syngas as its product, Fe_2O_3 has different product spectrums with its various oxidation states [14,15]. When the amount of oxygen resources is larger than that of CH_4, the total oxidation is boosted with the production of CO_2 and H_2O. On the other hand, the partial oxidation becomes the dominant reaction as the amount of oxygen resource decreases with the lowering oxidation state of the oxygen carrier. On the fully reduced metal, the carbon coking is generated by the promoted methane decomposition in the fuel reactor [16–19] and thus, CO or CO_2 byproduct is inevitably mixed with N_2 in the air reactor, while causing the greenhouse gases emission [20].

Especially in a fixed bed process, the immobilized oxygen carrier is gradually reduced under the continuous CH_4 stream. Therefore, the gradient of the oxidation state of the oxygen carrier occurs along the longitudinal axis of the fixed bed reactor [21], which worsens the change of the product spectrum in CLP. To produce a high-purity syngas with the minimization of the oxidation state gradient, perovskite or Ce-based materials have been exclusively used for CLP due to their

high syngas selectivity.

When perovskite materials are used as oxygen carriers of the chemical looping process, the products varied with their structures and compositions [22–32]. The crystallite size [33] and textural property [34] of the perovskite oxygen carrier also affected the product spectrums. However, the high costs of rare earth metals used in the perovskite restricted the industrial implementation.

When CLP is conducted on Ce-based materials, Fe-Ce mixed oxides have been used to compensate for the high cost of Ce. Also, the incorporation of Fe^{3+} into Ce^{4+} created the structural defect with the high oxygen mobility of the mixed oxide and then, its redox property was enhanced for the syngas production [35,36]. However, a large amount of Ce is still required to selectively produce syngas despite the enhanced redox activity of the Fe-Ce mixed oxide. CLP has been conducted on the Fe-Ce mixed oxides prepared through the co-precipitation or hydrothermal method. However, the H_2 and CO selectivities were higher than 70% with the H_2/CO ratio of 2 only when the molar ratio of Ce to Fe was higher than 2.3 [37,38].

Both syngas and H_2 were produced from the fuel and water reactors, respectively, through the combined chemical looping and steam reforming process. However, the isomolar amount of Ce to Fe was needed to achieve the high syngas selectivity and the H_2/CO ratio of 2 [39]. The high-purity syngas was produced through CLP on the Fe-Ce mixed oxide whose molar Ce/Fe ratio was almost equal to 0.5. However, the reduction degree of the oxygen carrier was precisely controlled to suppress the total combustion. Moreover, the weight hourly space velocity was kept low (100 mg of oxygen carrier under 1 sccm of CH_4) to prevent the generation of the carbon coking [21].

This work aims to produce the high-purity syngas with the H_2/CO ratio of 2 on the Ce-enhanced Fe_2O_3/Al_2O_3 oxygen carrier whose molar Ce/Fe ratio of 0.15 that is much lower than those of previous studies [21,35–39], implying that the oxygen carrier is economically competitive by reducing the amount of Ce. Toward this goal, a Ce-enhanced mesoporous Fe_2O_3/Al_2O_3 oxygen carrier is synthesized by a sol-gel method. It will be shown that CeO_2 particles are highly dispersed in the mesoporous Al_2O_3 supporting matrix due to the incorporation of ceria precursor during the hydrolysis of Al precursor. According to the previous research, the highly dispersed Ce in the porous structure facilitated the soot combustion with the increased catalytic activity [40,41]. Therefore, it is speculated that the accessibility of reactant to CeO_2 particles and the suppression of carbon coking can be also achieved on the Ce-enhanced mesoporous Fe_2O_3/Al_2O_3 oxygen carrier for a chemical looping process.

In addition to the novel oxygen carrier, the co-feed of CO_2 is supplied to the fuel reactor with CH_4 as the external oxygen resource [42,43] for promoting dry reforming of methane [2,44–47]. Therefore, the novel chemical looping partial oxidation with dry reforming of methane (CLPD, Fig. 1) is introduced by supplying the CH_4-CO_2 mixture feed into the fixed bed system. By adding the external oxygen resource of CO_2, the syngas selectivity can dramatically increase and the carbon coking by the catalytic methane decomposition can be remarkably suppressed. Moreover, the CO_2/CH_4 feed ratio is optimized with the reaction time to minimize the fluctuation of the produced H_2/CO ratio and the gradient of the oxidation state in the fixed bed reactor.

2. Experimental

2.1. Preparation of the oxygen carriers

Oxygen carriers containing Fe_2O_3 or Fe_2O_3-CeO_2 on the Al_2O_3 supporting matrix with 40 wt% of the total metal loading were synthesized by the impregnation method. In a typical synthesis, the required amount of $Fe(NO_3)_3 \cdot 9H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ (supplied by Sigma-Aldrich) was dissolved in an aqueous solution. Then, 2.0 g of Al_2O_3 (S_{BET} = 80–120 m^2/g, supplied by Alfa Aesar) was added and stirred for 12 h. The obtained slurry was dried at 100 °C and the