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Syngas production on a Ni-enhanced Fe_2O_3/Al_2O_3 oxygen carrier via chemical looping partial oxidation with dry reforming of methane

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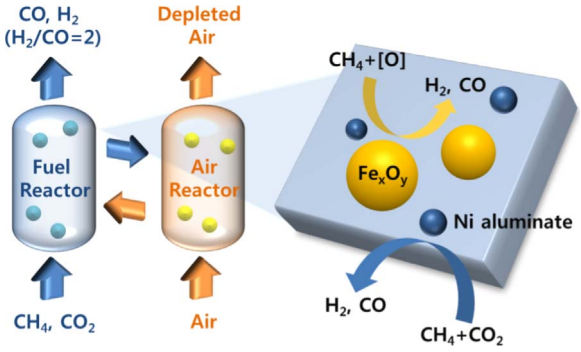
HIGHLIGHTS

- CLPD was derived by merging dry reforming into chemical looping partial oxidation.
- Results of CLPD were calculated using the ASPEN Plus simulator.
- Syngas with a H_2/CO ratio of 2 was produced through the CLPD process.
- Ni-enhanced Fe_2O_3/Al_2O_3 showed the enhanced CLPD activity without rare earth metals.
- Stabilized Ni in Al_2O_3 promoted dry reforming with suppressed carbon deposition.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel chemical looping process was introduced by combining partial oxidation and dry reforming of methane on a cost-effective iron-based oxygen carrier to produce high-purity syngas with a H_2/CO ratio of 2. The rationale for the proposed chemical looping process was substantiated with the thermodynamic data, which showed increased syngas purity and an H_2/CO ratio close to 2 by introducing the CH_4-CO_2 mixture feed. Compared with the general chemical looping process, the calculated carbon deposition with the CO_2 emission of the proposed process was dramatically decreased by using CO_2 as a co-feed with CH_4. Due to the exothermic heat from the oxidation reaction of the oxygen carrier, the net heat duty of the novel chemical looping process was much lower than that of the dry reforming process. To validate the thermodynamic results, a Ni entrapped Fe_2O_3/Al_2O_3 oxygen carrier was synthesized by increasing the metal-support interaction through a sol-gel route. It is striking that the formation of Ni aluminate phase in the Ni-reinforced oxygen carrier facilitated dry reforming with partial oxidation while suppressing methane decomposition. By supplying a nonstoichiometric CH_4-CO_2 mixture feed (CO_2/CH_4 ratio = 0.38) to the 1 wt% Ni-entrapped Fe_2O_3/Al_2O_3 oxygen carrier at 900 °C, an H_2/CO ratio of 2.09 and high CO selectivity of 96.76% were achieved with minimized carbon deposition. These results were close to the calculated equilibrium value while a Ni-impregnated Fe_2O_3/Al_2O_3 oxygen carrier showed an increased H_2/CO ratio of 2.36 with severe carbon deposition by the promoted methane decomposition. In addition, the Ni-reinforced oxygen carrier also showed stable redox activity during successive reduction and oxidation cycles.

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1. Introduction

The economical accessibility of shale gas reservoirs has been increasing due to advances in horizontal drilling and hydraulic fracturing technologies, which will almost double shale gas production by 2040 [1]. This increased production has attracted public attention as not only a promising fuel for power production but also as a chemical raw material [2]. However, when methane (CH_4), a primary resource of shale gas, is directly used as a combusted fuel, anthropogenic carbon dioxide (CO_2) is emitted, contributing to global warming [3]. The direct conversion of CH_4 to chemicals is also difficult due to localized C−H bonds with a high bond energy of 413 kJ mol^{-1} and the absence of empty orbitals with a low bond energy [4].

The conversion of CH_4 to syngas, a mixture of CO and H_2, should be done first to synthesize valuable liquid hydrocarbons, because syngas is as an essential intermediate [5]. Steam reforming of CH_4 [SRM, Eq. (1)] is mainly adopted to produce syngas from CH_4 in the current mature industry. However, its endothermic reaction requires an energy intensive process, and the stoichiometric syngas ratio (H_2/CO) of 3 is unsuitable for the syngas-to-liquid hydrocarbon process, where a H_2/CO ratio of 2 is preferred [6,7].

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H^0_{298\ K} = 206\ \text{kJ mol}^{-1} \tag{1}$$

$$CH_4 + (1/2)O_2 \rightarrow CO + 2H_2 \quad \Delta H^0_{298\ K} = -36\ \text{kJ mol}^{-1} \tag{2}$$

Partial oxidation of CH_4 [POM, Eq. (2)] is a promising alternative to SRM, which achieves both auto-thermal operation by its exothermic reaction and a H_2/CO ratio of 2. Despite these advantages of POM over SRM, the safety issue related to mixed oxygen (O_2) and flammable gases makes it difficult to scale up POM. There is also an economic burden because an air separation unit (ASU) is required to produce the concentrated syngas by supplying high-purity O_2 [8].

Chemical looping partial oxidation of methane (CLP) is a deployable solution that can achieve sustainable syngas production with minimized safety and air separation cost issues, because the concept of chemical looping divides the oxidizing/reducing reactions into two separated reactors [9–17]. In CLP, the reducible oxygen resource is transported from air to CH_4 via a metal oxide without being diluted by N_2. The oxidized MeO_x is reduced by CH_4 in the fuel reactor with the production of syngas, and the reduced MeO_y is re-oxidized by air with the generation of heat in the air reactor, where MeO_x and MeO_y represent the oxidized and reduced transition metal oxides, referred to here as the oxygen carrier (Fig. 1a). Therefore, direct contact of oxygen with flammable gases is avoided [18–20]. Also, an ASU is not required, because the produced gaseous streams are not diluted by N_2.

However, a suitable oxygen carrier and its supporting matrix to achieve a H_2/CO ratio of 2 are very limited in CLP. To the best of our knowledge, ceria (Ce)-containing materials [21–26] or perovskite-type oxides [27–30] with rare earth metals have been almost exclusively studied for CLP due to their high CO selectivity from the abundant oxygen vacancies. Although CeO_2 preferentially yields syngas as the product from the reaction with CH_4, not H_2O and CO_2 [31], the scarcity and high cost of CeO_2 make Fe-Ce mixed oxides an attractive alternative to pure CeO_2 [22–26]. In addition to the low cost of Fe based materials, the smaller size and lower valence state of Fe^{3+} relative to that of Ce^{4+} create structure defects, which enhance the redox activity of the Fe-Ce mixed oxide [32–34]. However, the dissolution of Fe^{3+} into bulk Ce was restricted to only 15% of the dopant content by a hydrothermal route [35], thus suggesting a high cost for the Fe-Ce mixed oxide oxygen carrier.

Perovskite-type oxides have emerged as an attractive candidate oxygen carrier for CLP due to the high oxygen mobility originating from the capability of the concentrated oxygen vacancies [36]. Various kinds of rare earth and transition metals have been used for their synthesis depending on the applications [27–30,37–41]. Nevertheless, the economic concern of using rare earth metals has not yet been solved and mechanical stabilities of perovskite particles in CLP should be evaluated further so that they can be used in a scaled-up process [12].

In addition to the type of oxygen carrier, the feed composition of CLP also plays an important role in determining the product composition. CO_2 has been utilized as an oxidizing reagent to remove the deposited carbon and oxidize the reduced oxygen carrier [42–47]. CO_2-utilized chemical looping combustion was initially proposed, which produces a H_2O-CO_2 mixture from CH_4 in the fuel reactor and high-purity CO from CO_2 in the oxidation reactor [42]. Various oxygen carriers have been investigated for this CO_2-utilized chemical looping combustion such as Fe/barium hexaaluminate [43], CeO_2-modified Fe_2O_3 [44], and iron nickel oxide [45]. CO_2-utilized chemical looping reforming, which produces syngas from CH_4 in the fuel reactor and CO from CO_2 in the oxidation reactor, was subsequently proposed [46,47]. However, the produced H_2/CO ratio was not closely monitored [47] or fluctuated during the reduction reaction [46], because CH_4 and CO_2 were separately supplied to the fuel and oxidation reactor, respectively. CO_2 have only recently begun to be considered as the co-feed with CH_4 [48–50]. In a moving bed reactor system, the CH_4-CO_2 mixture was reacted with iron-titanium composite metal oxide to produce a high-purity syngas while reducing the CH_4 feed usage [49]. The chemical looping process with the CH_4-CO_2 mixture feed was also modularized, potentially providing economic and environmental benefits [50].

The aim of this study is to achieve a H_2/CO ratio of 2 produced through a chemical looping process in a fixed bed reactor system without using expensive oxygen carriers such as CeO_2 and perovskites. To this end, Fe_2O_3 on a supporting matrix of Al_2O_3 is used as the oxygen carrier due to its abundance and low cost, contributing to the economic feasibility of the chemical looping process. To compensate for the high H_2/CO ratio caused by the catalytic methane decomposition [CMD, Eq. (3)] of Fe_2O_3/Al_2O_3 oxygen carrier, an external oxygen resource is supplied by CO_2 with co-feeding of CH_4 to the fuel reactor (Fig. 1b). Because the stoichiometric H_2/CO ratio is 1 by the reaction of CH_4 with CO_2, which is dry reforming of CH_4 [DRM, Eq. (4)], we conjecture that the addition of CO_2 can adjust the produced H_2/CO ratio to 2 even on a Fe_2O_3/Al_2O_3 oxygen carrier by promoting DRM with the production of additional CO.

$$CH_4 \rightarrow C(s) + 2H_2, \quad \Delta H^0_{298\ K} = 75\ \text{kJ mol}^{-1} \tag{3}$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H^0_{298\ K} = 247\ \text{kJ mol}^{-1} \tag{4}$$

In this way, this study introduces the concept of CLP combined with DRM, hereafter called chemical looping partial oxidation with dry reforming of methane (CLPD), by controlling the molar ratio of CO_2 to CH_4 in the feed stream (CO_2/CH_4). To increase the catalytic activity toward DRM, a small amount of Ni, known as an effective catalytic metal [51], will be added to the oxygen carrier. However, Ni is highly active for not only DRM but also for CMD [52,53], which leads to increases in both the H_2/CO ratio and carbon deposition. Thus, to promote DRM while suppressing CMD, this study will show how the Ni and support interaction is enhanced by mixing the Ni precursor and the Al precursor before the hydrolysis of Al precursor through a sol-gel synthesis route. It will be demonstrated that this increased interaction between the Ni particles and the supporting matrix can minimize the carbon deposition by preventing the separation of the Ni particles from the supporting matrix. The Ni-enhanced Fe_2O_3/Al_2O_3 oxygen carrier can achieve the production of high-purity syngas with a H_2/CO ratio of 2 through repeated reduction/oxidation cycles, implying the feasibility of the proposed CLPD process.

2. Experimental

2.1. Thermodynamic analysis

Because the RGIBBS module in ASPEN Plus minimizes the Gibbs free energy, chemical equilibrium compositions of the gaseous products of