

Syngas production in chemical looping reforming process over ZrO₂ promoted Mn-based catalyst

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ABSTRACT

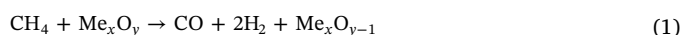
Chemical looping reforming (CLR) of methane is a familiar process for the production syngas or hydrogen, which could be applied as one of the most important energy sources. In this process, reforming of methane takes place in the fuel reactor in contact with lattice oxygen of oxygen carriers (OCs), while the reduced OCs are re-oxidized in the air reactor. In this study, two different alumina supports are promoted using zirconium oxide to improve Mn-based oxygen carriers. Different synthesized oxygen carriers were evaluated in CO₂-modified chemical looping reforming process at different conditions such as reaction temperature (500–750 °C), CH₄/CO₂ ratio (0.5–3), alumina support base, ZrO₂ position and manganese loading weight percentage (10–30). The presence of ZrO₂ in the support structure significantly inhibited the deposition of coke on the surface of oxygen carrier. The characterization and process results revealed the noteworthy effect of Zr incorporation to the structure of alumina support. The redox results revealed that 20Mn/20Zr-Al oxygen carrier exhibited the highest activity even at low reduction temperatures. This oxygen carrier exposed the highest activity and stability with lowest coke deposition during 16 redox cycles at 650 °C. The methane and CO₂ conversion, H₂ yield and H₂/CO molar ratio of about 99.0%, 96.6%, 65.2% and 2.55 were achieved at 650 °C using the optimized oxygen carrier. The synthesized samples were characterized by X-ray powder diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) and N₂ adsorption-desorption (BET) techniques.

1. Introduction

During recent decades, global warming has attracted much attention due to its undesired impact on the earth and human life according to earth warming. Previous studies revealed that the main reason for global warming is the greenhouse influence of CO₂ in the atmosphere [1,2]. The consumption of fossil fuels is the main source of increasing the concentration of carbon dioxide. Therefore, the reduction in carbon dioxide emission is attracted much attention. On the other hand, using clean energy sources such as hydrogen and utilization of produced CO₂ are applied in large scales recently [3–7]. Hydrogen as a clean energy source has been considered for fuel cell and combustion in engines [8,9]. Methane is one of the main source of hydrogen and a good option due to high hydrogen to carbon ratio, high availability, cleanness, lower costs and fewer byproducts compared to other hydrocarbons [10–12]. Steam reforming, partial oxidation and dry reforming (CO₂ reforming) are the most important processes for the conversion of methane to synthesis gas. However, the reforming of methane with carbon dioxide is mentioned to be appropriate due to CO₂ consumption, which is

cheaper than the formerly considered CO₂ capture-storage [13,14]. As an alternative method, chemical looping reforming process is proposed for the reforming of methane [15–17]. In this process, methane is reformed with lattice oxygen of a solid metal oxide called oxygen carrier [18,19]. The modification of chemical looping reforming with CO₂ reforming could help the reduction in CO₂ emission and regulation of H₂/CO molar ratio [2,20].

In this process methane is partially oxidized to syngas (H₂ and CO) in the fuel reactor, while the metal oxide (Me_xO_y) used as an OC, transfers the lattice oxygen and is reduced to Me_xO_{y-1}. The main reactions in the fuel reactor are as follows:



Then air is applied to re-oxidized the reduced OC at high temperature in the air reactor through the following reaction:



In CO₂ modified chemical looping reforming, dry reforming of methane takes place in parallel with the first reaction [2]. Therefore,

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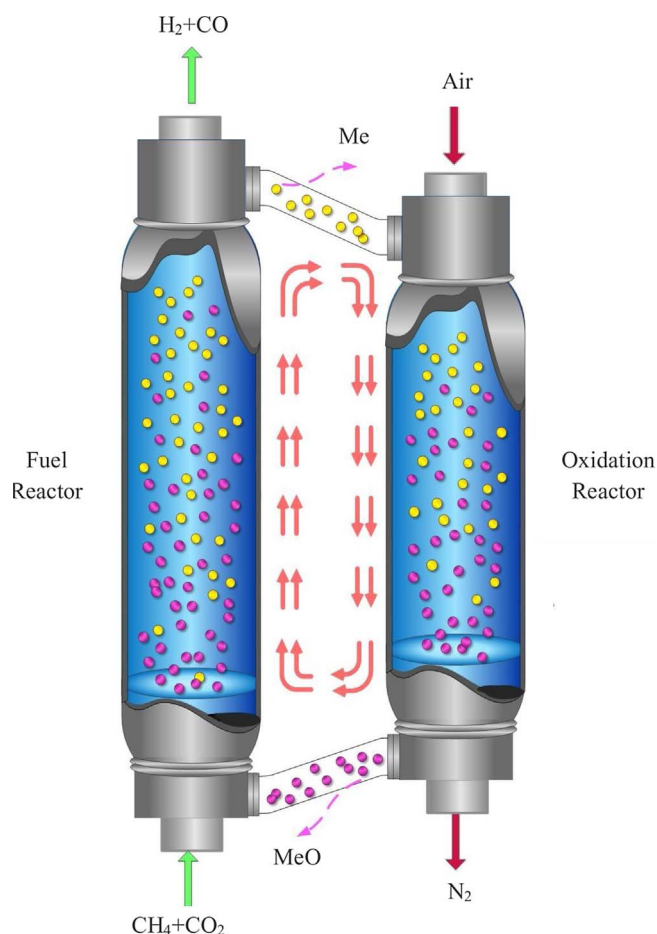


Fig. 1. Conceptual scheme of chemical looping reforming process.

development of a suitable oxygen carrier is one of the most essential issues in chemical looping process. A typical chemical looping reforming scheme consisting of two interconnected reactors with no direct mixing of fuel and air is demonstrated in Fig. 1.

As stated above, an appropriate metal oxide with high oxygen capacity as oxygen carrier could improve the CLR process, significantly. The required oxygen carrier should be capable of performing successive redox cycles. Some possible transition metals including active oxides of nickel, copper, cobalt, iron and manganese, possess the conditions mentioned above [21–25]. Manganese has a high oxygen storage capacity and a suitable resistance against agglomeration at high reduction temperatures [26].

The coke deposition and structural resistance are the most important drawbacks of oxygen carriers. A popular strategy in order to avoid carbon formation, preventing sintering and agglomeration and/or stabilizing active site nanoparticles in the channels of supporting material is the utilization of promotional oxides such as Ce₂O₃, La₂O₃, CaO, ZrO₂, MgO and Y₂O₃ [27–31]. Li et al. [30] prepared Ce promoted Ni/SiO₂ catalyst using co-impregnation method and applied for producing syngas in the combined partial oxidation of methane with CO₂ reforming. The results revealed that nickel-based catalyst has better performance in the presence of cerium promoter. Hafizi et al. [22,23] showed the improvement in structural properties, coke inhibition and durability of iron-based oxygen carrier using Ce, Ca and Mg promoters in CLR process. Recently, ZrO₂ has been widely applied as promoter and support in different reforming processes due to its high coke resistance (high oxygen storage-release capacity) and improving the structural properties to enhance thermal and mechanical stability [32,33].

The main purpose of this research is to investigate the influence of support type and promotional behavior of ZrO₂ in the framework of manganese-based oxygen carrier in CO₂ modified chemical looping reforming process. The effect of reduction temperature, support type, Zr promoter, CO₂/CH₄ ratio and Mn loading weight percentage are studied on the performance of oxygen carriers. Moreover, various characterization techniques such as XRD, BET, EDX and FESEM are applied to analyze the fresh and used samples. Finally, the life time and stability of optimized oxygen carrier over 16 redox cycles are investigated.

2. Experimental

2.1. Oxygen carrier preparation

In order to investigate the effect of support type, promoter position and Mn weight percentage, the supports and oxygen carriers were synthesized by three distinct methods including co-precipitation, impregnation and sequential impregnation methods.

2.1.1. Co-precipitation (CP)

The 20 wt.% zirconium modified alumina support was synthesized using a co-precipitation method. Therefore, a 1 M solution of ammonium was applied as the precipitant agent. The precipitant was added dropwise to a mixture containing a solution of Cl₂OZr·8H₂O (Merck) and Al(NO₃)₃·9H₂O (Merck) with the molarity of 0.05 M. The addition of the ammonia was continued to adjust the pH to about 10. The resulted slurry was aged for 15 h at 60 °C with continuous stirring to facilitate the precipitation. In the next step, the obtained precipitant was filtered and washed several times with warm deionized water, and dried in oven at 90 °C during the night. Finally, the samples (abbreviated as 20Zr-Al) were calcined at 700 °C for 3 h in static air, crushed

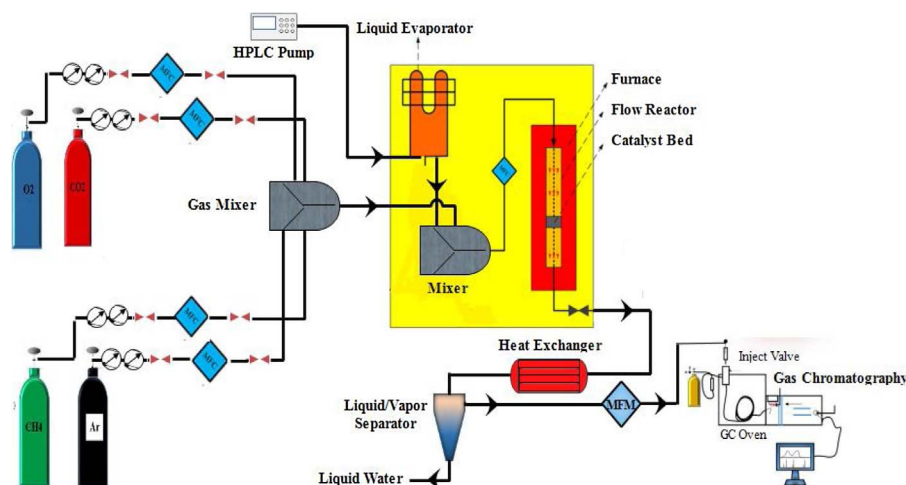


Fig. 2. Laboratory scale reactor experimental set up.

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