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Hydrogen production by chemical looping steam reforming of methane over Mg promoted iron oxygen carrier: Optimization using design of experiments

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ABSTRACT

In the chemical looping reforming (CLR) process, methane is converted to hydrogen and carbon monoxide through cyclic reduction–oxidation reactions of fuel with active lattice oxygen (O^{2-}) of an oxygen carrier. In this research, Mg promoted iron based oxygen carrier was used in the process. The response surface method (RSM) based on Box–Behnken design was applied to examine the operating conditions of chemical looping steam methane reforming process. Independent variables including reaction temperature (550–750 °C), Mg loading (0–10%) and oxygen carrier preparation method (co-impregnation and sequential impregnation methods) were selected for investigation and optimization of methane conversion, hydrogen production yield and CO/CO_2 molar ratio using RSM. The characterization of samples was accomplished by means of X-ray diffraction (XRD), N_2 adsorption–desorption (BET test) and transmission electron microscope (TEM). The Design expert software suggested several optimized solutions; among them, the best choice was $15Fe/5Mg/Al_2O_3$ oxygen carrier synthesized with sequential impregnation method at reaction temperature of 650 °C. However, $15Fe/5Mg/Al_2O_3$ oxygen carrier is consistently stable in chemical looping reforming with high hydrogen producing capacity over redox cycles.

1. Introduction

In today's world, hydrogen is undoubtedly one of the most important chemicals which not only is used in different industries such as petroleum refining, methanol and ammonia production, and high-purity metal extraction, but it also is considered as an environmentally friendly energy carrier [1–4]. Over the last few decades, there was a sharp rise in the hydrogen demand which is predicted to sustain in next decades [5]. In order to satisfy this demand, the problems involving in large-scale production of this crucial chemical should be resolved.

Hydrogen can be derived from different sources including natural gas, coal, oil, biomass and water by using various methods such as hydrocarbon reforming, biomass gasification, thermochemical water splitting, photoeletrolysis, electrolysis of water *etc.* [1,6–9]. Currently, nearly 49% of hydrogen is produced from natural gas and the dominant technology for direct production is steam reforming but considerable amount of energy must be consumed for the complex hydrogen purification processes [5,10,11]. Methane reforming is the main hydrocarbon used for hydrogen production in reforming process, because of its low costs and the emission of lower airborne pollutants and greenhouse gases in comparison with other hydrocarbons [12]. Steam reforming, partial oxidation, auto-thermal reforming, and CO_2 reforming have been widely investigated as primary processes for converting methane into hydrogen [13]. Another issue associated with produced hydrogen is the fact that only if CO_2 is captured within the reforming process, the produced H_2 could be used as a CO_2-free fuel for vehicles, as well as for other applications [4].

Chemical looping is a breakthrough technology that provides the means to convert carbonaceous fuel to desired products, such as heat/electricity or hydrogen, and provide carbon capture without significant efficiency or cost penalties [14–17]. In this process, the fuel is oxidized by oxygen from a solid oxygen carrier in the "fuel reactor". The oxygen carrier is then re-oxidized in the "air reactor".

When the chemical looping concept is used for steam reforming of methane, it is called chemical looping steam methane reforming (CL-SMR) which is of two major benefits. Firstly, the produced syngas is not diluted with N_2 which would remove the need for costly

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gas separation, and secondly, the higher purity of produced hydrogen [18]. Generally, CL-SMR involves two general steps. The first step is the partial oxidation of methane to syngas. In this stage, the needed oxygen for oxidation is provided from the lattice oxygen of the oxygen carrier.

$$Me_xO_y + \delta CH_4 \rightarrow Me_xO_{y-\delta} + \delta(2H_2 + CO) \quad (1)$$

Also, other reactions like steam methane reforming, water gas shift reaction, CO oxidation and methane decomposition would occur in the reaction media. Therefore, the presence of carbon dioxide in the reactor effluent gas with a low concentration is expected.

$$CH_4 + H_2O \leftrightarrow CO + H_2 + CO_2 \quad (2)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (3)$$

$$CO + MeO \leftrightarrow CO_2 + Me \quad (4)$$

$$CH_4 \leftrightarrow C + 2H_2 \quad (5)$$

In the second step, the reduced oxygen carrier is reoxidized to its initial form (Me_xO_y) [19–21].

$$Me_xO_{y-\delta} + O_2 \rightarrow Me_xO_y \quad (6)$$

One of the key factors in the efficiency of chemical looping process is the usage of a suitable oxygen carrier [22–24]. It not only should have acceptable rate of conversion during redox reactions, but it also should have high comminution and agglomeration resistance. Economic and environmental aspects of the chosen oxygen carrier should also be taken into account. Because of their appropriate thermodynamic properties, the first row transition metal oxides such as Ni, Cu, Fe, Co, and Mn are considered as good candidates for this purpose [25–30]. In order to improve the long-term performance of the oxygen carrier (such as reactivity, durability, and stability), a support, which is usually chosen from ceramic materials, is added to the primary oxide. Perovskite-type complex metal oxides have also been proposed as oxygen carriers. Although they have high thermal stability, good mechanical properties, and decent activity, they usually have small specific surface area [31].

Several oxygen carriers have been synthesized and tested for chemical looping steam methane reforming. Diego et al. [32] studied $21NiO\text{-}\gamma Al_2O_3$ oxygen carrier over 50 h of operation and assessed the influence of different operating variables such as fuel reactor temperature, H_2O/CH_4 molar ratio and solid circulation rate. Their results showed high CH_4 conversion (> 98%) in all of the studied operating conditions. It was also revealed that the NiO/CH_4 circulation rate was the most important variable in the gas product distribution. Ortiz et al. [33] investigated the catalytic activity of $18NiO\text{-}\alpha Al_2O_3$ and $21NiO\text{-}\gamma Al_2O_3$ in a fixed-bed reactor at different operating conditions. They found that catalytic activity of both of these oxygen-carriers were the same but poorer than that of conventional Ni catalysts. They also reported that the degree of the oxygen-carrier oxidation affects the catalytic activity of the oxygen-carriers for the steam methane reforming. Jiang et al. [29] studied the effect of $Ni/NiAl_2O_4$ oxygen carrier for hydrogen production in the chemical looping steam reforming of glycerol. The results showed the effective conversion of glycerol and steam to H_2 by redox reactions in the reduction temperature of 450–600 °C. The glycerol conversion of near 100% and hydrogen purity of about 69% was attained at 600 °C. Hafizi et al. [19] investigated the effect of oxygen carrier preparation method, iron loading percentage, calcium promoter percentage, and reduction temperature in chemical looping steam methane reforming. The obtained results revealed that oxygen carrier composed of 15 wt.% iron and 5 wt.% Ca has the highest activity in CL-SMR process at 700 °C.

Determining the sensitivity analysis and optimum conditions for evaluating the catalytic performance of an oxygen carrier is a tedious and difficult procedure including many steps, variables and complex interactions among the variables. The most of previous researches involved using the one-factor-at-a-time experimental approach [3,34]. As for disadvantages of this method, it not only is time consuming and expensive, but it also does not consider the interaction of various treatment parameters. Therefore, it results in accuracy reduction in the process optimization and tends to functionalize only for a single varied factor.

The application of design of experiments (DOE) procedure seems to be one of the best methodologies for studying and improving the catalytic processes efficiency [35–39]. Box–Behnken method is one of the DOE applicable multivariate methods that can be applied in experimental design, process statistical modeling and optimization. This method is useful for studying the relationship between one or more responses and a set of quantitative or qualitative experimental parameters [40,41].

Iron oxide has been widely used as an oxygen carrier material (OCM) for hydrogen production by chemical looping due to its favorable thermodynamic properties. Consequently, the present study was undertaken to optimize the process variables of chemical looping steam methane reforming by performing a three-level, tree-factor response surface method. The performance of iron based oxygen carrier in CL-SMR process was improved with Mg addition to its structure. Furthermore, we studied the oxygen carrier's lifetime and stability over the cycles.

2. Experimental

2.1. Oxygen carrier preparation

With the purpose of studying the effect of oxygen carrier synthesis method, the samples were synthesized by two different methods including co-precipitation and sequential impregnation. Moreover, co-impregnation and sequential impregnation methods were applied to examine the influence of magnesium promoter position.

2.1.1. Co-impregnation method (CIM)

The wetness co-impregnation method was applied to synthesize the $15Fe\text{-}xMg/Al_2O_3$ oxygen carrier ($x = 0$, 5, 10 wt.%). Prior to the synthesis, the alumina support was calcined in an oven at 350 °C for 3 h in air in order to remove water and volatile compounds from support structure. Typically, a known amount of $Fe(NO_3)_2{\cdot}6H_2O$ (Merck) and $Mg(CH_3COO)_2{.}4H_2O$ (Merck) were dissolved in distilled water separately to make a 0.5 M solutions. The precursor solutions were added simultaneously to the glass balloon containing alumina support and sonicated in an ultrasonic bath at 30 °C for 15 min for better diffusion of Mg precursor to alumina pores. Then the obtained mixture was stirred for 6 h in a rotary evaporator at 80 °C. The impregnated OCs were dried at 90 °C for 15 h and subsequently calcined at 800 °C in static air for 2 h with the heating ramp of 4 °C/min. Finally, the calcined samples were crushed and sieved to a mesh size of 100–200.

2.1.2. Sequential impregnation method (SIM)

To synthesis $Fe/Mg/Al_2O_3$ oxygen carrier the pretreated $\gamma\text{-}Al_2O_3$ was impregnated with Mg and Fe precursors, consecutively. The Mg loading on the support was carried out by wetness impregnation method. For this purpose, magnesium acetate dissolved in deionized water (0.5 M) was added to alumina support and impregnated in a rotary evaporator at 80 °C for 6 h. After the first step impregnation, the samples were dried at 90 °C and subsequently calcined in air at 600 °C for 2 h. Then, the iron, as active phase,

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