Journal of CO_2 Utilization 14 (2016) 112–121

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

journal homepage: www.elsevier.com/locate/jcou

Application of zirconium modified Cu-based oxygen carrier in chemical looping reforming

I. Alirezaei[a], A. Hafizi[a], M.R. Rahimpour[a,b,*], S. Raeissi[a]

[a] Chemical Engineering Department, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz 71345, Iran
[b] Department of Chemical Engineering and Materials Science, University of California, Davis, CA 95616, USA

ARTICLE INFO

Article history:
Received 14 November 2015
Received in revised form 3 March 2016
Accepted 21 April 2016
Available online 28 April 2016

Keywords:
Chemical looping reforming
CO_2 utilization
Oxygen carrier
Hydrogen production

ABSTRACT

The modification of alumina support of copper-based oxygen carrier using zirconium oxide is investigated in this study. The CO_2 modified chemical looping reforming (CO_2-CLR) process is applied to evaluate the synthesized oxygen carriers at different reduction temperatures (550–750 °C). The presence of ZrO_2 in the support structure of oxygen carrier inhibited the deposition of coke on the samples. The results revealed that the addition of 20% zirconium oxide could effectively improve the efficiency of oxygen carrier at different reduction temperatures. In addition, the effect of CH_4/CO_2 ratio in feed (0.5–3) and copper loading percentage (10, 15, 20, 25, 30) are investigated on methane and carbon dioxide conversion, hydrogen production yield and CO/CO_2 ratio. The synthesized oxygen carriers were characterized by X-ray powder diffraction (XRD), field emission scanning electron microscopy (FESEM), BET and energy dispersive X-ray spectroscopy (EDX) techniques. The 15Cu/20Zr-Al as optimized oxygen carrier exposed a mesoporous structure with a high surface area of 315.9 $m^2 g^{-1}$. The redox results revealed that 15 Cu/20 Zr-Al oxygen carrier exhibited the highest activity and showed about 99.2% CH_4 conversion at a low temperature of 650 °C. This oxygen carrier revealed high stability for CH_4 and CO_2 conversion, hydrogen production yield and CO/CO_2 ratio during 16 redox cycles at 650 °C.

1. Introduction

The first studies of the global warming started by Arrhenius and a Swedish chemist about 100 years ago. Arrhenius showed that global warming is mainly due to greenhouse effect of carbon dioxide in the atmosphere. Studies show that the oceans can only absorb one-third of the carbon dioxide produced by human activity and the other two-third remains in the atmosphere, so it could intensify the global warming [1]. Studies on global warming in the past 15 years by the intergovernmental panel on climate change (IPCC) showed that the temperature of earth is increased between 0.4–0.8 °C each 10 years due to increasing the concentration of greenhouse gases in the atmosphere. Carbon dioxide is the main part of greenhouse gas that has major effect on global warming. The carbon dioxide concentration in the nearby atmosphere reached to about 398 ppm in 2013 that shows about 100 ppm increase in comparison with the middle of the 19th century [2]. The CO_2 concentration in the atmosphere is increased mainly due to the consumption of fossil fuels [3]. Consequently, the necessity for mitigating the emission of carbon dioxide is now widely accepted. There are different known methods that could be applied in order to reduce CO_2 emission such as: increasing the internal combustion engines efficiency [4,5], changing fossil fuels to biofuels [6,7], separating and utilizing the produced carbon dioxide [8,9] and using clean energies [10,11].

Reforming of hydrocarbons is an important process in the refining and petrochemical industries for the production of synthesis gas (H_2 and CO). Synthesis gas could be applied to produce ammonia, methanol and synthetic fuels [12,13]. Different reforming reactions that are conventionally used for synthesis gas production are as follows:

Steam reforming: this process is suitable for producing H_2 and CO from light fuels such as natural gas [14–17].

$$C_nH_m + nH_2O \rightarrow nCO + (n + \frac{1}{2}m)H_2 \quad (1)$$

* Corresponding author at: Chemical Engineering Department, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz 71345, Iran.
E-mail addresses: rahimpor@shirazu.ac.ir, mrahimpour@ucdavis.edu (M.R. Rahimpour).

http://dx.doi.org/10.1016/j.jcou.2016.04.007
2212-9820/

Partial oxidation: this reaction is appropriate for the heavier fuels such as oil or coal [18–20].

$$C_nH_m + (\frac{1}{2}n)O_2 \rightarrow nCO + (\frac{1}{2}m)H_2 \quad (2)$$

Carbon dioxide reforming: this process could be applied for the production of synthesis gas with high concentration of carbon monoxide along with reducing the CO_2 emission [21].

$$C_nH_m + nCO_2 \rightarrow (2n)CO + (\frac{1}{2}m)H_2 \quad (3)$$

Hydrogen or synthesis gas production from hydrocarbon sources using modified technologies has been investigated and applied in industrial scale during the recent decades. Chemical looping technology is known as a novel process for the efficiently conversion of carbonaceous fuels to the desired products with reduced carbon footprints. In general, chemical looping process occurs in two different reactors with an active metal oxide circulating between the reactors as oxygen source [22,23]. Chemical looping combustion (CLC) and chemical looping reforming (CLR) processes are the most known chemical looping processes.

Chemical looping combustion is used for energy production via burning of methane with lattice oxygen of a metal oxide as oxygen carrier (OC) [11,24,25]. This process is used for heat production through burning hydrocarbon sources as an unmixed or indirect process. In this process, fuel and air do not mix while reaction between oxygen and fuel takes place in the interface of oxygen carrier. This process produces pure carbon dioxide, which can be separated from steam easily [26].

Chemical looping reforming of methane is a novel technology for partial oxidation of CH_4 with lattice oxygen of the OC. The concepts of CLR process are similar to those of CLC with the difference of keeping air to fuel ratio low to prevent the complete conversion of fuel to CO_2 and H_2O [20,27]. The oxidization of fuel to hydrogen and carbon monoxide with lattice oxygen of the OC takes place in the fuel reactor. Then, the reduced OC is re-oxidized with air at high temperature in the air reactor as indicated in Fig. 1 [28].

There are two main side reactions taking place simultaneously with the main reduction reaction (Eq. (4)) in fuel reactor [29].

$$Me_xO_y + CH_4 \leftrightarrow Me_xO_{y-1} + 2H_2 + CO \quad (4)$$

$$H_2O + CO \leftrightarrow H_2 + CO_2 \quad (5)$$

$$Me_xO_y + CO \leftrightarrow Me_xO_{y-1} + CO_2 \quad (6)$$

The reduced oxygen carrier is re-oxidized by air flowing to the air reactor as indicated in the following reaction [28,29]:

$$Me_xO_{y-1} + 0.5O_2 \leftrightarrow Me_xO_y \quad (7)$$

The deposition of coke on the oxygen carrier is one of the most important complications of CLR process. The presence of carbon dioxide in the reaction media promotes CO_2 reforming reaction along with CLR reactions, which is preferred because it could be effective on coke removal. In addition, it leads to the utilization of industrially produced CO_2 with the aim of decreasing greenhouse gas emission [30]. The CO_2 modified CLR process could be applied in GTL process in which low H_2/CO molar ratio is needed.

In CLR process, oxygen carrier has the major effect on the reaction performance. Ideal oxygen carrier has two advantages including high oxygen transfer capacity and low deactivation rate. CuO is one of the best oxygen carriers because of its high oxygen capacity and transfer rate [29,31,32]. However, the main disadvantage of this metal oxide is its low melting point and thus high tendency to agglomeration of CuO particles.

Our recent studies on CO_2 modified CLR process with different oxygen carriers showed the complete conversion of methane at relatively high reduction temperature in the range of 900–1050 °C. For instance, Forutan et al. [29] used iron, copper, magnesium and cobalt metal oxides supported on alumina in CO_2-CLR process and obtained optimum temperature of each OC to be 900, 1030, 800, and 1025 °C, respectively. Also, Karimi et al. [30] used different metal oxides supported on Al_2O_3 and TiO_2 prepared by co-precipitation method in the same process. The results showed better performance of Al_2O_3 support for all metal oxides at about 1000 °C. In addition, Rydén and Lyngfelt [33] studied the effect of pressure on CLR process. The results showed that pressure does not have a significant effect on the performance of oxygen carriers. Zafar et al. [25] synthesized Ni, Cu, Fe supported on SiO_2 using impregnation method. They showed that these oxygen carriers have acceptable capacity for oxygen transfer in the temperature range of 800–950 °C.

The high reaction temperature could be one of the drawbacks of this process. In addition, the coke deposition is the other problem that is intensified at high temperatures of reforming reactions. Generally, Al_2O_3 is one of the most applicable supports of catalytic materials. However, it causes the coke deposition due to its acidic properties [30]. Zirconium oxide has been used recently as promoter to prevent coke deposition on catalyst structure. It could also increase the mechanical resistance and adjust the pore size distribution of supporting materials [34,35].

The purpose of this study is to investigate the potential of copper-based oxygen carriers in CO_2 modified chemical looping reforming process. In addition, some fresh and used oxygen carriers were characterized with various physicochemical methods to understand the surface and structural properties of them. The process and synthesis variables including methane to carbon dioxide ratio, Zr loading percentage in support, Cu loading percentage and reduction temperature were studied. Finally, we have studied the oxygen carrier lifetime and its performance over the cycles.

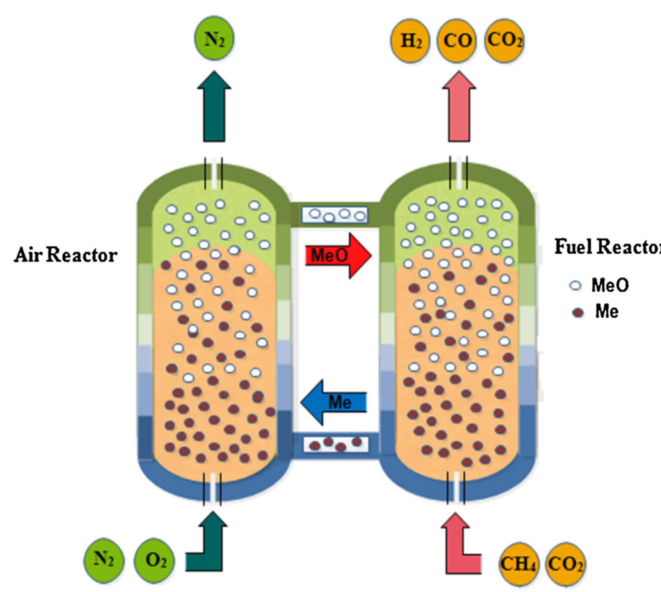

Fig. 1. Conceptual scheme of chemical looping reforming process.