Chemical Engineering Journal 325 (2017) 322–331

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Carbon formation on iron-based oxygen carriers during CH_4 reduction period in Chemical Looping Hydrogen Generation process

Min Zhu, Shiyi Chen, Shiwei Ma, Wenguo Xiang*

Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing, China

HIGHLIGHTS

- Carbon deposition process on Fe_2O_3/Al_2O_3 in methane reduction is investigated.
- The active phase Fe or Fe_3C in the reduction results in the carbon deposition.
- Carbon deposition is affected by temperature and methane concentration.
- $MgAl_2O_4$ and alkali additive K_2CO_3 could alleviate the carbon deposition.
- Carbon deposited is in the form of iron carbide.

ARTICLE INFO

Article history:
Received 2 March 2017
Received in revised form 3 May 2017
Accepted 4 May 2017
Available online 6 May 2017

Keywords:
Iron-based oxygen carriers
Chemical Looping Hydrogen Generation
Carbon deposition
Methane decomposition

ABSTRACT

Chemical Looping Hydrogen Generation (CLHG) is promising hydrogen production technology with inherent capture CO_2 and high-purity hydrogen production simultaneously. Although the reactivity and durability of oxygen carriers can be improved by the combination of inert materials. Carbon deposition over oxygen carrier in the reduction period is still a serious problem in the process of CLHG with CH_4 as fuel, and it affects the purity of hydrogen in steam oxidation period and the carbon capture efficiency. In this study, oxygen carriers, Fe_2O_3/Al_2O_3 and $Fe_2O_3/MgAl_2O_4$, composed of 60 wt% Fe_2O_3, were prepared by mechanical mixing method. Moreover, different contents of K_2CO_3 were incorporated into the Fe_2O_3/Al_2O_3 oxygen carriers by using impregnation method. Experiments were performed in a fluidized bed reactor by exposing the oxygen carriers to alternating methane reducing, steam oxidizing and air oxidizing conditions. The effects of inert supports and alkali additive on the carbon formation performance of iron oxides with different methane concentration were investigated. Results indicate that carbon was formed on the oxygen carriers Fe_2O_3/Al_2O_3 during the reduction, the cracking reaction of CH_4 on the surface of iron-based oxygen carrier starts as active phase Fe or Fe_3C formed. However, the methane decomposition promoted the reduction rate of oxygen carriers and it increased with the temperature and CH_4 concentration. Lower carbon deposition rate was found on $Fe_2O_3/MgAl_2O_4$ compared with Fe_2O_3/Al_2O_3. Furthermore, the addition of K_2CO_3 exhibited a beneficial effect on suppressing carbon formation but decreased the reduction activity of oxygen carrier.

1. Introduction

Hydrogen is currently regarded as one of the key energy carriers for the 21st century, and it will contribute significantly to a reduction in environmental impact and creation of new energy industries. It is well known that natural gas based on steam–methane reforming (SMR) holds the largest share of the H_2 production [1,2]. SMR includes at least three steps: steam reformer, water-gas shift, and pressure swing adsorption, and the energy consumption of pressure swing adsorption are huge. H_2 production in the future not only demands high purity and efficiency but also need to eliminate greenhouse gas CO_2 [3,4].

However, it is notable that introducing CO_2 capture into original process would reduce the energy efficiency and increase the cost of products. Currently great efforts have been carried out to develop the low-cost CO_2 capture technology, the chemical-looping concept was suggested as the promising approach to reduce the economic cost of CO_2 capture [5]. The principle of chemical looping is dividing the process of fuel combustion into two spatially independent steps: a fuel is fully oxidized in fuel reactor (FR) to yield a pure steam of CO_2 and H_2O for obtaining the high-concentration

---

* Corresponding author.
E-mail address: wgxiang@seu.edu.cn (W. Xiang).

http://dx.doi.org/10.1016/j.cej.2017.05.027
1385-8947/© 2017 Elsevier B.V. All rights reserved.

stream of CO_2 after condensing [6], while oxygen atom was provided form oxygen carrier (typically a metal oxide) for combustion; and then, the oxygen carriers regain the oxygen atoms in air reactor (AR) by reacting with air, and circulating back into the FR to complete the materials 'loop'.

Chemical looping thus far facilitates a novel process configuration for H_2 production which can be realized in at least two different ways. In the first configuration, there are two reactors, i.e. FR and AR, which constitutes is similar to chemical looping combustion process (CLC), also named as "chemical-looping reforming process" (CLR) or "chemical-looping partial oxidation of methane process" (CL-POM). The proposed routine is as follows: a fuel is co-fed with steam or air in FR, resulting in steam reforming of methane (SRM) or catalytic partial oxidation of methane (POM) via oxygen carrier; air or steam are adopted in AR for oxygen carrier regeneration or H_2 production. However, the target product of CLR and CL-POM were syngas not H_2, the oxygen carrier is chosen to ensure the highest selectivity towards H_2 and CO. Form the common materials in this configuration, i.e. Fe-, Ni-, Cu-, Co- and Mn-based oxygen-carriers, the Ni-based oxygen carrier showed the highest selectivity while unable to split water for H_2 production [7]. Fe-based oxygen carrier was proved to be ideal for water splitting reaction (WSR) but suffering lower selectivity towards H_2 and CO. Alternatively, there is another configuration, using iron oxide as oxygen carrier normally due to its reasonable kinetics, cheaper cost and environmental properties, which consisting of three reactors: a FR, a steam reactor (SR), and an AR. This configuration is also a development process form CLC and is thus named "Chemical Looping Hydrogen Generation" (CLHG). In CLHG, Fe_2O_3 is reduced to FeO/Fe by methane in FR, and then, FeO/Fe is transported to SR where reacting with steam to produce pure H_2, however, due to the limit of thermodynamic constrains [5,6], the transformation from Fe_2O_3 to Fe_3O_4 is suitable for total oxidation of CH_4 but the iron oxide can be oxidized only to Fe_3O_4 by steam, so further oxidation of Fe_3O_4 to Fe_2O_3 occurs in the AR. The schematic of the CLHG process using CH_4 as fuel is shown in Fig. 1.

CLHG offers several advantages: (i) the overall reaction is exothermic; (ii) theoretically, stream of CO_2 and H_2O can be obtained in FR, high purity CO_2 is easily to be separated by condensation; (iii) avoid the product purification unit due to H_2 was produced by splitting water. Kathe et al. have conducted a thermal efficiency analysis between CLHG and SMR with more than 90% CO_2 capture, it was found that CLHG has better the cold gas efficiency and six percent more the effective thermal efficiency than SMR [10].

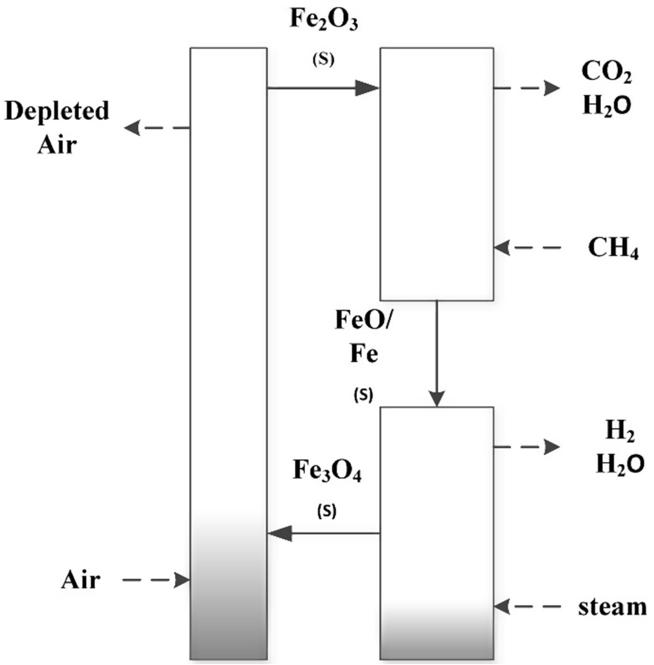

Fig. 1. The schematic of the CLHG process using CH_4 as fuel.

When pure hematite was used as an oxygen carrier, the reduction of Fe_2O_3 to Fe led to sintering on the particle surface and generated rapid deactivation within the first few cycles [11]. In order to increase the reactivity and durability of the oxygen carrier, hematite was often supported with some inert materials, i.e., Al_2O_3, TiO_2, SiO_2, ZrO_2, CeO_2 or $MgAl_2O_4$ [12,13]. These supports were used to provide higher surface area, better mechanical properties and more efficient ionic conductivity of the oxygen carriers [8–10]. When Al_2O_3 and TiO_2 were used as supports, $FeAl_2O_4$ and $FeTiO_3$ would generate with Fe^{2+} formed during the reduction of hematite, but these materials have the ability to be oxidized back by air [14]. Chen et al. [15] prepared Fe_2O_3 supported on Al_2O_3 and TiO_2 with different ratios, it was shown that 60 wt% Fe_2O_3/Al_2O_3 was the best candidate, porous structure and higher surface area were supported by Al_2O_3 that promoted better crushing strength and reactivity than TiO_2. Fe_2O_3/SiO_2 maybe the formation of silicate at high temperature [16]. $FeAl_2O_4$, as the major stable Fe-based phase during the reduction reaction, reduced the reactivity of Fe_2O_3/Al_2O_3 and was formed based on the interaction of Fe_2O_3 with Al_2O_3 [17]. In order to inhibit the formation of $FeAl_2O_4$, $MgAl_2O_4$ support has been proposed due to its stability at high temperature [15,18]. Galinsky et al. [19] investigated the reduction reactivity of $Fe_2O_3/MgAl_2O_4$ and Fe_2O_3/CeO_2 with CH_4. Deactivation of CeO_2 supported samples resulted from formation $CeFeO_3$ by solid-state migration of iron cations which decreased the surface area. Mattisson et al. [20] found that Fe_2O_3 supported by Al_2O_3 or ZrO_2 showed high reactivity with CH_4. Hence Al_2O_3 was still widely used as support for iron-based oxygen carrier due to its great thermal stability, good mechanical properties and lower cost of the resulting oxygen carriers [21,22].

Syngas and natural gas were usually used for the reduction of iron oxides in CLHG. When methane was used as a reducing agent, carbon deposition on the oxygen carrier is serious compared with syngas under high temperature [23,24,25]. If coke formation during the reducing step, it would be transported back to the SR by particles, causing CO_2 or CO formation and decreasing the purity of hydrogen. Ghose et al. [26] measured the reduction rate of Fe_2O_3 in the TGA with purity methane in the temperature range of 800–1025 °C. They suggested that the overall reaction may be consisted of decomposition of CH_4 into C and H_2, and reduction of Fe_2O_3 by the resulting H_2 [27]. Mendiara et al. [28] found that carbon deposition on the iron oxide surface while residual oxygen mole content in the oxygen carrier dropped to 0.5%. Bao et al. [29] found that the deposition of carbon rapidly increased when Fe formed.

As carbon formation occurs during the CH_4 reducing process, it was suggested that increase in adsorption and activation of CO_2 or H_2O would accelerate the gasification of the surface active carbons and retard the carbon sedimentary [30,31]. A certain amount of alkaline metal or alkaline-earth metal oxide could improve active carbons gasification and modify the acid-base properties of the supports [32,33]. Carrero et al. [34] prepared and tested the Cu–Ni/SiO_2 catalysts with alkaline-earth elements (Mg and Ca) modified silica support for hydrogen production through ethanol steam reforming, they observed that the coke resistance ability was improved by Ca and Mg additive, the deposition carbon was less order and it was more reactive for steam gasification. Specifically, alkaline metal K was proved to be the best performing alkaline metals which promoted carbon gasification [35]. Liu et al. [36]