Effects of supports on reduction activity and carbon deposition of iron oxide for methane chemical looping hydrogen generation

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HIGHLIGHTS

- Carbon resistance of oxygen carrier was enhanced by inner supports.
- Four supports $MgAl_2O_4$, CeO_2, ZrO_2, and $CeZrO_4$ were combined with iron oxide.
- Reduction activity is related to the surface area of oxygen carriers.
- Carbon resistance depends on the oxygen transfer capacity.
- Oxidation of deposited carbon causes oxygen carrier sintering.

ARTICLE INFO

ABSTRACT

Chemical looping hydrogen generation is a promising technology which has the potential to efficiently produce hydrogen and capture CO_2 with the aid of iron-based oxygen carriers. The properties of the iron-based oxygen carrier, such as carbon resistance, redox activity, and cycle stability, are critical factors for the development of CLHG process. In this study, four different supports, $MgAl_2O_4$, CeO_2, ZrO_2, and $CeZrO_4$, were incorporated with iron oxide by a co-precipitation method. The reduction activity, carbon resistance and redox stability of the oxygen carriers with methane were investigated in a bench-scale fluidized bed reactor. The redox activity and oxygen transfer capacity were also tested by temperature programmed reduction (TPR) and temperature programmed oxidation (TPO). Carbon formation was observed during the reduction period through the methane decomposition reaction. It was revealed that the carbon resistance of the oxygen carriers was partially determined by the oxygen transfer capacity. For the fresh oxygen carriers, the incorporation of $MgAl_2O_4$ led to a better carbon resistance because more lattice oxygen can be released compared to the other supports before carbon deposition. After 10 redox cycles, the $Fe_2O_3/CeZrO_4$ oxygen carrier performs the best oxygen transfer capacity, but the oxygen transfer capacity of the $Fe_2O_3/MgAl_2O_4$ oxygen carrier reduced obviously. In addition, the specific surface area could dramatically affect the reduction activity of the oxygen carriers. Crystalline graphite was observed on the reduced oxygen carriers, which posed a negative effect on the reduction activity, leading to sintering of the oxygen carriers.

1. Introduction

Hydrogen is one of the promising clean energy carriers for future generations. Currently, most hydrogen is produced by steam methane reforming (SMR) process which releases 0.3–0.4 Nm^3 CO_2 with 1 Nm^3 H_2 generated [1–3]. Therefore, the hydrogen production cost would inevitably go up by about 10 percent when the carbon sequestration unit is added in the SMR process [4]. In recent years, great efforts have been made to develop the low-cost CO_2 capture technologies. The chemical looping combustion (CLC) process was suggested as the cheapest one among those new technologies [5,6], since the pure

stream of CO_2 could be separated inherently in the CLC process without extra energy.

For hydrogen production, there are two main technological routes related to the Chemical-Looping (CL) principle, i.e. Chemical Looping Reforming (CLR) process and Chemical Looping Hydrogen generation (CLHG) process. In case of the CLR process, the target product is syngas, which needs additional water-gas shift (WGS) and pressure swing adsorption (PSA) systems to obtain the high purity H_2 [7]. CLHG process is derived from the 'steam-iron' process, which can produce pure H_2 continuously with inherent CO_2 capture [8–10].

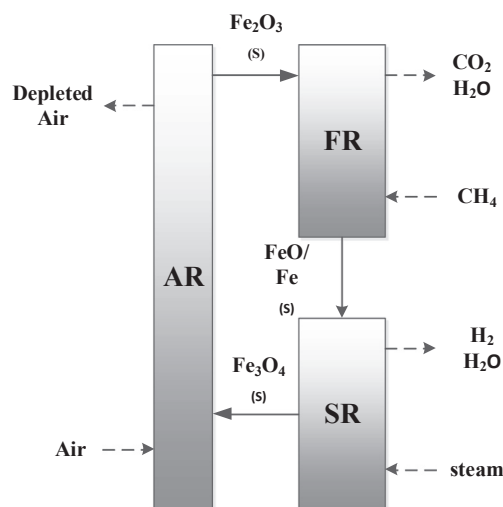Iron oxide (Fe_2O_3) is an ideal oxygen carrier (OC) for the CLHG

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

process, as it has lower cost, higher equilibrium partial pressure of H_2 for the water splitting and less environmental impact than other metal oxides (e.g. NiO, CuO, Mn_3O_4, CoO and CeO_2). In case of using methane as fuel, the schematic diagram of the CLHG process is shown in Fig. 1.

CLHG process includes three reactors: a fuel reactor (FR), a steam reactor (SR) and an air reactor (AR). In the FR, a hydrocarbon fuel (CH_4) is used to reduce Fe_2O_3 to FeO or Fe^0, and the pure CO_2 can be obtained at the outlet of the FR after condensation. In the SR, high purity H_2 is subsequently generated by the water-splitting reaction. However, due to the thermodynamic limitation of the iron oxide, and the reduced oxygen carrier (FeO or Fe^0) can only be oxidized by vapor to Fe_3O_4. An additional AR must be included after the SR to oxide the Fe_3O_4 to Fe_2O_3 completely.

The reduction step in the FR is expected to be the limiting step in the CLHG process [11]. In the FR, CH_4 is sequentially dissociated over the surface of oxygen carriers to form C and H atoms. The H atoms are oxidized by lattice oxygen to produce H_2O or combine together to generate H_2 [12], while the C atoms are oxidized to produce CO or CO_2 or diffuse through the bulk of Fe particle, causing carbon deposition [13].

It is essential to avoid carbon deposition in the FR, otherwise, the deposited carbon will react with the vapor in the SR, which leads to CO/CO_2 formation and H_2 purity reduction. Carbon formation is strongly dependent on the amount of the available oxygen, whether it comes from H_2O, CO_2 or oxygen carriers [7], since the deposited carbon would be oxidized by the H_2O/CO_2 or lattice oxygen to carbon oxides [14,15]. For the iron oxide, carbon deposition did not happen before the Fe^0 formation [16], for the dissociation of CH_4 was the dominant rate-determining step while the transform of iron oxide was Fe_2O_3 to FeO [17]. However, after the Fe^0 formed on the surface of the oxygen carrier, methane decomposition became favoured over the Fe^0, being in accordance with the rapid increase in reduction rate of the oxygen carrier, as well as the subsequently intensive rise of C atoms formed resulting in carbon deposition [18].

It is known that incorporating metal supports with iron oxide can improve the redox activity and stability. Al_2O_3 is the most common support, which has been proved to show a good performance on reducibility of the oxygen carrier by taking the advantage of its high Tammann temperature and good mechanical stability during the reduction period [19]. But problems did exist if using methane as fuel: (i) increased acid sites by Al_2O_3, (ii) formed spinel $FeAl_2O_4$ in the reduction period [20]. $FeAl_2O_4$ was formed after the generation of FeO, inevitably decreasing the oxygen ion migration speed and slowing down the reduction rate. Moreover, the acid site would promote the cracking of the C−H bond significantly, leading to a negative consequence on the

carbon elimination [21,22]. $MgAl_2O_4$ as an alternative for Al_2O_3 was proposed by the researchers [23–25], for it can avoid the formation of $FeAl_2O_4$ and promote the basicity of oxygen carrier [26]. Additionally, $MgAl_2O_4$ provides more favourable CO_2 affinity [27], which facilitated the gasification of carbon to CO through the reverse Boudouard reaction (C + CO_2 → 2CO) [28]. ZrO_2 has good chemical inertness and did not form solid solution with iron oxide [29]. Yüzbasi et al. [30] found that Fe_2O_3 supported on ZrO_2 showed a high ion conductivity than the unsupported Fe_2O_3. However, after many cycles, the large-scale phase separation phenomenon was observed for the Fe−Zr mixed oxides, reducing the reduction activity. CeO_2-based materials have received widespread attentions for its good oxygen storage capacity and redox property [31,32]. The addition of CeO_2 was found to modify the distribution of Fe_3O_4 phase by the Ce−Fe interaction, which enhanced the oxygen mobility and the reactivity of iron-based oxygen carrier. The presence of the $CeZrO_x$ solid solution could induce the growth direction of the carbon filament, resulting in a loose contact between the carbon filament and the catalysts [33].

This work focuses on the role of supports for the carbon resistance and reduction stability of iron-based oxygen carriers in the CLHG process. Although many experimental investigations have been performed on the redox stability of iron oxide by adding different supports, a detailed understanding of the relationship between the reduction activity and carbon formation is still lack. Additionally, enhancing the oxygen storage can improve the carbon resistance of oxygen carrier, but it strongly depends on the support nature and operating conditions. However, these factors have not been well reported. In this work, we used four different supports, i.e. $MgAl_2O_4$, CeO_2, ZrO_2 and mix oxide $CeZrO_4$ to modify the iron oxide, and the tests on reduction activity with CH_4 and carbon deposition property during the redox cycles were performed in a bench-scale fluidized bed. The oxygen transfer capability of the fresh and reacted oxygen carriers was investigated with TPR-CH_4 method and the chemical and physical property of deposited carbon were also studied by TPO and transmission electron microscopy (TEM) tests.

2. Experimental methods

2.1. Oxygen carrier preparation

Four Fe-based oxygen carriers were prepared using co-precipitation method. The mass ratio of Fe_2O_3 was 60% and the simplified label for those oxygen carriers are shown in Table 1. The required amounts of precursor nitrates $Fe(NO_3)_3 \cdot 9H_2O$ (AR, ≥98.5% purity), Ce $(NO_3)_3 \cdot 6H_2O$ (AR, ≥99.5% purity), $Zr(NO_3)_3 \cdot 5H_2O$ (AR, ≥99% purity), $Al(NO_3)_3 \cdot 9H_2O$ (AR, ≥99% purity) and $Mg(NO_3)_3 \cdot 6H_2O$ (AR, ≥99% purity) were dissolved in deionized water. The solution was heated to 70 °C with frequent agitation until nitrates dissolved. Ammonia solution was applied as the precipitant which was added dropwise to the nitrates solution to increase the PH to 9. The solution was stirred for 1 h and aged for 6 h. The solid sediment in the solution was repeatedly filtered and washed with deionized water. After that they were subsequently dried at 110 °C for 24 h, calcined at 300 °C for 2 h, and then increased temperature to 900 °C for 3 h. After cooling, the solid residues were crushed and screened to the final particle size in the range of 0.180–0.300 mm.

Table 1
Nomenclature for the oxygen carriers.

Oxygen carrier	Lable
Fe_2O_3/$MgAl_2O_4$	FeMgAl
Fe_2O_3/CeO_2	FeCe
Fe_2O_3/ZrO_2	FeZr
Fe_2O_3/ZrO_2:CeO_2(1:1 M ratio)	FeZrCe