EVALUATION OF Fe-BASED OXYGEN CARRIERS SUPPORTED WITH Al₂O₃, ZrO₂ AND CeO₂ IN CHEMICAL LOOPING HYDROGEN GENERATION

Shiwei Ma, Wengu Xiang*, Shiyi Chen
Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education,
Southeast University, 210096Nanjing, China
*Email: wgxiang@seu.edu.cn

Abstract – Chemical looping hydrogen generation (CLHG) is a promising technology that can produce high-purity hydrogen with inherent CO₂ capture. It is composed of three steps, reduction by fuel gas, steam-iron process and air oxidation. Fe₂O₃ is currently the best candidate for CLHG with high CO₂ and H₂O selectivity and H₂ mole fraction in iron-steam reaction, and it is also of low cost and abundance in nature. However, pure Fe₂O₃ cannot meet the requirement of oxygen carriers in multi-cycles. It should be combined with support to improve its reactivity and stability, and eliminate potential sintering and carbon deposition. In this paper, Fe-based oxygen carriers, which consisted of 60wt% iron oxide and 40wt% support, were prepared by co-precipitation method with three supports including inert and reducible ones, i.e. Al₂O₃, ZrO₂, and CeO₂. Experiments were conducted in a batch fluidized bed with CO as fuel during multiple redox cycles for CLHG. The H₂ yield, carbon deposition, reactivity and redox stability of the oxygen carriers were analyzed to investigate the effects of supports as well as the fundamental mechanism. The experiments results showed that the properties of the oxygen carriers highly relied on the support and its interaction with iron oxide. The oxygen carrier supported by Al₂O₃ exhibited poor reactivity and stability, and the oxygen carrier supported by ZrO₂ led much carbon deposition, decreasing H₂ purity. However, the reducible support CeO₂, rendering fast oxygen transfer rate and the formation of perovskite-type CeFeO₃, demonstrated reactivity enhancement for Fe₂O₃, counteracted the negative effect originating from sintering and guaranteed the reactivity and stability of Fe₂O₃/CeO₂. In addition, the oxygen carrier supported by CeO₂ suppressed carbon deposition and H₂ with high purity could be attained. Overall, CeO₂ is a potential support for H₂ production with consideration of H₂ yield and purity.

INTRODUCTION

Hydrogen is an ideal energy carrier with a net calorific value of 121.00MJ/kg, higher than any other known fuel, and no pollutants or greenhouse gases are emitted into the atmosphere during the process of hydrogen utilization, as can be found in Chauvey et al. (2013). So hydrogen is an optimal solution for the energy supply in future. Also, Holladay et al. (2009) wrote that hydrogen was an important industrial material which can be widely used in the production of ammonia, gasoline, methanol, ethanol, etc. However, there is no hydrogen existing on the earth, owing to its highly active property, and it must be generated from other energy sources. It can be found in (Adanez et al., 2012) that steam methane reformation (SMR) is commercially proven, and it is currently the predominant technology for hydrogen production. Nevertheless, the process for SMR is complex and expensive, especially when CO₂ capture process is implemented.

Chemical looping hydrogen generation (CLHG) is a promising hydrogen production technology developed from chemical looping combustion (CLC). It can not only produce high purity hydrogen but also separate CO₂ inherently. CLHG consists of three reactors: fuel reactor (FR), steam reactor (SR) and air reactor (AR). The oxygen carrier, mostly iron oxide, circulates among the three reactors, converting hydrocarbons into hydrogen. For CO as fuel, the reactions in these three reactors can be described as follow.

In the FR, Fe₂O₃ is reduced to Fe or FeO, as shown in Eq. (1) to Eq. (3).

\[ 3\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2 \] (1)
\[ \text{Fe}_3\text{O}_4 + \text{CO} \rightarrow 3\text{FeO} + \text{CO}_2 \] (2)
\[ \text{Fe}_3\text{O}_4 + 4\text{CO} \rightarrow 3\text{Fe} + 4\text{CO}_2 \] (3)

In the SR, Fe and FeO are oxidized into Fe₂O₃, releasing H₂, as listed in Eq. (4) and Eq. (5).

\[ 3\text{FeO} + \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2 \] (4)
The present work investigates how to improve the steam reforming process. It would be an effective way to develop new oxygen carriers that can convert more fuel into hydrogen, but also decrease the carbon deposition and obtain H2 of high purity. Kang et al. (2010a) wrote that although Fe2O3, CeO2 and WO3 could be all applied to CLHG, Fe2O3 was the most suitable oxygen carrier regarding to the CO2 and H2O selectivity and H2 concentration at the outlet of SR. Moreover, Fe2O3 is attractive owing to its abundance, low cost and low toxicity.

In addition to the active metal oxides, supports are also indispensable parts to the oxygen carriers for high reactivity and resistance to sintering, carbon deposition and attrition. There are many investigations on the comparison of different supports, such as Al2O3, MgAl2O4, TiO2, SiO2, ZrO2, YSZ (yttrium-stabilized zirconia), for related CLC and CLR (Chemical Looping Reforming) regarding to the Fe-based oxygen carriers, which can be found in (Galinsky et al., 2015; Adánez et al., 2004; Chen et al., 2014). But the results cannot be directly applied in CLHG. The difference of CLHG from CLC/CLR is the reduction. Fe2O3 must be reduced to Fe/FeO in CLHG rather than merely FeO in CLC. However, Lin et al. (2016) wrote that Fe and FeO could facilitate carbon deposition, but this can be avoided in CLC because Fe2O3 is only reduced to FeO. In addition, Tang et al. (2015) wrote that FeO could react with some supports, so the selection of supports is important for Fe-based oxygen carriers in CLHG. Many researchers focused on the effects of the different inert supports for CLC and CLR, but the inert effects for CLHG are limited. Chen et al. (2011) wrote that H2 yield of Fe-based oxygen carrier supported by Al2O3 was superior to that of TiO2 due to the formation of unreactive FeTiO3. It can be found in (Kosaka et al., 2015) that oxide ion conductors YSZ and GDC (gadolinia-doped ceria) could accelerate the reduction of Fe2O3 for H2 storage, while CeO2 and GDC would distinctly boost the reduction kinetics from FeO to Fe; furthermore, all these three supports could improve the steam-iron reaction rates compared to ZrO2.

CeO2 is a reducible support that is widely used in redox catalysis, such as automotive exhaust abatement, water gas shift and catalytic methane oxidation. It can be found in (Shi et al., 2008) that the promotion role of CeO2 for the active metal in catalyst is due to its property of storing and releasing oxygen, which could accelerate the reduction of active metal. CeO2 has been used in CLC as a reducible support. Bhavsar and Veser (2013a, 2013b) wrote that CeO2, as a support for Ni-based and Fe-based oxygen carriers in CLC, could accelerate the reaction kinetics and enlarged the time window for total oxidation of methane compared to inert supports Al2O3 and SiO2; more striking was that CeO2 allowed for complete carrier conversion with H2 or CH4 as fuel. Liu et al. (2014) wrote that the oxygen carrier Fe2O3/Al2O3 with CeO2 additive provided better average reaction rates in CLC with CO as fuel, for the vacancies inspired by CeO2 could transfer oxygen quickly to the surface of the oxygen carrier by vacancy diffusion or even through oxygen tunnels formed by vacancies. Similarly, the improved performance for methane total oxidation with CeO2 additive to Fe2O3 can be found in (Miller and Sirirwardane, 2013). Furthermore, Bhavsar et al. (2016) wrote that oxygen carriers supported by gadolinia doped-ceria or lanthana-doped ceria showed even higher reactivity and oxygen capacity for CLC. For CLR, Li et al. (2010) wrote that the oxygen carrier Fe2O3/CeO2 maintained high catalytic activity and selectivity during the conversion of methane to synthesis gas due to the oxygen mobility enhancement by the solid solution originated from Fe2O3 and CeO2. Moreover, there are some researches on the chemical-looping steam methane reforming (CL-SMR) over the Fe2O3/CeO2 oxygen carrier. It can be found in (Zhu et al., 2013) that Fe2O3/CeO2 was a promising oxygen carrier in CL-SMR for its high redox activity and desired product yield of syngas and hydrogen. Zhu et al. (2014a) also wrote that CeO2 modified Fe2O3 was a suitable material for the chemical hydrogen storage and production and Ce addition could decrease both the hydrogen reduction temperature and the temperature for water splitting reaction. In addition, Ce could be used to eliminate carbon deposition due to its redox properties and oxygen buffering capacity. Zheng et al. (2017) wrote that CeO2 could reduce the carbon deposition for the reforming of methane. Sun et al. (2015) wrote that the oxygen carrier Fe2O3/Al2O3 modified by CeO2 could effectively inhibit carbon deposition or Fe-C formation in CLHG. Based on those findings, CeO2 may be a promising support for Fe-based oxygen carriers with excellent performance in CLHG.

The present work investigated the effects of supports on H2 yield, carbon deposition, reactivity and redox stability of Fe-based oxygen carriers for CLHG in batch fluidized bed. Al2O3 and ZrO2, which are frequently encountered and perform well in chemical looping process, are included for comparison apart from CeO2.

\[
3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2 \quad (5)
\]

In the AR, Fe3O4 is further oxidized and so Fe2O3 is regenerated, as can be seen in Eq. (6).

\[
4\text{Fe}_2\text{O}_3 + \text{O}_2 \rightarrow 6\text{Fe}_2\text{O}_3 \quad (6)
\]

Luo et al. (2015) wrote that the oxygen carrier material was the key issue related to the performance of chemical looping process. It would be an effective way to develop new oxygen carriers that can not only convert more fuel into hydrogen, but also decrease the carbon deposition and obtain H2 of high purity. Kang et al. (2010a) wrote that although Fe2O3, CeO2 and WO3 could be all applied to CLHG, Fe2O3 was the most suitable oxygen carrier regarding to the CO2 and H2O selectivity and H2 concentration at the outlet of SR. Moreover, Fe2O3 is attractive owing to its abundance, low cost and low toxicity.
EXPERIMENTAL SECTION

OXGEN CARRIER SYNTHESIS

The Fe-based oxygen carriers were prepared by co-precipitation, and the ratio of Fe$_2$O$_3$ and the inert support was kept 6:4. The calculated precursor nitrates for Fe$_2$O$_3$, Fe(NO$_3$)$_3$·9H$_2$O (AR, Nanjing Chemical Reagent Co., Ltd), and metal oxide supports, Ce(NO$_3$)$_3$·6H$_2$O (99.5%, Aladdin), Al(NO$_3$)$_3$·9H$_2$O (AR, Greagent), or Zr(NO$_3$)$_4$·5H$_2$O (AR, Greagent), were put into solution with deionized water. The solution was sufficiently blended and heated in a magnetic stirrer until the temperature reached 70°C. Then a 25%~28% ammonia solution was gradually introduced into the mixture to increase the PH of the solution to 9. It was then aged for 12 h under room temperature. Afterwards, the resulting precipitate was filtered and dried at 110°C in a drier for 24 h. The resulting solids are subsequently subjected to decomposition at 350°C for 2 h and sintered at 900°C for 2 h in a muffle oven. Then the particles were crushed and sieved to get powder in the size range of 0.150~0.250 mm for experiments.

OXGEN CARRIER CHARACTERIZATION

X-ray powder diffraction (XRD) was implemented to study the crystal phase compositions. XRD patterns were recorded using a Rigaku SmartLab X-ray diffractometer with Cu-Kα radiation operating at 3 kW. The sample scans were performed in a step-scan mode between an angle range of 20~90° (2θ), with a step size rate of 0.1°/s. Scanning electron microscopy (SEM) and Energy Dispersive Spectrometer(EDS) was performed on an Ultra Plus (Carl Zeiss AG) microscope to study the morphology of oxygen carriers.

EXPERIMENTAL REACTOR AND PROCEDURE

A laboratory-scale batch fluidized bed reactor was used in the test as shown in Fig.1. This system was comprised of three parts, a gas distribution system, a fluidized bed reactor, and an off-gas treatment system. In the gas distribution system, distilled water was pumped into a steam generator and heated into steam, whereas CO, N$_2$ and O$_2$ were sent into the reactor through the mass flow controllers. The reactor was a quartz fluidized bed, which had a length of 750 mm and an inner diameter of 22 mm with a porous quartz plate placed 150 mm from the bottom. The quartz tube was heated by an electric furnace with a temperature controller. In the off-gas treatment system, the outlet flue gas was first condensed to remove water, and then dried by silica gel. The off-gas was finally sent into the gas analyzer.

In each test, the oxygen carrier was 10 g, which was placed on the porous quartz plate, and the furnace was heated to the desired temperature under nitrogen atmosphere, then the particles were exposed to reducing and oxidizing atmosphere. There were three stages in a cycle, including CO reduction stage (35 min), steam oxidation stage (20 min) and air oxidation stage (15 min). The experiments were carried out at isothermal condition with a constant total flow rate of 0.5 L/min, while, in steam oxidation stage, nitrogen flow rates was 0.35 L/min and the H$_2$O (l) injected into the furnace was 0.20 mL/min. The minimum fluidized velocity, $u_{mf}$, of the particles was 0.018 m/s at 850 °C, and the gas velocity $u_g$ was 0.101 m/s, i.e., $5.6 u_{mf}$, sufficient to fluidize the oxygen carrier. Gas flow rates were adjusted so that there was 30% CO in reduction stage and 16% O$_2$ in air oxidation stage balanced with nitrogen. Nitrogen blowing stage was conducted after every stage. In order to investigate the carbon deposition of the oxygen carriers and to avoid CO contamination from the reduction period, the nitrogen blowing stage between reduction stage and steam oxidation stage lasted for 40~50 min until the concentration of CO and CO$_2$ went down to zero.

Fig. 1. Schematic diagram of the experimental setup
The total volume flow rate of the off-gas $F_{\text{out}}$ is defined as:

$$F_{\text{out}} = \frac{F_{N_2,\text{in}}}{1 - X_{CO} - X_{CO_2} - X_{H_2}}$$  \hspace{1cm} (7)

Where $F_{N_2,\text{in}}$ is the volume flow rate of the inlet nitrogen, $X_{CO}$, $X_{CO_2}$, and $X_{H_2}$ are the measured concentrations of CO, CO$_2$, and H$_2$ respectively.

The volume flow rate of CO$_2$ in the off-gas is:

$$F_{CO_2} = F_{\text{out}} X_{CO_2}$$  \hspace{1cm} (8)

The volume flow rate of H$_2$ in the off-gas for the steam oxidization period is:

$$F_{H_2} = F_{\text{out}} X_{H_2}$$  \hspace{1cm} (9)

The H$_2$ yield in the steam oxidizing period is:

$$Y_{H_2} = \int_{0}^{t} F_{H_2} dt$$  \hspace{1cm} (10)

The gas yield of carbonaceous gases, including CO and CO$_2$, in the steam oxidation period is:

$$Y_{CO} = \int_{0}^{t} F_{\text{out}} \left( X_{CO_2} + X_{CO} \right)$$  \hspace{1cm} (11)

The H$_2$ purity in the steam oxidization period is:

$$a_{H_2} = 1 - \frac{Y_{CO}}{Y_{\text{total}}}$$  \hspace{1cm} (12)

**RESULTS AND DISCUSSION**

**EFFECT OF SUPPORTS ON H$_2$ YIELD**

![Graph showing the effect of cycle number on H$_2$ yield for oxygen carriers with different supports at 850°C](image)

Fig. 2 shows the H$_2$ yields in 10 redox cycles for oxygen carriers with different supports at 850°C. After three cycles, the H$_2$ yields for all the investigated oxygen carriers came to a relatively stable state, decreasing slightly with cycle number, which indicated that the structure of the oxygen carriers tended to stabilize. The H$_2$ yields followed the sequence: Fe$_2$O$_3$/ZrO$_2$ > Fe$_2$O$_3$/CeO$_2$ > Fe$_2$O$_3$/Al$_2$O$_3$. And the average H$_2$ yields from the 3rd to 10th cycle were 1.60 L, 1.30 L, 0.61 L, respectively. Fe$_2$O$_3$/ZrO$_2$ showed high H$_2$ yield due to the high phase stability and thermal stability of ZrO$_2$. For Fe$_2$O$_3$/CeO$_2$, it can be found in (Galinsky et al., 2015) that the poor performance of Fe$_2$O$_3$/CeO$_2$ resulted from solid-state migration of iron cations and subsequent enrichment on the oxygen carrier surface, which led to sintering and lowered lattice oxygen accessibility. As a note of caution, however, Bhavsar and Veser (2013b) wrote that although CeO$_2$ demonstrated reducibility compared to no reducibility for ZrO$_2$ and Al$_2$O$_3$, the oxygen carrying capacity was negligible compared to typical metals, such as Fe$_2$O$_3$ and NiO. The terrible H$_2$ yield for Fe$_2$O$_3$/Al$_2$O$_3$ could be attributed to the generation of inactive spinel FeAlO$_4$, which can be found in (Svoboda et al., 2007), or sintering problem that can be found in (Nandy et al., 2016). Although the oxygen carrier Fe$_2$O$_3$/ZrO$_2$ is the best one in view of H$_2$ yield, carbon deposition is another important factor which have a serious impact on the H$_2$ purity and should be sufficiently considered, especially when the hydrogen is intended to applied in the fuel cell.
CARBON DEPOSITION

The hydrogen produced in CLHG with CO as fuel and Fe₂O₃ as oxygen carrier can reach high purity above 99%, the reason why the purity cannot achieve 100% is the carbon deposition generated in the FR, as can be found in (Cho et al., 2014). The related reaction is called as Boudouard reaction, see below in Eq. (13).

\[ 2\text{CO} \rightarrow \text{CO}_2 + \text{C} \]  

The carbon deposition generated will then react with H₂O, leading to the production of CO and CO₂, leading to the contamination of H₂, as shown in Eq. (8) and (9).

\[ \text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \]  

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]

Many factors can influence the carbon deposition, such as reaction pressure, temperature, composition and concentration of fuel gas, and the quality of the available lattice oxygen from oxygen carrier, which can be found in (Wang et al., 2008).

Carbon deposition could be converted to CO or CO₂ both in steam oxidation stage and air oxidation stage, however, the attention was paid to the steam oxidation stage in this paper, which exerted direct influence on the H₂ purity. CO and CO₂ could not detected by the gas analyzer under the experimental condition described above, viz. the concentrations of CO and CO₂ in the steam oxidation stage were beyond the detection limits (50ppmv) of the gas analyzer. Therefore, 100% CO (flow rate 0.5L/min) was sent into the fluidized bed instead of 30% to investigate the resistance of the oxygen carriers to carbon deposition. The H₂ purities corresponding to the three oxygen carriers are illustrated below in Fig.3.

```
Fe₂O₃/CeO₃  Fe₂O₃/ZrO₂  Fe₂O₃/Al₂O₃

| H₂ Purity (%) | 99.9975 | 99.7957 | 100.000 |
```

Fig. 3. Effect of different supports on H₂ purity at 850°C

It can been seen in Fig.3 that the H₂ purities followed the sequence: Fe₂O₃/Al₂O₃ > Fe₂O₃/CeO₃ > Fe₂O₃/ZrO₂. Interestingly, this sequence is quite the opposite to that of H₂ yields. It can also be found in (Kang et al., 2010b) that ZrO₂ supported oxygen carrier showed more carbon deposition than that of CeO₂. The reason for low carbon deposition on Fe₂O₃/CeO₃ is that CeO₂ can provide oxygen species from lattice oxygen to oxidize the surface carbon, producing CO or CO₂. However, for Fe₂O₃/ZrO₂, plenty of Fe or FeO originating from deep reduction promote the Boudouard reaction, leading to much carbon deposition. The gas analyzer could not detect CO or CO₂ generated from the carbon deposition for Fe₂O₃/Al₂O₃ probably due to the sintering of the particle surface and the resulting reduction of active sites Fe or FeO. In addition, the element distribution of the oxygen carriers obtained after the 11th reduction stage (30% CO) was characterized by EDS. The result showed that the weight ratios of carbon element on the surface of the reduced oxygen carriers were 2.46%, 4.56% and 11.45% for Fe₂O₃/Al₂O₃, Fe₂O₃/CeO₃ and Fe₂O₃/ZrO₂ respectively, which was consistent with the result indicated by Fig.3.

It can be found in (Hotza and Diniz Da Costa, 2008) that the fuel cell with a polymeric electrolyte membrane (PEM) had been chosen by most of the automotive companies as the power source for future vehicles, however, Bohn et al. (2008) wrote that the level of CO contamination for the hydrogen used in a PEM fuel cell must be kept below ~50 ppm, so as not to poison the platinum clusters on the anode. Therefore, only the hydrogen yielded by Fe₂O₃/Al₂O₃ and Fe₂O₃/CeO₃ can meet the requirement. However, the H₂ yield for Fe₂O₃/Al₂O₃ was lower and the reduction rate from the 3rd to 10th cycle was 19.0%, versus 5.0% for that of Fe₂O₃/CeO₃. To sum up, Fe₂O₃/CeO₃ was the most suitable oxygen carrier for H₂ production with consideration of H₂ yield and purity in CLHG.
REACTIVITY AND REDOX STABILITY

The reactivity and stability of Fe$_2$O$_3$/CeO$_2$ was investigated, since Fe$_2$O$_3$/CeO$_2$ showed the best performance, by comparing the CO$_2$ concentration for the reduction stage in redox cycles. As can be seen in Fig.4, the peak values of CO$_2$ concentration decreased from 16.6% to 14.9% from the 1st to 3rd cycle, but those for the 3rd and 10th cycles were very close to each other, and the CO$_2$ concentration curves were almost the same, which indicated the satisfactory stability of reactivity for Fe$_2$O$_3$/CeO$_2$. It can also be found in Fig.4 that the CO$_2$ concentration at the end of the reduction stage in the 3rd and 10th cycles was higher than that in the 1st cycle, with the highest one in the 10th cycle. This phenomenon can be attributed to the perovskite-type CeFeO$_3$ formed in the redox cycles, which could intensify the oxygen mobility, promoting the reactivity of Fe$_2$O$_3$/CeO$_2$, counteract the negative impact originating from sintering and guarantee the stability of Fe$_2$O$_3$/CeO$_2$, as can be found in (Zhu et al., 2014b).

Fig. 4. CO$_2$ concentration in reduction stage for Fe$_2$O$_3$/CeO$_2$ in the 1st, 3rd and 10th cycles at 850°C

MORPHOLOGY AND COMPONENTS

The oxygen carrier Fe$_2$O$_3$/CeO$_2$ was further investigated in view of morphology and components by SEM and XRD. The SEM and XRD analysis of Fe$_2$O$_3$/CeO$_2$ are shown in Fig. 5 and Fig. 6, respectively. As can be seen in Fig.5, grains with a size of 0.2–0.5μm over the surface of the particles led to the porous structure for fresh oxygen carrier, however, smaller grains agglomerated together and sintering occurred after redox cycles, blocking the pores and preventing sufficient contact between reactant gas and oxygen carrier. Nevertheless, the oxygen carrier still kept high reactivity and H$_2$ yield along with the redox cycles due to the reducible support, CeO$_2$, as shown in Fig.2 and Fig.4.

Fig.5. SEM images of the oxygen carrier Fe$_2$O$_3$/CeO$_2$

Fig.6 shows XRD patterns of Fe$_2$O$_3$/CeO$_2$. In its fresh state, only Fe$_2$O$_3$ and CeO$_2$ existed. After air oxidation in the 10th cycle, the intensity of CeO$_2$ decreased seriously, indicating the iron enrichment on the oxygen carrier surface, which promoted sintering. The XRD pattern of Fe$_2$O$_3$/CeO$_2$ for the reduction state verified not only the existence of Fe and FeO, but also CeFeO$_3$, which could intensify the oxygen mobility and promote the reactivity of Fe$_2$O$_3$/CeO$_2$, just as the illustration in Fig.4.
CONCLUSIONS
Three Fe-based oxygen carriers, supported by Al₂O₃, ZrO₂ and CeO₂, were prepared by co-precipitation and investigated in a batch fluidized bed at 850°C using CO as fuel for CLHG. The conclusions were drawn as below. (1) The properties of the oxygen carriers, e.g. reactivity and stability, mainly depended on the support and its interaction with iron oxides; (2) The reactivity and H₂ yield for the oxygen carriers followed the sequence: Fe₂O₃/ZrO₂ > Fe₂O₃/CeO₂ > FeO/Al₂O₃, however, the resistance to carbon deposition followed the reverse sequence: Fe₂O₃/Al₂O₃ > Fe₂O₃/CeO₂ > Fe₂O₃/ZrO₂; Fe₂O₃/CeO₂ was the most suitable one for CLHG with the consideration of H₂ yield and carbon deposition in CLHG; (3) Fe₂O₃/CeO₂ suffered sintering in redox cycles, but it still kept high reactivity, redox stability and H₂ yield; (4) XRD analysis verified the iron enrichment on the oxygen carrier surface, which promoted sintering, and the formation of perovskite-type CeFeO₃ that could guarantee the reactivity and stability of Fe₂O₃/CeO₂.

ACKNOWLEDGEMENTS
The authors gratefully express thanks to the National Natural Science Foundation of China (51576042), National Program on Basic Research Project (2016YFB0600802), and Natural Science Foundation of Jiangsu (BK20160672) for financial support of this research.

NOTATION
$F$  gas flow rate, L/min  $X$  gas volume concentration, %
$V$  volume, L  $u_g$  gas velocity, m/s
$u_{mf}$  minimum fluidized velocity, m/s  $a_{H_2}$  H₂ purity, %

REFERENCES


