

# Reaction characteristics research of coal char chemical looping gasification for hydrogen production with an Fe-Zr oxygen carrier modified by $K_2CO_3$

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**Abstract:** An Fe-Zr oxide ( $Fe_2O_3$  and  $ZrO_2$ ) modified by  $K_2CO_3$  was prepared as the oxygen carrier (denoted as K3-Fe70Zr30) to examine the effects of temperature and char mass/oxygen carrier (OC) ratio on gas yield and composition during coal char chemical looping gasification for hydrogen production. The results of temperature-programmed experiments show that the reaction of oxygen carrier and coal char starts at 500°C, and the reaction rate increases sharply above 750°C. The reduced oxygen carrier begins to react with steam at 400°C, and the concentration of hydrogen significantly increases above 500°C. The results of isothermal experiments indicate that the reaction rate is accelerated with increasing reaction temperature. However, the  $H_2$  production yield decreases as the temperature rises when the ratio of  $CO/CO_2$  volume ratio increases. In addition, with the increase of char/OC ratio, the ratio of  $CO/CO_2$  in the outlet gas increases. As a result, the hydrogen production firstly increases and reaches a maximum value of 1.734 L/g, and then decreases. The activity of oxygen carrier can keep stable during the first 2 redox cycles, but decreases in the 3rd one. The activity can be renewed by the supplement of  $K_2CO_3$ , suggesting that the decreased activity of oxygen carrier can ascribe to the loss of  $K_2CO_3$ .

**Key words:** oxygen carrier;  $K_2CO_3$ ; coal char;  $H_2$  production

Hydrogen is an important energy carrier which could meet the sustainable development of both the resource and environment. The industrial processes of  $H_2$  production mainly consist of coal gasification, steam methane reforming, and water electrolysis<sup>[1–3]</sup>. However,  $H_2$  production from these processes presents several drawbacks. For example, the coal gasification has the disadvantages of high investment, long process flow, and low efficiency<sup>[4]</sup>. The steam methane reforming is also restricted by several factors including limited resource, vast water consumption, and severe requirements of equipment material. The energy cost of water electrolysis for  $H_2$  production is too large. Therefore, it is important to explore an efficient and reasonable way for  $H_2$  production from consideration of environment protection and reasonable resource utilization.

Zeng et al<sup>[5–8]</sup> simulated the energy efficiency of chemical looping gasification for hydrogen production. It is found that this process has significant advantages in the aspect of environment protection and energy conversion efficiency in

comparison with other processes. The simulation result of Aspen Plus revealed that the chemical looping hydrogen process from coal is superior to that from syngas in efficiency and equipment investment. The hot efficiency of chemical looping for hydrogen production by using coal could reach 78%, which was 30% higher than that of hydrogen production from coal gasification. Besides, this process could capture 90% of carbon dioxide<sup>[5]</sup>. Yang et al<sup>[9]</sup> tried to evaluate the chemical looping for hydrogen production with a fluidized bed reactor. The result showed that iron-based oxygen carriers could meet the requirements of chemical looping for hydrogen production, but the process efficiency was not high. The moving bed reactor was more suitable for this process proposed by Fan et al<sup>[6]</sup>, by which  $Fe_2O_3$  is reduced to FeO and Fe, and the concentration of  $CO_2$  is very high in outlet for cheap capturing. However, few experimental data were provided to validate the simulation results.

The chemical looping process for hydrogen production consists of three steps, as shown in Figure 1.

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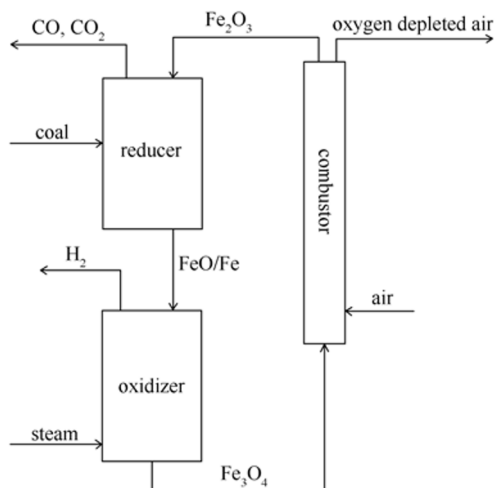
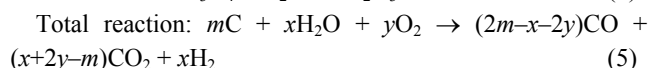
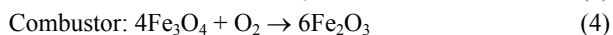
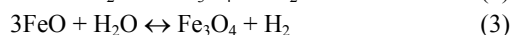
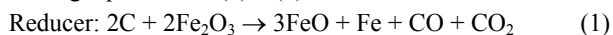


Fig. 1 Schematic diagram of chemical looping hydrogen production from coal based on iron oxide oxygen carrier

Firstly,  $\text{Fe}_2\text{O}_3$  is reduced to  $\text{FeO}$  and  $\text{Fe}$  by coal char in reduction reactor. Secondly,  $\text{FeO}$  and  $\text{Fe}$  are oxidized to  $\text{Fe}_3\text{O}_4$  by steam in oxidation reactor, releasing  $\text{H}_2$  at the same time. Finally, oxygen carrier is oxidized back to  $\text{Fe}_2\text{O}_3$  by air in combustion reactor. The main reactions are shown as following equations of (1) – (5):



The reaction rate of the oxygen carrier with solid fuel is very slow, so it is difficult to meet the requirements of industrial use. We proposed a means to add a catalyst into iron-based oxygen carrier in chemical looping based on our previous work<sup>[10–13]</sup>. It can be found that the reaction rate increased greatly with the addition of  $\text{K}_2\text{CO}_3$ , in fact the reaction ( $\text{C} + \text{CO}_2 \leftrightarrow 2\text{CO}$ ) was promoted by  $\text{K}_2\text{CO}_3$ . Thus,  $\text{K}_2\text{CO}_3$  was proved to be an efficient catalyst. Yu et al<sup>[13]</sup> conducted a more detailed study on the mechanism of chemical looping for gasification, but there is no data provided about the gas concentration in every section and the phase change in hydrogen production.

In this work, the effects of temperature and feed ratio on coal char direct chemical looping for hydrogen production with an Fe-Zr oxygen carrier modified by  $\text{K}_2\text{CO}_3$  was

comprehensively studied. In addition, the cycle performance of oxygen carrier was also investigated to provide foundation for the development of chemical looping gasification process.

## 1 Experimental

### 1.1 Preparation of oxygen carrier

The preparation of oxygen carrier can be referred to the literature<sup>[12]</sup>. The composite oxide with 70%  $\text{Fe}_2\text{O}_3$  and 30%  $\text{ZrO}_2$  is synthesized firstly. Then,  $\text{K}_2\text{CO}_3$  is immersed in the above composite oxide, and dried at  $110^\circ\text{C}$  until the constant weight. The ratio of  $m(\text{K}_2\text{CO}_3)/m(\text{Fe70Zr30})$  is 3%, and the oxygen carrier is denoted as K3-Fe70Zr30 for simplicity. Finally, it is ground to less than 0.15 mm for use.

### 1.2 Experimental materials

A Shenmu (SM) bituminous coal char (<0.15 mm) pyrolyzed at  $900^\circ\text{C}$  was used as the solid fuel. Proximate and ultimate analyses of Shenmu (SM) char is shown in Table 1.

### 1.3 Experimental apparatus

Figure 2 shows the schematic diagram of the fixed bed reactor of chemical looping for hydrogen production. The device consists of a horizontal quartz tube reactor, temperature and mass flow controller, steam generator and gas chromatography. The nitrogen (purity 99.99%) is used as protective gas and carrying gas in the reducer and oxidizer. The steam entering the reactor is controlled by water pump, and the water flowrate is 5 mL/h. The oxygen carrier is regenerated by air in the last step with air flowrate of 100 mL/min.

The gas composition was analyzed by gas chromatography (Haixin GC-950C). The X-ray diffraction (XRD) patterns of the reduction residue were obtained by using X-ray powder diffractometer (Bruker AXS D8 Advance), which was operated with  $\text{Cu K}\alpha$  radiation and a step size of  $0.02^\circ$  at a scanning speed of  $5^\circ/\text{min}$  from  $10^\circ$  to  $80^\circ$ . Field-emission scanning electron microscopy (FE-SEM, JSM-7001F) was applied to examine the sintering morphology of the oxygen carriers.

Table 1 Proximate and ultimate analyses of Shenmu (SM) char

Sample	Proximate analysis $w_{\text{ad}}/\%$				Ultimate analysis $w_{\text{daf}}/\%$				
	$V$	$M$	$A$	FC	C	H	$\text{O}^*$	N	$\text{S}_t$
SM char	1.27	0.68	19.30	78.75	93.81	1.23	3.19	1.06	0.71

\*: by difference

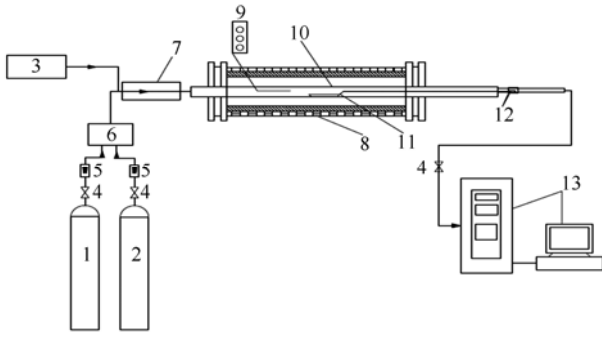


Fig. 2 Schematic diagram of the fixed bed reactor

1: N<sub>2</sub> cylinder; 2: air cylinder; 3: plunger pump; 4: stop valve;  
5: flowmeter; 6: premixer; 7: steam generator; 8: heating furnace;  
9: thermocouple and temperature controller; 10: quartz tube;  
11: alumina boat; 12: magnet; 13: gas chromatography

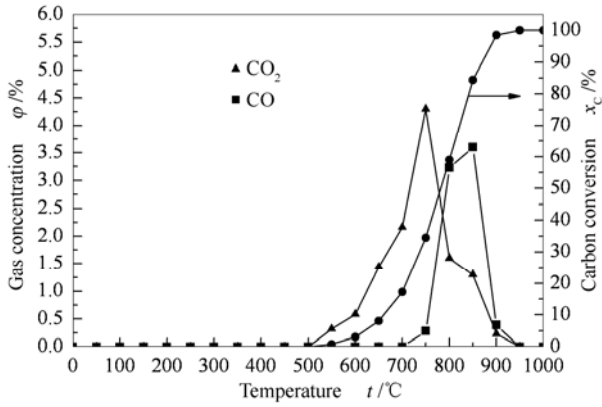


Fig. 3 Export gas concentration and carbon conversion as a function of temperature

The amount of CO and CO<sub>2</sub> generated per minute is calculated by:

$$n_{i,t}(\text{mol/min}) = \frac{\varphi_i \times q_{v,N_2}}{(1 - \varphi_{CO} - \varphi_{CO_2}) \times 22.4} \quad (6)$$

$i = \text{CO}, \text{CO}_2$ ,  $\varphi_i$  is the concentration of CO or CO<sub>2</sub> (by volume) in exit gas,  $q_{v,N_2}$  is the inlet flowrate of N<sub>2</sub>.

The whole amount of CO or CO<sub>2</sub> in  $t$  minutes is calculated by:

$$n_i(\text{mol}) = \int_0^t n_{i,t} dt \quad (i = \text{CO}, \text{CO}_2) \quad (7)$$

The carbon conversion of coal char is defined as:

$$x_C = \frac{n_{CO} + n_{CO_2}}{n_{C, \text{char}}} \times 100\% \quad (8)$$

Where  $n_{C, \text{char}}$  is the amount of fixed carbon in coal char.

The ratio of hydrogen production in  $t$  minutes is defined as:

$$y_t = \frac{\int_0^t n_{H_2,t} dt}{\int_0^\infty n_{H_2,t} dt} \times 100\% \quad (9)$$

The total hydrogen production yield is defined as:

$$H_2 \text{ production yield (L/g)} = \text{volume of } H_2 \text{ in oxidizer / mass of SM char in reducer} \quad (10)$$

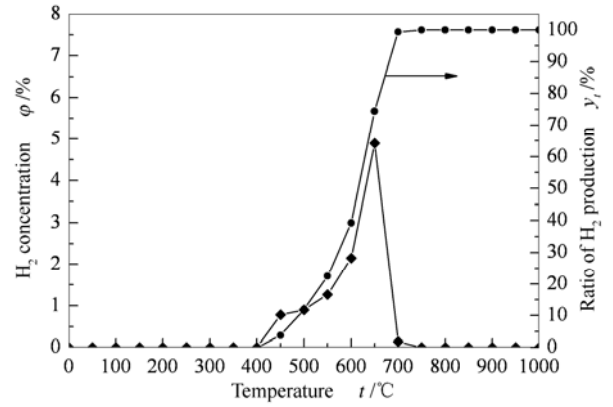


Fig. 4 H<sub>2</sub> concentration and the ratio of H<sub>2</sub> production as a function of temperature

## 2 Results and discussion

### 2.1 Effect of temperature

#### 2.1.1 Temperature-programmed experiments

Figure 3 shows exit gas concentration and carbon conversion as a function of temperature in the reducer heated at 5°C/min. As shown in Figure 3, the oxygen carrier starts reacting with coal char at 500°C, and the carbon conversion increases sharply at 750°C, which is consistent with literature<sup>[9]</sup>. It facilitates the formation of CO<sub>2</sub> from 500 to 700°C because the generation rate of CO is lower than the oxidation rate of CO by iron oxide, while the concentration of CO<sub>2</sub> decreases and CO increases above 700°C. As the temperature increases, the rate of CO production is accelerated significantly and the fresh iron-oxide is depleted, leading to the high content of CO in the bed. The carbon conversion of char reaches to 100% above 900°C, indicating the char reaction with oxygen carrier is complete.

Figure 4 shows H<sub>2</sub> concentration and ratio of H<sub>2</sub> production as a function of temperature in the oxidizer heated at 5°C/min. The reduced oxygen carrier starts reacting with steam at 400°C. With the increasing of temperature, H<sub>2</sub> concentration increases sharply above 500°C. The ratio of hydrogen production is up to 100% at 700°C, indicating that the reduced oxygen carrier is oxidized by steam completely.

#### 2.1.2 Isothermal experiments

The isothermal experiments were conducted using rapid heating method. Porcelain boat containing samples was quickly put into the central area of furnace (in N<sub>2</sub> atmosphere) to elevate the temperature to the testing values (800, 850, and 900°C) shortly. Figure 5 shows the gas concentration during the experiments at char/Fe<sub>2</sub>O<sub>3</sub> = 1:7 against temperatures. It is clear that the temperature has a positive influence on these reactions.

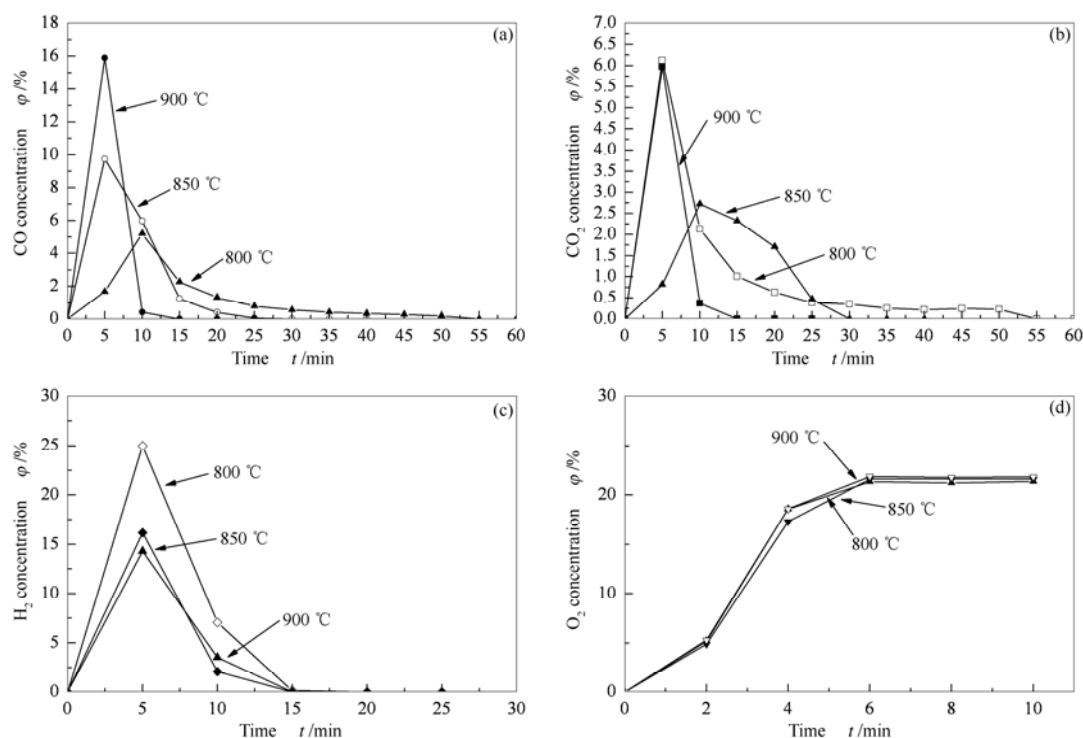


Fig. 5 Gas concentration during the fixed experiment at different temperatures

(a) and (b): oxygen carrier react with char directly; (c): reduced state of oxygen carrier react with steam; (d): oxygen carrier regenerate at air

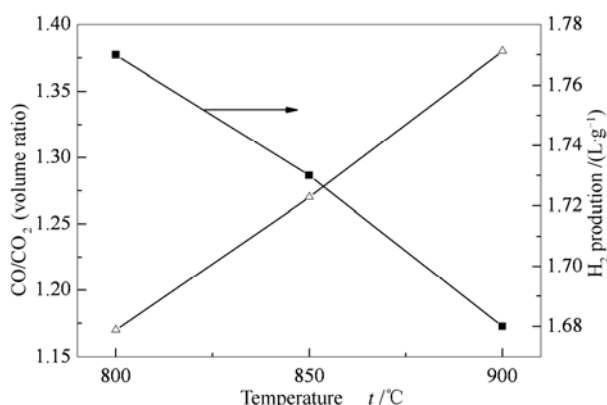


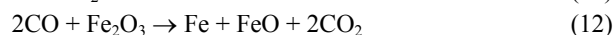
Fig. 6 Volume ratio of CO/CO<sub>2</sub> and H<sub>2</sub> production as a function of temperature

As shown in Figure 5(a) and (b), the time of oxygen carrier completely reacting with SM char is 55 min at 800°C, 30 min at 850°C, and 15 min at 900°C respectively. It indicates that the reaction rate of oxygen carrier with SM char increases with temperature, and the reaction time becomes short. The main reason is that SM char reaction with oxygen carrier is endothermic, and high temperature is favorable for the reaction. However, Figure 5(c) shows that the maximum of hydrogen concentration decreases with temperature. The increase in reducer temperature could have considerable negative effects on the FeO and Fe reacting with steam. It is in agreement with the thermodynamic law to the exothermic reactions of Eq.(2)–(3). On the other hand, the reaction rate

can be improved at higher temperatures. Therefore an appropriate temperature range should be chosen for practical use. In addition, the time of complete reaction at three temperatures is all about 15 min for H<sub>2</sub> production, and the reaction rate is fast.

Figure 5(d) shows that the reaction is quite fast at 800–900°C. The curves of oxygen carrier regeneration at air atmosphere at three temperatures are overlapped. In about 10 min the O<sub>2</sub> concentration in exit gas is consistent with the O<sub>2</sub> concentration in air.

Figure 6 shows the ratio of CO/CO<sub>2</sub> and H<sub>2</sub> production changes with temperature. With the increase of temperature, the ratio of CO/CO<sub>2</sub> increases at the first step, but H<sub>2</sub> production decreases at the second step. It was demonstrated by our previous studies<sup>[10–13]</sup> that oxygen carrier reacting with char includes two reactions:



When the temperature is low, the reaction (12) is easy to carry on from the point of thermodynamics, resulting in the formation of CO<sub>2</sub>, and the oxygen carrier is reduced extensively. However, higher temperature has a positive effect on reaction (11), leading to the formation of CO. Figure 6 indicates that the ratio of CO/CO<sub>2</sub> increases with temperature. When the amount of char is fixed, CO increasing leads to decrease of CO<sub>2</sub>. In other words, the remaining oxygen atom in the oxygen carrier reduces (more FeO and less Fe), resulting in the decrease in H<sub>2</sub> production.

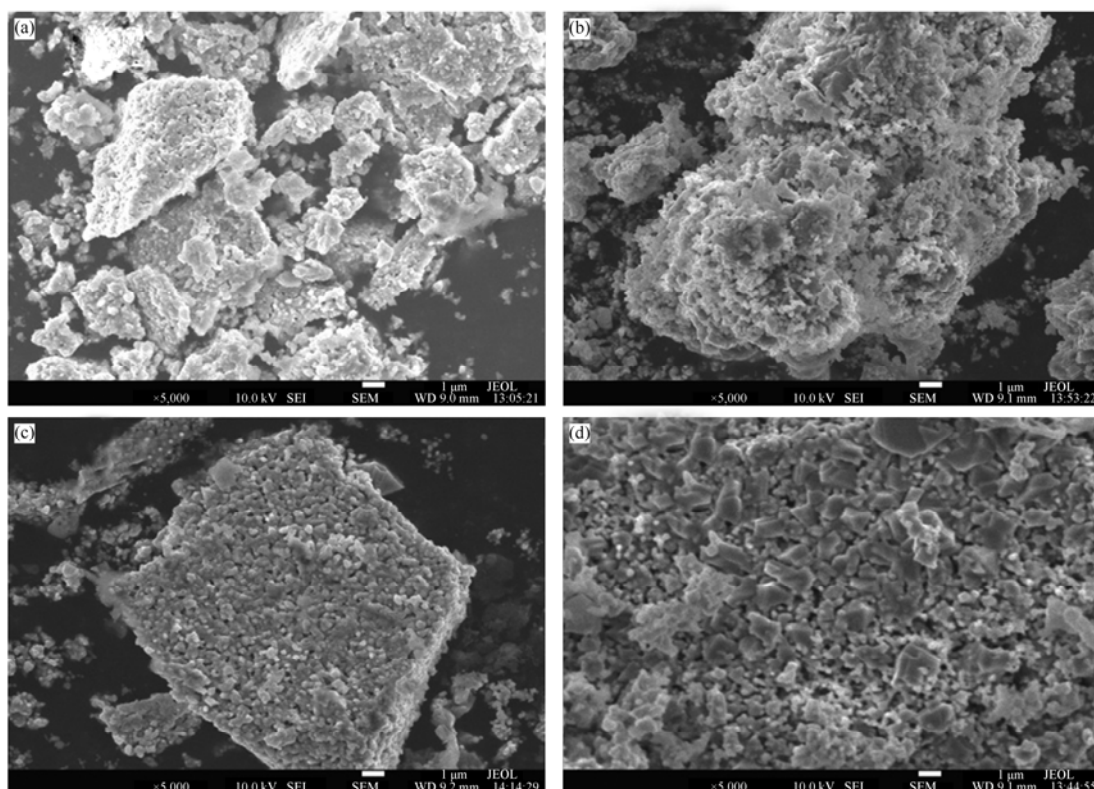


Fig. 7 SEM images of K3-Fe70Zr30 oxygen carrier

(a): fresh and after one recycle at different temperatures; (b): 800°C; (c): 850°C; (d): 900°C

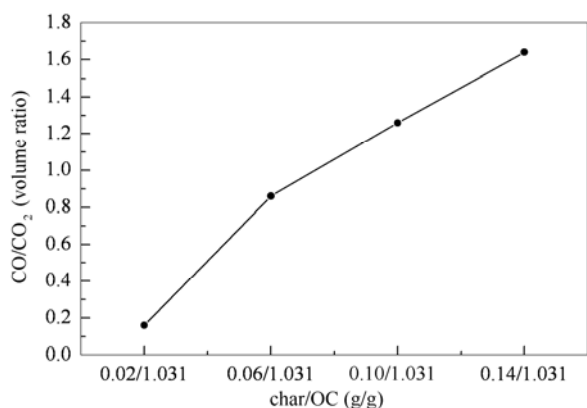


Fig. 8 Volume ratio of CO/CO<sub>2</sub> as a function of char/OC ratio

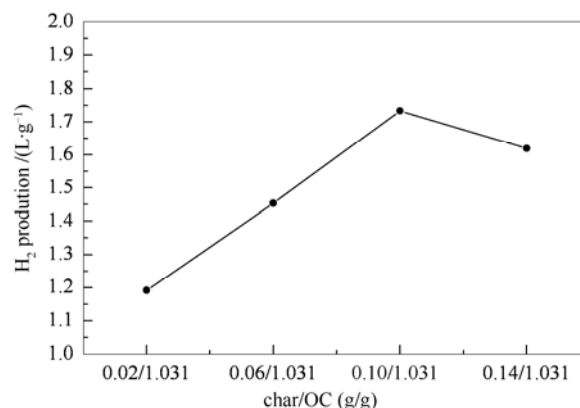


Fig. 9 Hydrogen production as a function of char/OC ratio

The reaction rate increases with the increase of temperature, but high temperature would lead to the sintering of oxygen carrier because the melting temperature of K<sub>2</sub>CO<sub>3</sub> is 891°C. Figure 7 shows some SEM images of K3-Fe70Zr30 oxygen carrier about fresh and after one recycle at different temperatures. The oxygen carrier maintains small grain size morphology after one recycle at 800 and 850°C, but the grain size of oxygen carrier grows a lot with recycling at 900°C. This is obviously caused by the sintering at higher temperature. Since the sintering of oxygen carrier is well-observed, the rest of other factors are investigated at 850°C in the subsequent experiments.

## 2.2 Effects of Char/K3-Fe70Zr30 on reaction characteristics

Figure 8 shows the volume ratio of CO/CO<sub>2</sub> as a function of char/OC ratio at 850°C. The volume ratio of CO/CO<sub>2</sub> increases with the increase of char/OC ratio. As oxygen atom in oxygen carrier is fixed, the increase of the amount of SM char results in the formation of CO and the increase in ratio of CO/CO<sub>2</sub>.

Figure 9 shows the H<sub>2</sub> production yield as a function of char/OC ratio. Firstly, the H<sub>2</sub> production yield increases, having a maximum value of 1.734 L/g.

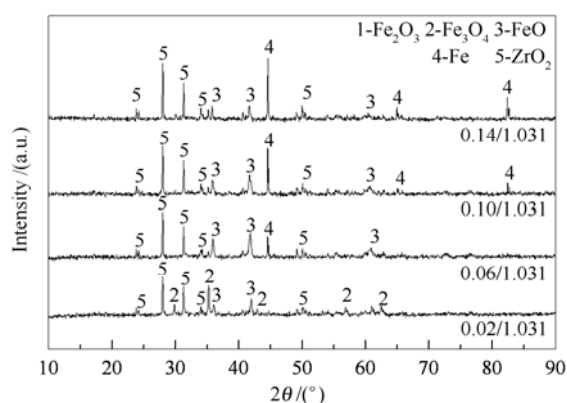


Fig. 10 XRD patterns of reduction residue of OC by SM char

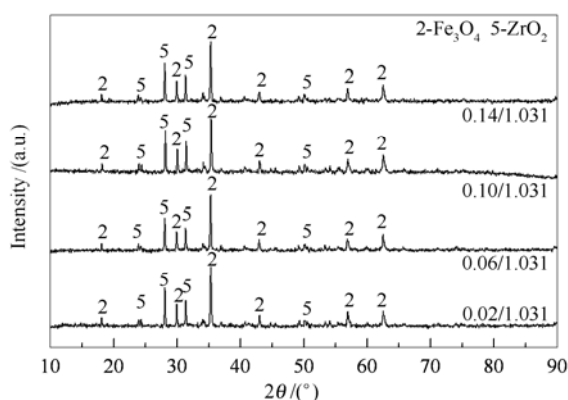


Fig. 11 XRD patterns of OC after steam oxidation

After that it decreases with increasing amount of SM char. This can be explained as follows: the reduction sequence of  $\text{Fe}_2\text{O}_3$  in oxygen carrier is  $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$ . Figure 10 shows the XRD patterns of reduced OC by SM char. The reduction degree of  $\text{Fe}_2\text{O}_3$  is enhanced with increasing char/OC ratio. The phase of oxygen carrier becomes stable after char/OC exceeds 0.10 g/1.031 g. Figure 11 is the XRD patterns of OC converting to  $\text{Fe}_3\text{O}_4$  after steam oxidation. The reduction degree of  $\text{Fe}_2\text{O}_3$  increases as a function of char/OC ratio from 0.02 g/1.031 g to 0.10 g/1.031 g, and more  $\text{Fe}_2\text{O}_3$  turns into Fe, so the volume of hydrogen increases by steam oxidation. However, when the ratio of char/OC reaches 0.14 g/1.031 g, the phase of oxygen carrier becomes stable comparing with the case of 0.10 g/1.031 g, and the volume of  $\text{H}_2$  determined by the amount of Fe and FeO increases little. Also, the increase of raw coal char, i.e., the increase of denominator of reaction (10), leads to the decrease of  $\text{H}_2$  production.

### 2.3 Multi-cycle reaction of OC for $\text{H}_2$ production

Figure 12 shows the carbon conversion and  $\text{H}_2$  production yield as a function of cycle number at  $850^\circ\text{C}$  when  $\text{Fe}_2\text{O}_3/\text{char}$  ratio is 7:1 in the mixture of OC and SM char.

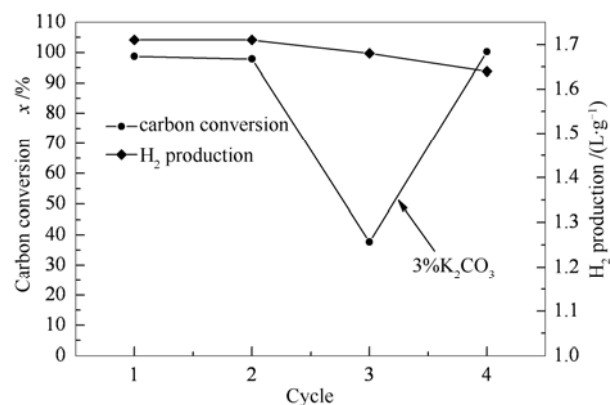
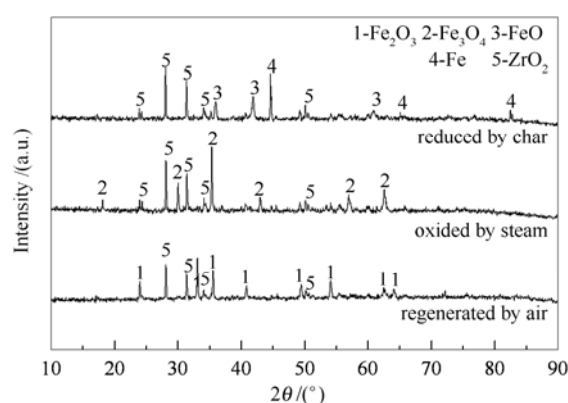

Fig. 12 Carbon conversion and  $\text{H}_2$  production as a function of cycle


Fig. 13 XRD patterns of OC in one cycle

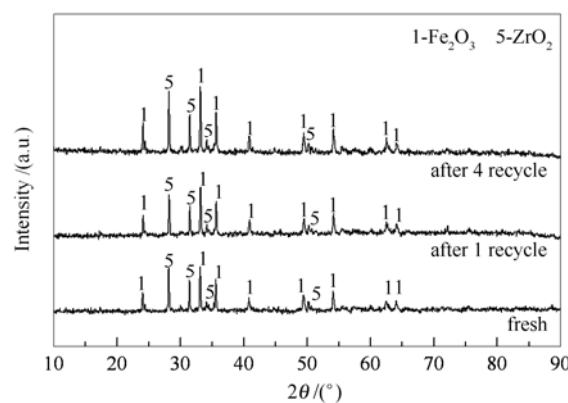


Fig. 14 XRD patterns of OC after several cycles

The activity of oxygen carrier keeps stable during the first 2 redox cycles, but decreases in the 3rd one. The  $\text{H}_2$  production yield does not decrease significantly, and CO and  $\text{CO}_2$  are detected in the oxidizing process with steam, indicating that the steam not only reacts with the reduced OC, but also with the residual char.

In order to investigate the reasons of decrease in the activity of OC, 3%  $\text{K}_2\text{CO}_3$  is added to the OC after 3 cycles. Figure 12 illustrates that the activity can be renewed by supplement of  $\text{K}_2\text{CO}_3$ , implying that the decreased activity can attribute to

the loss of  $K_2CO_3$ <sup>[13]</sup>.

Figure 13 shows the XRD patterns of OC in one cycle. The phase of OC during reactions is consistent with equation (1) to (4). Figure 14 is the XRD patterns of OC after several cycles. The OC after regeneration is the same as the initial OC, confirming that the phase of OC does not change after several cycles.

### 3 Conclusions

The temperature-programmed experiments reveal that the reaction of oxygen carrier and coal char starts at 500°C, and the reaction rate becomes rapid above 750°C. The reduced oxygen carrier begins to react with steam at 400°C, and the concentration of hydrogen significantly increases above 500°C. The isothermal experiments indicate that the reaction rate is accelerated with increasing reaction temperature. However, the ratio of CO/CO<sub>2</sub> increases, resulting in the decrease of H<sub>2</sub> production with increasing temperature. In addition, the ratio of CO/CO<sub>2</sub> increases with the increase of char ratio. Therefore, the hydrogen production firstly increases and then decreases. The activity of oxygen carrier keeps stable during the first 2 redox cycles, but decrease in the 3rd one. Its activity can be renewed by supplement of K<sub>2</sub>CO<sub>3</sub>, suggesting that the decreased activity can ascribe to the loss of K<sub>2</sub>CO<sub>3</sub>.

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