Experimental Study on Reaction Characteristic of Lignite CLC with NiFe$_2$O$_4$ as Oxygen Carrier

Yong LIU[1, a*], Wu QIN[2,b]

[1]Yancheng Polytechnic of Jiangsu, Yancheng 224002, China

[2]School of Renewable Energy Engineering, North China Electric Power University, Beijing 102206, China

[a]ycliuyong@qq.com, [b]qinwugx@126.com

*Corresponding author

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Abstract. In this work, NiFe$_2$O$_4$ was prepared as oxygen carrier (OC) and its redox performance with lignite was systematically studied by thermogravimetric analyzer (TGA) experiments. Surface structures of the fresh and reduced NiFe$_2$O$_4$ were characterized by SEM, BET, and XRD methods. In comparison with NiO and Fe$_2$O$_3$, the presence of Ni in the NiFe$_2$O$_4$ complex increases the specific surface and pore volume, enhancing its reactivity and oxygen transfer capacity during lignite CLC. Further, multi-cycles experiments confirmed the stability of high reactivity of NiFe$_2$O$_4$.

Introduction

Chemical-looping combustion is a novel and efficient technology to realize low cost CO$_2$ capture because of its unique CO$_2$ inherent separation characteristic [1]. As extra advantages, it can also reduce NOx emissions [2] by decreasing the combustion temperature compared to the conventional combustion model, and enhance the efficiency of energy utilization [3].

In CLC system, oxygen carrier (OC) plays an critical role of transferring oxygen and heat to maintain an excellent CLC performance. Thus, developing an efficient, good mechanical strength, low cost, and environmentally friendly OC is vital to realize industrial application of CLC. So far, some transition metal oxides (Ni, Cu, Cd, Mn, Fe, and Co oxides) have attracted great attentions of researchers. As for the aspect of CLC fuel, solid fuel used to direct CLC has been an investigation hotspot for the rich solid fuels resources [4], and its feasibility has been confirmed by lots of experiments.

To date, Fe$_2$O$_3$ has been commonly used as OC for its advantages of low cost, high mechanical strength and thermal stability, and good environmental friendliness [5]. Nevertheless, compared with NiO, CuO, *et al.*, iron oxide presents lower redox reactivity. To enhance its reactivity, that combined iron oxide with other components (Co, Ni, Cu, et al.) is an effective method, and many investigations confirmed the enhanced performance of CuFe$_2$O$_4$, BaFe$_2$O$_4$, CoFe$_2$O$_4$, et al [6]. NiO is such an oxide with excellent reactivity, whereas the high cost and toxicity restrict its large-scale application [7]. Therefore, we put forward to synthesize the nickel-iron combined OC, and then investigate its redox performance and stability with lignite by TGA experiments, the structure of which was further characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), and Brunauer–Emmett–Teller (BET). As for comparisons, the reaction characteristics of Fe$_2$O$_3$ and NiO with lignite were also investigated. This study can provide a fundamental understanding of the performance of NiFe$_2$O$_4$ OC and the reaction mechanism of NiFe$_2$O$_4$ with lignite, and make a preparation for large-scale application of NiFe$_2$O$_4$ in CLC with lignite as fuel.

Experimental Details

Materials and OC Preparation

The hydrothermal synthesis method was adopted to prepare NiFe$_2$O$_4$ OC in present work, and the detailed procedures were as follows. Firstly, dissolve certain Ni(NO$_3$)$_2$ 6H$_2$O and

Fe(NO$_3$)$_3$ 9H$_2$O (the mole ratio of 2:1) into deionized water and then slowly add NaOH aqueous solution until the PH of the solution was 9. The sediment was obtained by filtered and washed by deionized water several times. Subsequently, put the obtained products into high pressure reaction kettle and add appropriate deionized water and DTAB, and then maintain the temperature to 200 ˚C˚ for 4 hours. After cooled down to room temperature, filtered and dried, the NiFe$_2$O$_4$ powder was obtained. Finally, collect OC particles of 0.1 mm - 0.2 mm for further TGA experiments and characterizations. For comparisons, the referenced Fe$_2$O$_3$ and NiO OCs were synthesized by the same method. The proximate and ultimate analyses of lignite were conducted and results are listed in Table 1.

Tab. 1 Proximate and ultimate analysis of lignite

Proximate analysis [wt.%]				Ultimate analysis [wt.%]				
M_{ad}	V_{ad}	A_{ad}	F_{ad}	C_{ad}	H_{ad}	O_{ad}	N_{ad}	S_{ad}
12.569	23.885	22.958	40.588	50.380	4.135	22.142	0.670	0.385

M: moisture content; *V*: volatile matters; *A*: ash content; *F*: fixed carbon; ad: air-dried basis.

TGA and Characterization Methods

Firstly, put 20 mg mixture of the synthesized OCs and lignite with mass ratio of 27:1 sample to the ceramic pan of the simultaneous thermogravimetric analyzer (SAT6000, Perkin). Adjust the carrier gas (N$_2$) flow rate to 40 mL/min, and heat from ambient to 120 ˚C at 40 ˚C/min with duration at this temperature for 10 min to eliminate moisture. And then further heat up to 850 ˚C and keep 20 min to ensure sufficient reaction. The CLC reactions of coal and referenced Fe$_2$O$_3$ and NiO OCs were also conducted under the same conditions for comparison. The conversion rate (*X*) of OCs was calculated by following equation:

$$X = \frac{m_{ox} - m}{m_{ox} - m_{red}}$$

(1)

where *m* refers to the actual mass of sample, m_{ox} is the mass of the sample when it was fully oxidized, and m_{red} is the mass of the sample in its fully reduced state.

Moreover, the surface structure properties of fresh OCs and solid product of TGA reactions were characterized by using SEM, XRD, and BET methods.

Fig. 1 displays the XRD spectrum of the fresh prepared OCs (NiFe$_2$O$_4$, NiO, and Fe$_2$O$_3$), results show that we have successfully synthesized the nickel iron combined OC with only containing Ni-Fe spinel structure.
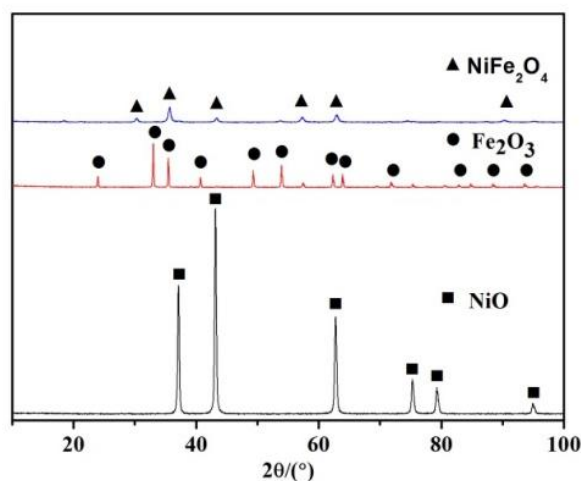

Fig. 1 XRD spectrum of the fresh NiFe2O4 OC

Results and Discussion

Reactivity of OCs

The CLC performances of the synthesized OCs ($NiFe_2O_4$, Fe_2O_3 and NiO) were investigated by TGA experiments, and results of TG and DTG curves are shown in Fig. 2. From Fig. 2, the net mass loss of LZ reaction with NiO is 26.30% and much higher than that of lignite with Fe_2O_3 as 2.73%, suggesting the superior reactivity of NiO than that of Fe_2O_3 during the CLC process of lignite. Whereas, the weight loss of mixture with adding $NiFe_2O_4$ is 14.37%, which is much higher than that of Fe_2O_3 while inferior to the sample with NiO, indicating the reactivity of the Fe_2O_3 OC has been effectively enhanced by combined Ni component. It is worth noting that a slight weight gaining occurs in the TGA curve with NiO OC, which may be caused by the serious carbon deposition on NiO surface [8].
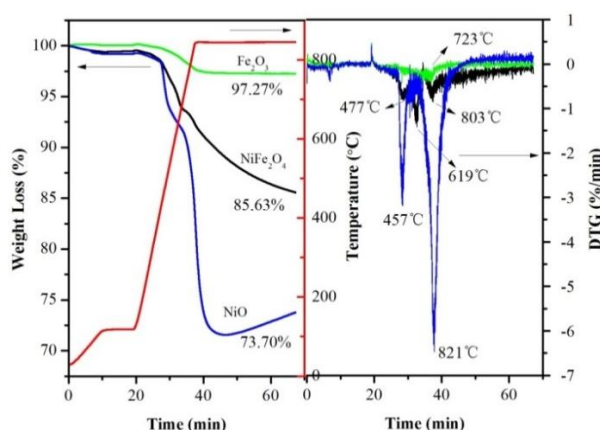

Fig. 2 CLC experiments of $NiFe_2O_4$, Fe_2O_3 and NiO with lignite

The specific weight loss rate of these three samples can be found in DTG curves. Results show that two distinct characteristic temperatures can be observed during the CLC of lignite with NiO, with large reaction rate of 3.6 Wt.%/min and 6.5 Wt.%/min at 457 ˚C and 821 ˚C, respectively. While there is only one characteristic peak can be found after adding Fe_2O_3 OC with a small weight loss rate of 0.6 Wt.%/min at 723 ˚C, which is much lower than that of NiO, corresponding to the slight weight loss in TG curve and previous experiments [6]. Nevertheless, three reaction stages after addition of $NiFe_2O_4$ OC occur, with the reaction rate of 1 Wt.%/min, 1.8 wt.%/min, and 0.8 Wt.%/min at 477 ˚C, 619 ˚C, and 803 ˚C, respectively. Moreover, the conversion rates of OCs are calculated and illustrated in Fig. 3. Results show that the reaction starts from 432 ˚C, and the final conversion rate of $NiFe_2O_4$, Fe_2O_3 and NiO is 50.42%, 8.99%, and 107.11%, respectively, suggesting more lattice oxygen was transferred to fuel of $NiFe_2O_4$ than Fe_2O_3.
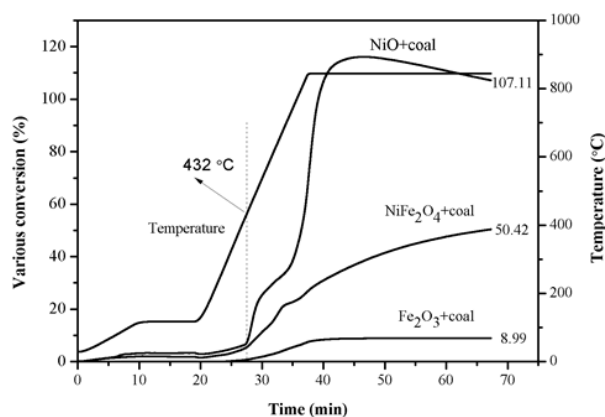

Fig. 3 The conversion rate of NiFe2O4, Fe2O3 and NiO OCs

Accordingly, combined Fe_2O_3 with NiO can improve its reactivity and oxygen transfer capacity. Based on the CLC system design theorem put forward by Mattisson [9], fewer OC inventory and lower OC transfer flow between the FR and AR would be required if $NiFe_2O_4$ were adopted as OC instead of Fe_2O_3.

In order to further study the oxidation property of $NiFe_2O_4$ OC, after reacted with lignite, the reduced OC was reoxidized by air in TGA and results are shown in Fig. 4. It can be found that the oxidation reaction of the reduced OC is much faster than the reduction reaction, whereas the weight of the regenerated OC is only around 90% of the initial mass, indicating the reduced OC cannot be fully reoxidized. This may be attributed to the adverse effect of coal ash, which covers the OC surface and inhibits the regeneration process. Apparently, after long running of CLC with coal, the ash will accumulate and further affect the fluidization and reactivity of OC. It is a great challenge to separate coal ash from OC during CLC with solid fuel, which needs researchers all over the world to continue to explore.
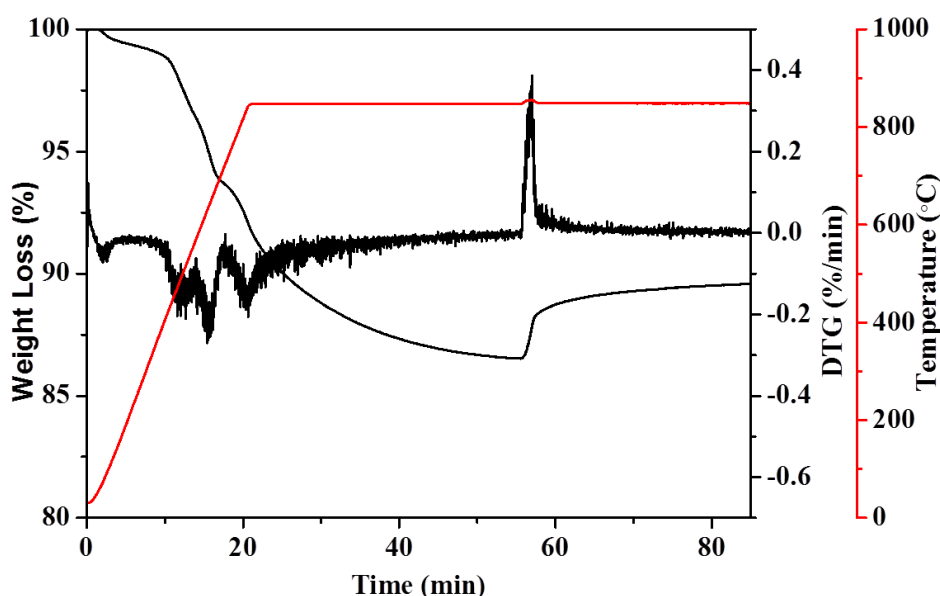

Fig. 4 The redox cycle experiment of $NiFe_2O_4$ OC with lignite

SEM Analysis

To further detect the micromorphology variation of OCs, SEM pictures of the fresh and reduced OCs after CLC reaction with lignite are displayed in Fig .5 (a ~ f). A slight agglomeration phenomenon occurs on the reduced NiO surface in Fig. 5b corresponding to the reported result [10], whereas no obvious difference can be found between the fresh and reduced OCs of $NiFe_2O_4$ and Fe_2O_3 (Fig. 5 c ~ f). These results are in good accordance to the BET values as listed in table 2, where a significant decrease of specific surface area and pore volume of NiO occurs, while the reduced $NiFe_2O_4$ shows comparable BET values to the fresh OC. As for the Fe_2O_3 OC, surface activation happens with slightly increasing its specific surface area and pore volume, which can be attributed to its excellent thermal stability. In addition, the combined Ni component in Fe_2O_3 can significantly increase its specific surface area and pore volume values, which will greatly reduce the resistance of coal pyrolysis products diffusing into oxygen carrier inner and promote the CLC reaction.
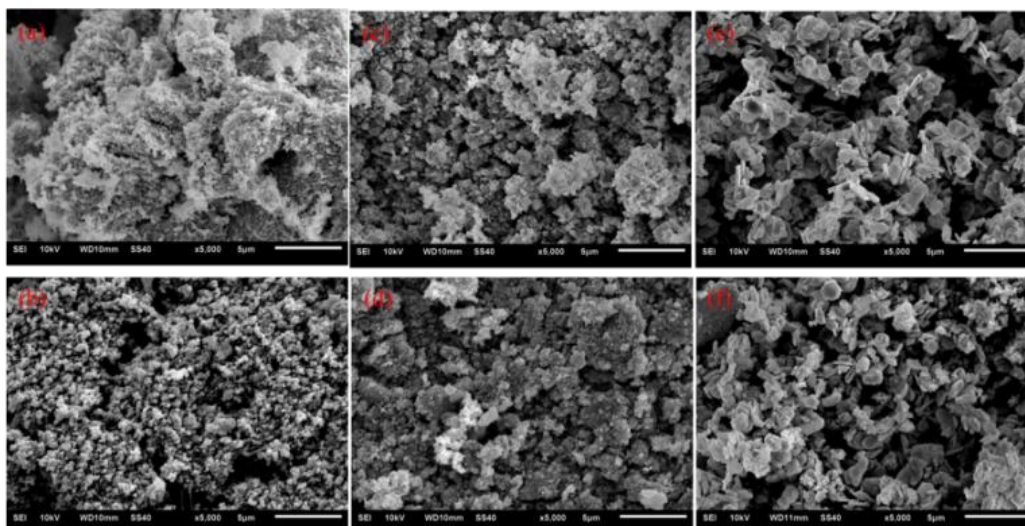
Fig. 5 SEM pictures of the fresh and reduced OCs, a, c, and e refer to the fresh NiO, NiFe$_2$O$_4$, and Fe$_2$O$_3$, respectively, while b, d, and f represent the reduced NiO, NiFe$_2$O$_4$, and Fe$_2$O$_3$, respectively

Tab. 2 the specific surface area (S) and pore volume (V) of the fresh and reduced OCs

Sample	*S* of the fresh/reduced OC [BET, m^2/g]	*V* of the fresh/reduced OC [cc/g]
NiO	12.26/1.71	0.20/0.036
NiFe$_2$O$_4$	29.66/26.44	0.26/0.20
Fe$_2$O$_3$	3.61/4.43	0.021/0.028

Reuse Analysis

Although the TGA experiments and characterization results confirm the good performance of the NiFe$_2$O$_4$ OC, the reactivity stability of OC is still critical for the actual application of OC. In order to eliminate the adverse effect of coal ash on its reactivity, we chose CO as probe molecule and conducted a 10 redox cycles experiments to further clarify the activity stability of NiFe$_2$O$_4$ in TGA. Keep reaction temperature at 850 ˚C and sequentially inlet CO (volume fraction of 30% with N$_2$ as balance gas), N$_2$ and air. Fig. 6 displays the multi-cycle experimental results. During the first two redox cycles, an activation phenomenon of NiFe$_2$O$_4$ occurs, and then its reactivity becomes stable. After regenerated, the final weight of OC is near to 100%. Comparing the third and the last cycle, the weight loss curve can be well repeated, which indicates the great reactivity stability of our synthesized NiFe$_2$O$_4$ OC.
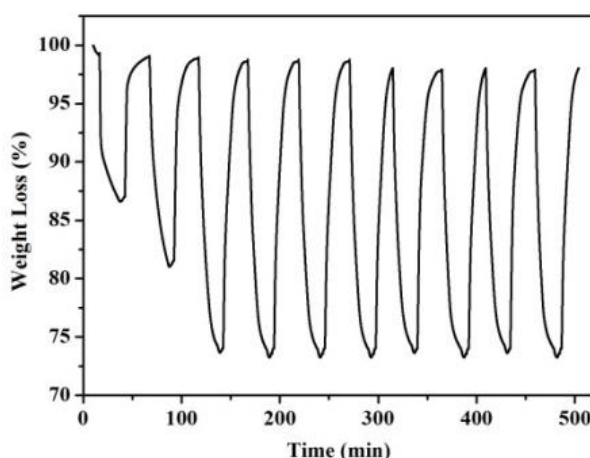

Fig. 6 ten redox cycles experiments of NiFe$_2$O$_4$ with CO

Summary

$NiFe_2O_4$ was prepared and characterized by SEM, BET, and XRD methods. Redox performance of $NiFe_2O_4$ with lignite was studied by TGA experiments. Results show that combined Ni component on Fe_2O_3 can optimize the surface structure with increasing the specific surface and pore volume, enhancing the reactivity and oxygen transfer capacity for lignite CLC. In addition, multi-cycles experiments further confirm the stability of high reactivity of $NiFe_2O_4$. Our findings suggest that $NiFe_2O_4$ OC is efficient and appropriate for lignite CLC.

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