Mechanistic investigation of chemical looping combustion of coal with Fe$_2$O$_3$ oxygen carrier

Baowen Wang$^a$, Rong Yan$^{b,c,a}$, Ying Zheng$^a$, Haibo Zhao$^a$, Chuguang Zheng$^a$

$^a$State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, PR China
$^b$School of Material Science and Engineering, Nanyang Technological University, Block N4.1, Nanyang Avenue, Singapore 639798, Singapore
$^c$Institute of Environmental Science and Engineering, Nanyang Technological University, Innovation Center, Block 2, Unit 237, 18 Nanyang Drive, Singapore 637723, Singapore

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**A B S T R A C T**

The reaction of three Chinese coals with Fe$_2$O$_3$ oxygen carrier (OC) was performed in a thermogravimetric analyzer (TGA), with special focuses on the effects of varying heating rate and coal rank on reactivity. Fourier transform infrared spectroscopy (FTIR) was used to in situ detect the emitted gases from TGA. Field scanning electron microscopy/energy-dispersive X-ray spectrometry (FSEM–EDX) was used to study the morphology and elemental compositions of the reaction residues collected from TGA and the related phase evaluation was further identified by X-ray diffraction (XRD). Through all these experiments, it was found that the pyrolysis of coal samples without Fe$_2$O$_3$ OC under N$_2$ atmosphere underwent the dehydration and the ensuing primary and secondary pyrolysis stages. The increasing heating rate shifted the characteristic temperature ($T_m$) of the primary pyrolysis to a higher temperature and favored a more rapid generation of volatile matters. When the three coals reacting with Fe$_2$O$_3$ OC, TGA results demonstrated even over 200 °C, the reaction still experienced the partial pyrolysis at the relatively low temperature and the ensuing two reactions of Fe$_2$O$_3$ with the pyrolysis products at the primary and secondary stages. The coal of low rank with high volatile content should be preferred for the full conversion of coal into CO$_2$. Furthermore, the activation energy of Fe$_2$O$_3$ OC reacting with PDS at its primary pyrolysis stage was the largest, more than 70 kJ/mol. Finally, SEM–EDX and further XRD analysis of the residues from the reaction of PDS with Fe$_2$O$_3$ OC indicated the reduced counterpart of Fe$_2$O$_3$ was Fe$_3$O$_4$, and some inert iron compounds such as Fe$_2$SiO$_4$ and FeAl$_2$O$_4$ were also generated, which might deteriorate the reactivity of Fe$_2$O$_3$ OC.

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1. Introduction

The large consumption of fossil fuels, especially coal, has been recognized as one of the main anthropogenic sources of CO$_2$ emission into the atmosphere, which exerts great concerns such as detrimental greenhouse effect and global warming. Actions to capture CO$_2$ from fossil fuel combustion are therefore of great necessity. The inherent separation of CO$_2$ does not require any extra gas separation unit [1]. Most of past CLC researches are considering gas fuels (such as natural gas and syngas etc.), using solid fuel (i.e. coal) in CLC application would be more beneficial in view of carbon reduction thus is attracting researchers’ interests.

There are two routes in applying coal in CLC, the first is to use the syngas derived from coal gasification as the fuel, and the other is to directly introduce coal particles into the CLC system. The latter route would apparently be more economically favorable as it doesn’t need the energy-intensive gasification of coal [2]. Leion et al. [3] investigated the direct use of coal from different sources in CLC in a laboratory fluidized bed reactor. Berguerand and Lyngfelt [4] designed a 10 kWth fluidized pilot reacting with a South African coal as the fuel, and Shen et al. [5] also started a CLC application with a Chinese coal on a spouted fluidized system with the same capacity. All these previous works demonstrated initially the feasibility of direct use of coal for CLC application. Also, they have uncovered that the dominant rate-determining step involved in the reaction of coal with OC was actually the coal gasification, instead of the reduction of OC with the gasification products generated in situ from the coal inside the CLC system [3–5]. It was also revealed that in relative to those metal oxides with even higher reactivity (such as NiO and CuO), the Fe$_2$O$_3$ OC was active enough for reacting with coal efficiently in CLC.

In order to improve the coal gasification in the coal-based CLC system and therefore to fully convert coal to CO$_2$ at a high efficiency facilitating the downstream sequestration, it is necessary...
to conduct an in-depth investigation on coal gasification with the presence of OC under well manipulated conditions to better understand the mechanism involved. To this end, using TGA, Cao et al. [6] investigated the reduction of CuO with a sub-bituminous coal, Zhao et al. [7] studied the reduction of Fe2O3 OC with a Chinese coal char, and Siriwardane et al. [8] attempted to study the reaction of CuO with coal to understand the effect of ash deposit on OC and reveal the potential difficulty in separating the reduced OC from the formed coal ash. Therefore, further researches should be properly addressed [2]. The interaction between the reduced OC and ash components would form some inert compounds, which might cause adverse effects, such as decreasing the content of active metal oxides present in OC and thus deteriorating the reactivity, lowering the melting point of the formed ash and possibly causing agglomeration of the reduced OC with ash [8,9]. These would suggest the potentially great difficulty in separating the reduced OC from the formed coal ash. Therefore, further researches are worthy to understand the effect of ash deposit on OC and reveal the possible interaction pathways involved under different CLC process conditions.

In this study, the reduction of Fe2O3 OC with three Chinese coals of different ranks was investigated using TGA, with focuses on the effect of heating rate and coal rank. FTIR coupled with TGA was used to characterize the emitted gases. The morphology and chemical properties of the reduced OC products were characterized using FSEM coupled with EDX, and their phases were further identified by XRD. This study could provide useful information for establishing a practical coal-based CLC system through a better understanding of the mechanisms involved.

2. Experimental procedures

2.1. Materials and characterization

Three Chinese coals of different ranks were selected, including Ping Ding Shan bituminous coal, Liu Pan Shui lean coal and Yang Quang anthracite, hereafter designed as PDS, LPS and YQ, respectively. The original coal samples were firstly dried at 105°C for 24 h to remove the containing moisture, and then ground and sieved to collect the samples in 63–106 μm for the ensuing use. The proximate and ultimate analyses of the three prepared coal samples are presented in Table 1. It was found that with the enhanced rank of three coals from PDS to LPS and to YQ, the content of volatile and the ratio of H to C descended whilst the content of fixed carbon increased. The ash contents of three coals were deducted and thus the remaining free hydrogen and oxygen could be determined. If 1 kg of coal samples were used, the content of different atoms (including C, H, O, N, S) contained in the coal samples could be determined and the relative chemical formula was represented as CxHySzOz(Nz)2r. Finally, for Fe2O3 OC, supposing the realistic oxidant product proceeded to be sintered in the same furnace at 950°C for 2 h. The more detailed procedure and the characterization of the formed oxides were elaborated elsewhere [10]. Similarly, after grinding and sieving, the oxides in 63–106 μm were used. Finally, the as-prepared coals were evenly mixed with the synthesized Fe2O3 OC at the designed mass ratio (as seen in Section 2.2) in a laboratory mortar.

2.2. Determination of oxygen excess number \( \phi \) for different coal samples

The full conversion of coal is determined by the availability of oxygen present in OC. Sufficient but not over supply of the OC is very important to operate the CLC system economically. Hereafter, the method of coal mass balance was adopted to determine the amount of Fe2O3 OC to be inputted into the CLC system. Similar to the reference [16], from the proximate and ultimate analysis results, the weight fractions of hydrogen and oxygen in the moisture were deducted and thus the remaining free hydrogen and oxygen could be determined. If 1 kg of coal samples were used, the content of different atoms (including C, H, O, N, S) contained in the coal samples could be determined and the relative chemical formula was represented as CxHySzOz(Nz)2r. Finally, for Fe2O3 OC, supposing the realistic oxidant product proceeded to be sintered in the same furnace at 950°C for 2 h. The more detailed procedure and the characterization of the formed oxides were elaborated elsewhere [10]. Similarly, after grinding and sieving, the oxides in 63–106 μm were used. Finally, the as-prepared coals were evenly mixed with the synthesized Fe2O3 OC at the designed mass ratio (as seen in Section 2.2) in a laboratory mortar.

\[
\begin{align*}
C_xH_yS_zO_z(N_z)^{2r} + 3 \left(2x + \beta/2 + 2\gamma - \delta\right)Fe_{2}O_3 \\
\rightarrow 2(2x + \beta/2 + 2\gamma - \delta)Fe_{2}O_4 + xCO_2(g) + \beta/2H_2O(g) \\
+ \gammaSO_2(g) + vN_2(g)
\end{align*}
\]

From Eq. (1), the theoretic stoichiometric oxygen needed for the full conversion of coal is \(3(2x + \beta/2 + 2\gamma - \delta)\), and supposing the realistic

Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Proximate analysis (wt.%)</th>
<th>Ultimate analysis (wt.%, d\text{b})</th>
<th>LHV\text{a} (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(M_\text{ad})</td>
<td>(V_\text{ad})</td>
<td>(A_\text{d})</td>
</tr>
<tr>
<td>PDS</td>
<td>1.11</td>
<td>29.18</td>
<td>24.92</td>
</tr>
<tr>
<td>LPS</td>
<td>3.09</td>
<td>22.84</td>
<td>25.38</td>
</tr>
<tr>
<td>YQ</td>
<td>2.39</td>
<td>8.05</td>
<td>29.24</td>
</tr>
</tbody>
</table>

\(a\) \(M\): moisture content; \(V\): volatile matters; \(A\): ash content; \(FC\): fixed carbon; \(ad\): air-dried basis.
\(b\) Dry basis.
\(c\) The O content was determined by difference.
\(d\) Low heating value.
oxygen contained in OC was Y(O), then the oxygen excess number \( \phi \) was determined below.

\[
\phi = Y(O)/(3(2x + \beta/2 + 2y - \delta))
\]

(2)

In Eq. (2), \( \phi = 1 \) referred that the Fe2O3 OC supplied theoretically just met the requirement of a full conversion of coal. According to the aforementioned method, the relative chemical formula of just met the requirement of a full conversion of coal. According to the aforementioned method, the relative chemical formula of coal, respectively, as \( C_{35.1}H_{20.2}N_{1.45}S_{0.13}O_{16} \), \( C_{37.9}H_{14.1}N_{0.66}S_{0.2}O_{13.5} \) and \( C_{36.8}H_{10.2}N_{0.54} \). To the previous report[12]. Meanwhile, in Fig. 1b, it was found that with the increase of the three coals decreased with the enhanced coal rank, similar to the finding of Burnham et al.[13].

The reaction characteristics of the synthesized Fe2O3 OC with three different coals at the oxygen excess number \( \phi = 1 \) were investigated using TGA (TA 2050, US). The mixture of coal and Fe2O3 OC was heated from ambient to 150 °C at the heating rate of 10 °C/min and held at the final temperature for up to 10 min so as to fully remove the moisture. Then, it was further heated up to 850 °C at 35 °C/min with holding the final temperature for 10 min to ensure the full conversion of coal. The flow rate of \( N_2 \) and the total mass for the mixture of coal and OC were determined, respectively, at 50 ml/min and ~15 mg after many pre-screening experiments, to eliminate the potential impact of mass transfer between gas and solid phases.

The evolved gases from the reaction of coal with Fe2O3 OC in TGA, were firstly dried through a portable tubular gas desiccator fully of Ca(SO4)2H2O, and were then in situ detected by FTIR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector (BioRad Excalibur Series, model FTS 3000). The FTIR was coupled with TGA 2050. The scanning range of IR was 4000–400 cm\(^{-1}\) with an accumulated voltage of 30 kV. The effect of coal rank was analyzed from the behaviors of three coals (PDS, LPS and YQ) also demonstrated two different pyrolysis stages, including primary pyrolysis and the ensuing secondary pyrolysis, of which the first one fell into 200–680 °C with the characteristic temperature \( T_m \) (i.e., DTG peak temperature) centering at 476 °C, and emitted approximately 25 wt.\% of volatile matter, mainly consisting of CH4, C2H6, CO2, H2O, etc., as evidenced in Fig. 3, and the corresponding mass loss rate reached 1.7 wt.\%/min. After the primary pyrolysis of PDS, another lower weight loss, almost indiscernible, occurred higher than 680 °C, with around 2.8 wt.\%/min emitted, resulting from the cleavage and condensation of the main carbon matrix [11].

The effect of coal rank was analyzed from the behaviors of three coal samples of different ranks. Similar to the pyrolysis characteristics of PDS, both LPS and YQ also demonstrated two different pyrolysis stages (see Fig. 1b) at above 200 °C, but their peak mass loss rate for the primary pyrolysis decreased rapidly from 1.7 wt.\%/min of PDS to 0.27 wt.\%/min of YQ, with the enhanced coal rank. On the contrary, the peak mass loss rate of the secondary pyrolysis of YQ (0.46 wt.\%/min) was even more significant compared to those of PDS and LPS, due to possibly the much higher fixed carbon content in YQ with the increase of coal rank. Furthermore, in Fig. 1a, after the pyrolysis, the emitted weight fraction of the three coals decreased with the enhanced coal rank, similar to the previous report [12]. Meanwhile, in Fig. 1b, it was found that the characteristics temperature \( T_m \) in both pyrolysis stages was shifted towards a higher value with the increase of coal rank, similar to the finding of Burnham et al. [13].

3. Results and discussion

3.1. Baseline experiment of coal pyrolysis without Fe2O3 OC

In order to gain an in-depth understanding to the reaction characteristics of coal in CLC, first as a basis, the pyrolysis of three Chinese coals (PDS, LPS and YQ) without the presence of Fe2O3 were performed in TGA under N2 atmosphere, with special focuses on the effect of different heating rates (10 and 35 °C/min). The results of mass loss (i.e., TG curve) are depicted in Fig. 1a, and those of differential mass loss rate (i.e., DTG curve) are shown in Fig. 1b and c for the heating rate of 10 and 35 °C/min, respectively.

Firstly, from Fig. 1a and b, taking PDS coal as an example, at the heating rate of 10 °C/min, it could be observed that the pyrolysis of PDS mainly occurred around 200–800 °C. After the dehydration occurred at below 200 °C, PDS mainly underwent two distinct pyrolysis stages, including primary pyrolysis and the ensuing secondary pyrolysis, of which the first one fell into 200–680 °C with the characteristic temperature \( T_m \) (i.e., DTG peak temperature) centering at 476 °C, and emitted approximately 25 wt.\% of volatile matter, mainly consisting of CH4, C2H6, CO2, H2O, etc., as evidenced in Fig. 3, and the corresponding mass loss rate reached 1.7 wt.\%/min. After the primary pyrolysis of PDS, another lower weight loss, almost indiscernible, occurred higher than 680 °C, with around 2.8 wt.\%/min emitted, resulting from the cleavage and condensation of the main carbon matrix [11].

The effect of coal rank was analyzed from the behaviors of three coal samples of different ranks. Similar to the pyrolysis characteristics of PDS, both LPS and YQ also demonstrated two different pyrolysis stages (see Fig. 1b) at above 200 °C, but their peak mass loss rate for the primary pyrolysis decreased rapidly from 1.7 wt.\%/min of PDS to 0.27 wt.\%/min of YQ, with the enhanced coal rank. On the contrary, the peak mass loss rate of the secondary pyrolysis of YQ (0.46 wt.\%/min) was even more significant compared to those of PDS and LPS, due to possibly the much higher fixed carbon content in YQ with the increase of coal rank. Furthermore, in Fig. 1a, after the pyrolysis, the emitted weight fraction of the three coals decreased with the enhanced coal rank, similar to the previous report [12]. Meanwhile, in Fig. 1b, it was found that the characteristics temperature \( T_m \) in both pyrolysis stages was shifted towards a higher value with the increase of coal rank, similar to the finding of Burnham et al. [13].

Heating rate also showed a significant influence on the coal pyrolysis. Compare Fig. 1c and b, it could be found that with the increase of heating rate from 10 to 35 °C/min, the peak mass loss rate of three coals greatly increased (note the different scales of mass loss rate). Especially for PDS at the primary pyrolysis stage, it was increased from 1.7 to 5.8 wt.\%/min. Furthermore, though the similar increasing trend of peak mass loss rate was found for LPS and YQ, the degree of increase was descended with the enhanced rank of coal. Meanwhile, the characteristics temperatures of all three coals were found to shift to a higher temperature with the enhanced heating rate, mainly due to the retardancy of the...
diffusion of volatile matters and heat transfer [14]. Overall, the heating rate increase benefited the pyrolysis of coal of all ranks and promoted the fast evolving of volatile matters in coal [15], especially for coal at low rank.

3.2. Investigation of the reduction of Fe\textsubscript{2}O\textsubscript{3} OC with three coal samples

3.2.1. TGA–FTIR analysis of the reduction of Fe\textsubscript{2}O\textsubscript{3} OC by different coals

The reactions of three coals with Fe\textsubscript{2}O\textsubscript{3} OC at the oxygen excess number $U = 1$ under N\textsubscript{2} atmosphere were performed in TGA. The heating rate of 35 $\degree$C/min was chosen. The temperature was increased to 850 $\degree$C with an isothermal period of 10 min for a full reaction of coal. The results are shown in Fig. 2a and Fig. 2b, with X-axis in time instead of temperature. Meanwhile, the inert support of OC (such as Al\textsubscript{2}O\textsubscript{3}) is also necessary for improving the resistance to sintering, abrasion and fragmentation over cyclic reactions in the CLC system. The reactions between three coals and Fe\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} were also investigated and the related results are depicted in Fig. 2c.

Firstly, from Fig. 2a, in the range of 200–850 $\degree$C, PDS reacted more easily with Fe\textsubscript{2}O\textsubscript{3} with a higher weight loss (2.5 wt.%) than other two coals of higher rank, especially for YQ with weight loss less than 1.0 wt.%. But the final weight losses for the reaction of different coal samples with Fe\textsubscript{2}O\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} oxygen carrier were found to be less than those corresponding losses for the reaction of coal with Fe\textsubscript{2}O\textsubscript{3} only, due to the introduction of the support Al\textsubscript{2}O\textsubscript{3}, which was inert to coal. In Fig. 2b, three reaction stages were observed from the DTG curves, different from the cases of without Fe\textsubscript{2}O\textsubscript{3} as shown in Fig. 1c. Similar finding of three-staged reaction was reported by Siriwardane et al. [8]. For PDS, the corresponding three characteristic temperatures were respectively at 496, 619 and 810 $\degree$C. The first reaction was most likely related to the partial pyrolysis of PDS in its mixture with Fe\textsubscript{2}O\textsubscript{3}, at the mass loss rate of 0.1682 wt.%/min. Note this value (0.1682 wt.%/min) was much lower than the pyrolysis rate (5.8 wt.%/min) seen for PDS at $\approx 484$ $\degree$C in Fig. 1c, but if multiplied by 38.2 (the mass ratio of Fe\textsubscript{2}O\textsubscript{3} to PDS at the oxygen excess number $U = 1$), the calculated mass loss rate of 6.4 wt.%/min was reasonable. The ensuing two reactions happened at 619 and 810 $\degree$C in Fig. 2b would be...
identified as the reaction of PDS coal with Fe$_2$O$_3$ through its primary and secondary pyrolysis. Such assumption could be further validated by the evolved gas products from the reaction of PDS with Fe$_2$O$_3$, which was identified by FTIR analysis at different reaction stages, and the result is shown in Fig. 3. The major gas product was CO$_2$ at 619 and 810 °C from the reaction of PDS coal with Fe$_2$O$_3$ for two-stage pyrolysis, indicating the full conversion of Fe$_2$O$_3$ samples used whilst the latter was synthesized by the reaction of PDS coal with Fe$_2$O$_3$, which was identified by FTIR analysis at different reaction stages, and the result is shown in Fig. 3. The major gas product was CO$_2$ at 619 and 810 °C from the reaction of PDS coal with Fe$_2$O$_3$, indicating the full conversion of Fe$_2$O$_3$ samples used whilst the latter was synthesized by Sirwardane et al. where a Illinos #6 coal reaction with commercial Fe$_2$O$_3$ was considered [8]. The big temperature discrepancy was expected to mainly arise from the reactivity difference of the two Fe$_2$O$_3$ samples used whilst the latter was synthesized by the home designed method.

Analyzing the effect of coal rank, from Fig. 2b, all the three coals demonstrated three stage reactions, but with the increase of coal rank, the corresponding characteristic temperature $T_m$ were found to shift to higher values, the same trend as observed for coal pyrolysis alone in Fig. 1c. This indicated that coal of higher rank reacted with Fe$_2$O$_3$ more difficulty [17]. In view of applying Fe$_2$O$_3$ OC in a coal-based CLC system, the coal of low rank with high volatile matters would be preferred. Finally, in Fig. 2c, the effect of inert support Al$_2$O$_3$ on the reaction of coal with Fe$_2$O$_3$ was shown. The mass ratio of Fe$_2$O$_3$ to Al$_2$O$_3$ was 8–2. Similarly three reaction stages occurred and the corresponding characteristic temperatures increased with the enhanced coal rank.

3.2.2. Kinetic analysis

In order to gain a better understanding to the reaction of three coals with Fe$_2$O$_3$ OC, the relevant kinetic parameters, including activation energy $E$ and pre-exponent $A$, were calculated by Eqs. (3)-(5). PDS was more selective to Fe$_2$O$_3$ OC and thus adopted as a representative. The TGA data obtained from Figs. 1c and 2 at the heating rate of 35 °C/min are selected and the calculated results are shown in Table 3.

From this table, all the correlation coefficients (CR) for the related kinetic parameters were larger than 0.99 with one exception for the reaction of PDS with Fe$_2$O$_3$/Al$_2$O$_3$. In relative to the activation energy $E = 44.9$ kJ/mol for the pyrolysis of PDS at 200–840 °C, with the inclusion of Fe$_2$O$_3$ and Fe$_2$O$_3$/Al$_2$O$_3$ OC the $E$ values of PDS pyrolysis at 220–530 °C decreased first slightly to 43.8 and 40.1 kJ/mol, respectively, indicating the catalytic effect of OC to coal pyrolysis. However, at 500–780 °C, the $E$ values increased a lot to 73.6 kJ/mol and to 96.1 kJ/mol for the reactions of PDS with Fe$_2$O$_3$ and Fe$_2$O$_3$/Al$_2$O$_3$, respectively. Furthermore, at 780–850 °C, the related reaction activation energy $E$ for both reactions of PDS with Fe$_2$O$_3$ and Fe$_2$O$_3$/Al$_2$O$_3$ decreased to below 70 kJ/mol, possibly because the products of secondary pyrolysis of coal contained a large fraction of H$_2$ and CO [11], which more easily reacted with Fe$_2$O$_3$ OC than those from the primary pyrolysis stage.

Table 3

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temperature (°C)</th>
<th>$E$ (kJ/mol)</th>
<th>$A$ (1/s)</th>
<th>CR$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDS</td>
<td>200–840</td>
<td>44.9</td>
<td>53.5</td>
<td>0.9971</td>
</tr>
<tr>
<td>PDS + Fe$_2$O$_3$</td>
<td>220–530</td>
<td>43.8</td>
<td>3.7</td>
<td>0.9981</td>
</tr>
<tr>
<td></td>
<td>530–750</td>
<td>73.6</td>
<td>726.9</td>
<td>0.9996</td>
</tr>
<tr>
<td></td>
<td>750–840</td>
<td>58.4</td>
<td>90.4</td>
<td>0.9945</td>
</tr>
<tr>
<td>PDS + Fe$_2$O$_3$/Al$_2$O$_3$</td>
<td>370–540</td>
<td>40.1</td>
<td>0.92</td>
<td>0.9947</td>
</tr>
<tr>
<td></td>
<td>540–780</td>
<td>96.1</td>
<td>7191.4</td>
<td>0.9969</td>
</tr>
<tr>
<td></td>
<td>780–845</td>
<td>67.5</td>
<td>5372.1</td>
<td>0.9839</td>
</tr>
</tbody>
</table>

$^a$ Correlated coefficient.

To help understand the issue of ash separation from the reaction of coal with OC, the morphology and elemental composition of both residues from PDS coal pyrolysis, and its reaction with Fe$_2$O$_3$ OC and Fe$_2$O$_3$/Al$_2$O$_3$ (mass ratio 8:2) were characterized using SEM–EDX. The results are shown in Fig. 4a-c, respectively.

In Fig. 4a for the pyrolysis of PDS, it could be observed in SEM pattern that the residue of PDS consisted of the fragmentary white discrete particle as shown in the spot 1 and the relatively dark bulk shown in spot 2. By the EDX analysis, the elemental composition of the spot 1 was identified as minerals, mainly composed of Si, Al, O and C. For the spot 2, it was possibly the carbon matrix left after pyrolysis of PDS with atomic fraction of C reached 81.71%, which was much higher than that presented in the spot 1 (32.0% of atomic fraction). The presence of Al, Si and S might be resulted from the minerals occurring inherently in the carbon matrix. Furthermore, as shown in Fig. 5a, XRD analysis of the residue from PDS pyrolysis indicated that SiO$_2$ and some silicates, such as Fe$_2$Si$_2$O$_5$(OH)$_4$, Al$_2$Si$_2$O$_5$(OH)$_4$ and CaAl$_2$Si$_2$O$_8$·4H$_2$O, were the main mineralogy compositions. Although the most part of residue should be ascribed...
to the carbon matrix by EDX analysis, it cannot be identified in XRD analysis due to its amorphous characteristics.

In Fig. 4b for the reaction of PDS with Fe$_2$O$_3$, it could be observed in SEM pattern that the reaction residue mainly consisted of discrete white particles, and the two optionally selected spots shown in the SEM pattern were scanned by EDX. It showed that the elemental compositions involved in the two spots were almost the same, which mainly consisted of Fe, O and C, with their atomic fractions equal to 44%, 50% and 5.6%, respectively. The contained iron oxide could be further inferred as Fe$_3$O$_4$ by the atomic ratio of Fe to O, which could be further validated from the XRD analysis presented in Fig. 5c. The valence of the reduced Fe$_2$O$_3$ was mainly determined by the mass ratio of Fe$_2$O$_3$ to carbonaceous material such as biomass [18,19]. When Fe$_2$O$_3$ OC was used in a CLC system, the potential defluidization of the fuel reactor was observed arising from the reduction of Fe$_2$O$_3$ further into the lower valence than Fe$_3$O$_4$ [20]. From this research, if such an undesirable circumstance would be avoided, high mass ratio of Fe$_2$O$_3$ to coal should be adopted, as suggested by Eq. (2).

Furthermore, to understand the role of inert support, the solid residues from the reaction of Fe$_2$O$_3$/Al$_2$O$_3$ with PDS were further investigated with FSEM–EDX, as shown in Fig. 4c. No sintering phenomenon was found due to the high resistance to sintering of Al$_2$O$_3$. The atomic fraction of C was ~3%, much less than the case of PDS reaction with Fe$_2$O$_3$, shown in Fig. 4b, which proved that the presence of Al$_2$O$_3$ improved the reactivity of Fe$_2$O$_3$ based OC and promoted the conversion of PDS. Meanwhile, although the Al compositions on the two spots were evenly distributed, with atomic fractions approaching ~15%, but the distribution of Si compositions on the two spots differed greatly, as such, the detailed phases

**Fig. 4.** SEM-EDX analysis of the PDS coal pyrolysis (a) and reaction with Fe$_2$O$_3$ (b) and reaction with Fe$_2$O$_3$/Al$_2$O$_3$ (mass ratio 8:2) (c) (The magnification number was 800 and the accumulated voltage was 30 kV.).
of residues from the reaction of PDS with Fe$_2$O$_3$/Al$_2$O$_3$ were further identified with XRD.

Finally, in order to identify the detailed phases involved after the reaction of PDS with Fe$_2$O$_3$ or Fe$_2$O$_3$/Al$_2$O$_3$, the residues left were identified by XRD, as presented in Fig. 5c and d. From Fig. 5c, after the reaction of Fe$_2$O$_3$ with PDS, the residue was mainly composed of Fe$_2$O$_3$, Fe$_3$O$_4$ and Fe$_2$SiO$_4$. The Fe$_2$O$_3$ left mainly resulted from the partial pyrolysis of PDS early at the pyrolysis characteristic temperature of 496 °C as shown in Fig. 2b and the pyrolysis products could not react further with Fe$_2$O$_3$ at such a low temperature. Of course, such circumstance would not occur in the real CLC system. The presence of Fe$_2$SiO$_4$ was closely attributed to the interaction of the reduced iron oxide with SiO$_2$ occurred inherently in the coal, especially in the local reducing atmosphere. Similar phase of Ni$_2$SiO$_4$ was found to occur in the reaction of NiO OC with coal char in our previous experiments [7].

While in Fig. 5d, for the reaction of PDS with Fe$_2$O$_3$/Al$_2$O$_3$ (mass ratio of Fe/Al at 8/2), the residue after reaction mainly consisted of Fe$_2$O$_3$, Fe$_3$O$_4$ and FeAl$_2$O$_4$. The left Fe$_2$O$_3$ was also owe to the partial pyrolysis of PDS at 487 °C prior to the initiation of PDS reacting with Fe$_2$O$_3$. The FeAl$_2$O$_4$ was resulted from the interaction of the reduced iron oxide with Al$_2$O$_3$ which was included in the Fe$_2$O$_3$/Al$_2$O$_3$ OC [21]. But here Fe$_2$SiO$_4$ inherent was not identified in the XRD pattern, likely because the reduced iron oxide reacted more easily with Al$_2$O$_3$ instead of SiO$_2$. At the possible reaction temperature (≈850 °C), the reaction enthalpy of the reduced iron oxide with Al$_2$O$_3$ is -14 kJ, far less than that of the reduced oxide with SiO$_2$ (i.e., -4 kJ). In addition, the identified phases by XRD for the PDS ashing sample (see Fig. 5b) contained SiO$_2$, Fe$_2$O$_3$, Al$_2$Ti$_2$SiO$_12$, CaAl$_2$Si$_2$O$_8$, several silicates were observed.

Of course, more attention should be paid to the inert iron compounds such as Fe$_2$SiO$_4$ and FeAl$_2$O$_4$, which were formed from the interactions of the reduced iron oxide with SiO$_2$ occurring inherently in coal or with Al$_2$O$_3$ included in the Fe$_2$O$_3$ OC. These compounds would not only lower the melting point of Fe$_2$O$_3$ OC, but also deteriorate the reactivity of OC [9]. Thus, further researches on the mechanisms of forming the inert iron compounds and effective separation of coal ash from the reduced OC through density or magnetic differences in the practical CLC system (such as an interconnected fluidized beds system) with a long duration of continuous operation should be performed.

4. Conclusions

The reaction of Fe$_2$O$_3$ OC with three Chinese coals was performed in TGA, with special focuses on the effect of heating rate and coal rank. The evolved gases from the reaction were detected using on-line FTIR. The morphology and elemental compositions of residues after reactions were analyzed by SEM–EDX, and finally the mineral phases from the reaction residues were further identified by XRD. Through all these measures, such conclusions were reached as follows.

(1) As the baseline, through the pyrolysis of the three coal samples of different ranks without Fe$_2$O$_3$ OC at the two different heating rates (10 and 35 °C/min), it would be found that coal pyrolysis underwent three different stages, related to the dehydration below 200 °C and the ensuing primary and secondary pyrolysis stages. The related characteristic temperatures $T_m$ at the two pyrolysis stages shifted to a higher value with the enhanced heating rate and coal rank. Overall, the high heating rate but coal of low rank favored to generate a large amount of volatile matter rapidly.

(2) TGA analysis of three coals reacting with Fe$_2$O$_3$ or Fe$_2$O$_3$/Al$_2$O$_3$ demonstrated that at over 200 °C, the reaction of three coals experienced three stages, ascribed to the partial pyrolysis of PDS at the relatively low temperature and the following reaction of Fe$_2$O$_3$ with the pyrolysis products at the primary and secondary stages. For PDS, rather than the other two coals of higher rank, was preferred for the full conversion of coal into CO$_2$ in the CLC system using Fe$_2$O$_3$ OC, though Fe$_2$O$_3$ OC benefited to improve the pyrolysis rate of all the studied coals of different ranks.

(3) The activation energy of Fe$_2$O$_3$ or Fe$_2$O$_3$/Al$_2$O$_3$ reacting with PDS at its primary pyrolysis stage was the largest among all the reaction stages, i.e., more than 70 kJ/mol.
(4) SEM–EDX and further XRD analysis of the residues from the reaction of PDS with Fe₂O₃ or Fe₂O₃/Al₂O₃ indicated that the reduced counterpart of Fe₂O₃ was Fe₃O₄, and some inert iron compounds such as Fe₃SiO₄ and FeAl₂O₄ were generated, which could lead to the deterioration of Fe₂O₃ OC. Further investigations are needed to understand this issue better.

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