Sulfur Fate during the Lignite Pyrolysis Process in a Chemical Looping Combustion Environment

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ABSTRACT: Chemical-looping combustion (CLC) is a novel technology with the feature of CO₂ inherent separation in which the fuel is converted via lattice oxygen (instead of gaseous oxygen) provided by the oxygen carrier that circulates between two structurally interconnected but atmosphere-isolated reactors, i.e., fuel reactor and air reactor. In the fuel reactor of in situ gasification CLC (iG-CLC), the pyrolysis and gasification products of coal are oxidized by lattice oxygen in the O₂-free environment. Therefore, the characteristics of sulfur species evolution and distribution in the coal pyrolysis products are significantly different from those in the conventional combustion, gasification, and pyrolysis processes. In this study, a two-stage fluidized bed reactor was utilized to investigate the reaction between the oxygen carrier and in situ coal pyrolysis products, in which the coal and oxygen carrier particles are separately loaded in two reactors. In this way, the influence of oxygen carrier on the coal pyrolysis process could be eliminated. As obtained from the experiment, the distribution of sulfur species in coal pyrolysis products changed significantly after being oxidized by the oxygen carrier. To be more specific, the sulfur species were 70.1% H₂S, 0.2% SO₂, 0.8% COS, and 13.1% CS₂, respectively, during the coal pyrolysis process in the blank experiment loaded with silica sand, whereas the concentrations of the sulfur species (in the same order) changed to 26.0%, 68.2%, 0%, and 0%, respectively, once the pyrolysis products went through the Fe₂O₃/Al₂O₃ oxygen carrier. The result indicates that most of the H₂S, COS, and CS₂ contents could be oxidized by the oxygen carrier to generate SO₂ in the CLC environment. The sulfurous gas conversion rate at the CLC experiment was higher than that at blank experiment due to the fast evolution of sulfur in tar, which was also converted by oxygen carrier to enhance the sulfur conversion at the CLC experiment. Most of the H₂S could be oxidized by the oxygen carrier to generate SO₂ via the reaction H₂S(g) + 9Fe₂O₃ = 6Fe₃O₄ + H₂O(g) + SO₂(g), and this has been confirmed by both experiment and HSC simulation. Moreover, scanning electron microscopy and energy-dispersive X-ray spectroscopy results indicated that no metallic sulfide was formed on the surface of reduced oxygen carrier.

1. INTRODUCTION

Chemical looping combustion (CLC) of coal is a novel way to realize low-cost CO₂ capture and cascade energy utilization at the same time. For a CLC system, it usually consists of two separated reactors: fuel reactor (FR) and air reactor (AR), where the oxygen carrier (OC, mainly transition-state metal oxides) circulates between them to transport the lattice oxygen needed for fuel conversion. During the in situ gasification CLC (iG-CLC) process, the coal undergoes two important steps occurring in FR: the fast pyrolysis process of raw coal and the relatively slow gasification process of residual char. The produced combustible gases (mainly CO, H₂, CH₄, H₂S, et al.) are finally oxidized by the OC to generate CO₂, H₂O, SO₂, and other byproducts.

Because almost all coals are sulfur-containing substance, the sulfur behavior is thus a key issue within iG-CLC process: on the one hand, the OC could be sulfurized in the presence of sulfur contaminants, resulting in the deactivation of OC; on the other hand, the sulfur-containing flue gases will reduce the purity of the captured CO₂, which demonstrates adverse effect to CO₂ compression and air cleaning. Several researches have evaluated the effects of H₂S on the performance of various OCs for CLC or chemical looping with oxygen uncoupling (CLOWU), usually using H₂S-containing synthesis gas as fuel. Francisco et al. first investigated the reaction between Ni-based OC and H₂S via HSC thermodynamic simulation, and then a series of experiments were conducted in a 500 Wth CLC unit. The results showed that Ni₃S₂ was formed under all experimental conditions due to the presence of H₂S in CH₄ in the fuel reactor. Cristina et al. showed that the reactivity of Al₂O₃ supported NiO oxygen carrier decreased when reacting with H₂S-containing CH₄ in the 500 Wth CLC unit because of the formation of nickel sulfides and sulfates. Diego et al. investigated the performance of Fe-based OC in the same 500 Wth CLC unit for conversion of sour gas with high H₂S content. The result showed that complete conversion of H₂S to SO₂ was attained when the oxygen carrier to fuel ratio was above 1.5, and meanwhile, the formation of iron sulfides could be avoided in FR. Wang et al. found that Cu₂S and FeS were the main sulfide products and H₂S was easier to react with CuO than Fe₂O₃ in the CLC process, using coal-derived synthesis gas (also with H₂S contained) as fuel. Tian et al. investigated the performance of different types of OCs in a thermogravimetric analyzer (TGA) using coal-derived synthesis gas mixed with 4042 ppm of H₂S as fuel. The results showed that the OC would first react with CO and H₂ and then react with H₂S to form metal sulfides. Shen et al. concluded that Ni₃S₂ was the...
only metal sulfide when NiO-based OC was used, and it was completely reversible in redox process. The reaction rate between NiO and H2S was higher than that of NiO and CO. Gu et al.\textsuperscript{11} found that the iron ore could be sulfurized in the presence of H2S, resulting in the formation of FeS, and the released sulfurous gases mainly consisted of COS, SO2, and CS2. Moreover, they claimed that H2S was mainly oxidized by Fe2O3 rather than by Fe3O4 or FeO. Ewelina et al.\textsuperscript{12} investigated the stability of Fe−Mn OC during CLC redox cycles with H2S-containing coal-derived synthesis gas. It was found that the presence of H2S would significantly decrease the reduction rates, but the oxidation rates of the reduced oxygen carrier increased. Solunke et al.\textsuperscript{13} studied the redox kinetics of nanostructured Ni-BHA and Cu-BHA with H2S-containing CS2. Moreover, they claimed that H2S was mainly oxidized by the sulfur migration path in CLC of in situ coal pyrolysis further understand the sulfur evolution in experiments. Finally, simulated using the HSC-Chemistry software version 6.0 to synthesis gas in TGA. The results showed that the oxygen numbers and temperature on the sulfur evolution using HSC integration, and pyrolysis processes. With respect to the current research on the reaction between H2S and OC in CLC, most of them are investigated by using H2S-containing synthesis gas as fuel.\textsuperscript{9,12,13} Actually, the reaction characteristics and the evolution of sulfurous gases were rather complicated in the real CLC process. Therefore, careful identification and a full understanding of the sulfur distribution and evolution characteristics during the coal-derived CLC process are certainly required. The objective of this work was to investigate the characteristics of sulfur species (H2S, SO2, COS, and CS2) evolution and distribution during the coal pyrolysis process (which, as the first step of iG-CLC of coal, occurs very rapidly with a large proportion of sulfur in coal released) in a two-stage fluidized bed reactor. Well-organized experiments were conducted for the comparison of the CLC process and simple coal pyrolysis process (using OC and silica sand as bed materials in the second reactor, respectively) to identify the sulfur behaviors. By using the two-stage fluidized bed reactor, the reaction between oxygen carrier and in situ coal pyrolysis gases (generated in the first pyrolysis reactor) can be directly evaluated, meanwhile minimizing the influence of oxygen carrier on the coal pyrolysis process because coal and oxygen carrier particles are separately loaded in two reactors. The sulfur balance was calculated based on the difference of sulfur in coal and in char. The interaction of OC and sulfurous gases (H2S, COS, CS2, and SO2) was simulated using the HSC-Chemistry software version 6.0 to further understand the sulfur evolution in experiments. Finally, the sulfur migration path in CLC of in situ coal pyrolysis products was deduced.

### Table 1. Proximate and Ultimate Analyses of XLT Coal and XLT Char

<table>
<thead>
<tr>
<th>Type</th>
<th>M</th>
<th>V</th>
<th>FC</th>
<th>A</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>XLT coal</td>
<td>10.59</td>
<td>49.56</td>
<td>33.40</td>
<td>6.45</td>
<td>45.52</td>
<td>4.20</td>
<td>1.28</td>
<td>0.60</td>
<td>31.36</td>
</tr>
<tr>
<td>XLT char</td>
<td>3.64</td>
<td>6.45</td>
<td>77.79</td>
<td>12.12</td>
<td>78.60</td>
<td>0.60</td>
<td>1.17</td>
<td>0.68</td>
<td>3.19</td>
</tr>
</tbody>
</table>

M, moisture content; V, volatile matters; A, ash content; FC, fixed carbon; ad, air-dried basis.

The O content was determined by difference.

### 2. EXPERIMENTAL SECTION

#### 2.1. Materials

A typical Chinese low-rank coal (Xiaolongtan, XLT in short) is used as solid fuel. The XLT coal was dried at 105 °C in air for 10 h and sieved in range of 100−350 μm. The relevant XLT char was prepared in an Ar atmosphere and heated to 950 °C at 15 °C/min. The proximate and ultimate analyses of XLT coal and XLT char (the char was prepared in the tube furnace at constant temperature of 950 °C and Ar atmosphere) are listed in Table 1. The Fe-based OCs in the range of 200−300 μm were prepared by the sol−gel method\textsuperscript{17} with 54 wt % Fe2O3 and 46 wt % Al2O3.

#### 2.2. Experimental Procedure

The two-stage fluidized bed reactor (shown in Figure 1) consists of a pyrolysis reactor, where the coal releases the volatile contents, and a CLC fuel reactor, in which the volatile-containing gases without cooling process are introduced to fluidize either OC or silica sand. In this way, the mixing of OC and coal is avoided, which eliminates the influence of OC on the coal pyrolysis process. The inner diameter of both reactors is 35 mm, with the height of 150 mm for the coal pyrolysis reactor and 250 mm for the CLC fuel reactor, respectively. The pore diameter of the distribution plate is 74 μm, located in the CLC fuel reactor, which could prevent the entrainment of coal and ash particles into the CLC fuel reactor. For each experiment, 0.232 g of XLT coal was first fed into the first-stage pyrolysis reactor, using Ar as fluidizing gas. Next, the in situ pyrolysis products were rapidly carried into the CLC fuel reactor by Ar, where OC (or silica sand as blank experiment) was loaded to investigate the distribution and evolution characteristics of sulfurous gases during the CLC process of pyrolysis products (or the O2-free coal pyrolysis process). An online Fourier transform infrared spectroscopy (FTIR, GASMET DX4000) was employed to measure the contents of sulfurous gases (SO2, COS, and CS2). The infrared absorption band of FTIR was in the range of 600−4250 cm⁻¹. The infrared peaks of COS, CS2, and SO2 were at 2051, 1527, and 1371 cm⁻¹, respectively. H2S was measured by the online H2S detector (MS600-H2S). The online gas analyzer (Gasboard Analyzer 3100) was used to determine the concentrations of CO2, CO, CH4, O2, and H2, within the range of 0−10 vol % for CO, CH4, O2, and H2 and 0−100 vol % for CO2. The measurement accuracy was 1% of full scale. To guarantee the reliability of the experiment, the FTIR and the H2S detector were calibrated. The range of H2S, SO2, COS, and CS2 was 500 ppmv with the accuracy lower than 1% of full scale, respectively. Moreover, to avoid the interference of the H2O infrared peak, the

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**Figure 1.** Schematic view of the two-stage fluidized bed reactor.
outlet gas was dehydrated by the electric condenser, and the tar was removed by the tar removing unit before flowing into the FTIR.

There were three steps in each experiment. The first step is used Ar as the fluidizing and carrier gas during the coal pyrolysis process, with the flow rate of 2000 mL/min, corresponding to 8 \( U_{\text{mf}} \) of OC (\( U_{\text{mf}} \) the minimum fluidized gas velocity, is calculated as 0.018 m/s at 950 °C and Ar atmosphere). Valve 1 was switched on, and valve 2 was closed. The in situ volatile is carried to the second CLC fuel reactor loaded with 40 g of oxygen carrier. The outlet gas was measured at the out of the CLC fuel reactor. After the pyrolysis process, the second step is to introduce 1600 mL/min Ar and 400 mL/min \( \text{O}_2 \) into the first reactor to burn out the residue char produced during step 1. The char was totally oxidized by switching on the valve 1 while closing valve 2.

Next, the in situ volatile is carried to the second CLC fuel reactor to burn out the residue char produced during step 1. The gas was cut off into the CLC fuel reactor by switching on the valve 2 while closing valve 1. The char was totally combusted in the pyrolysis reactor, and the outlet gas was exhausted through the outlet of the pyrolysis reactor until the \( \text{CO}_2 \) gas concentration was zero. The third step was switched the mixture gas of 1600 mL/min Ar and 400 mL/min \( \text{O}_2 \) to the CLC fuel reactor to oxidize the oxygen carrier by switching on the valve 1 while closing valve 2.

The blank experiment was also conducted to evaluate the sulfur distribution during the \( \text{O}_2 \)-free coal pyrolysis process. By comparing the results of the blank experiment and the CLC experiment, it is possible to explore the effect of the presence of Fe-based oxygen carrier on the sulfur distribution of coal pyrolysis products. All the experiments have been repeated three times to ensure data reliability.

2.3. Data Evaluation. The total volume of outlet gas from the CLC fuel reactor (\( F_{\text{out}} \)) was calculated by Ar balance:

\[
F_{\text{out}} = \frac{F_{\text{Ar}}}{1 - \Sigma\gamma_i}
\]

where \( F_{\text{Ar}} \) was the flow rate of Ar introducing into the pyrolysis reactor, \( \Sigma\gamma_i \) was the volume fraction of gas i (except for Ar) in the outlet of the CLC fuel reactor.

The volumes of the generated sulfurous gases (\( \text{SO}_2 \), \( \text{CS}_2 \), \( \text{COS} \), and \( \text{H}_2\text{S} \)) were calculated as:

\[
Y_i = \int_{t_0}^{t_f} Y_i \times F_{\text{out}} \, dt
\]

The mass of sulfur content in the volatile (\( m_{\text{s-v}} \)) was determined by:

\[
m_{\text{s-v}} = m_{\text{coal}} \cdot w_{\text{s-v}} - m_{\text{coal}} \cdot \gamma_{\text{char}} \cdot w_{\text{s-char}}
\]

where \( m_{\text{coal}} \) was the mass of coal fed into the pyrolysis reactor, \( \gamma_{\text{char}} \) was the char yield (\( \gamma_{\text{char}} = 0.43 \) through weighting the raw coal and the residue char), and \( w_{\text{s-v}} \) and \( w_{\text{s-char}} \) were the mass fraction of sulfur in coal and char (shown in Table 1), respectively.

The sulfurous gases conversion (\( X_S \)) was defined as the mole of sulfurous gases (\( \text{SO}_2 \), \( \text{H}_2\text{S} \), \( \text{COS} \), and \( \text{CS}_2 \)) released from the beginning to time \( t \) to the sulfur content in XLT coal volatile, as seen in eq 4, and the sulfurous gases conversion rate (\( \dot{X}_S \)) was the differential of sulfurous gases conversion (as seen in eq 5):

\[
X_S = \frac{\int_{t_0}^{t_f} F_{\text{out}} (Y_{\text{H}_2\text{S}} + Y_{\text{SO}_2} + Y_{\text{COS}} + 2 \times Y_{\text{CS}_2}) \, dt / 22.4}{m_{\text{s-v}} / 32}
\]

\[
\dot{X}_S = \frac{dX_S}{dt}
\]

The mass balance of sulfur species during the pyrolysis process was calculated as:

\[
w_i = \frac{Y_i \cdot M_i}{22.4 \cdot m_{\text{s-v}}} \cdot 100\%
\]

where \( w_i \) and \( M_i \) were the mass fraction and molecular weight of species \( i \), respectively, and \( i \) represented \( \text{SO}_2 \), \( \text{H}_2\text{S} \), \( \text{COS} \), and \( \text{CS}_2 \).

The carbon conversion, \( X_C \), the carbon conversion rate, \( \dot{X}_C \), and the \( \text{CO}_2 \) yield, \( Y_{\text{CO}_2} \), were calculated in the same way as in ref 16, as shown below:

\[
X_C = \left( \frac{\int_{t_0}^{t_f} F_{\text{out}} (Y_{\text{CO}_2} + Y_{\text{CH}_4} + Y_{\text{CO}}) \, dt / 22.4}{m_{\text{c}} / 12} \right)
\]

\[
\dot{X}_C = \frac{dX_C}{dt}
\]

\[
Y_{\text{CO}_2} = \left( \frac{\int_{t_0}^{t_f} F_{\text{out}} (Y_{\text{CO}_2} + Y_{\text{CH}_4} + Y_{\text{CO}}) \, dt}{m_{\text{c}} / 12} \right)
\]

where \( m_{\text{c}} \) was defined as the mass of carbon content in the coal.

3. RESULTS AND DISCUSSIONS

3.1. Thermodynamic Simulation. \( \text{H}_2\text{S} \) is the main sulfur-containing substance released during the coal pyrolysis process (as indicated in Figure 6 of section 3.3). The active component, \( \text{FeO}_y \), in the oxygen carrier could provide lattice oxygen to convert \( \text{H}_2\text{S} \) into \( \text{SO}_2 \), as shown in R1. Moreover, ferric sulfides may be formed by the reaction between \( \text{H}_2\text{S} \) and \( \text{Fe}_2\text{O}_3 \) in CLC of coal pyrolysis products, as in R4, resulting in the degradation of the OC reactivity. The iron oxide with different chemical valence could react with \( \text{H}_2\text{S} \) in the fuel reactor as follows:

\[
\text{H}_2\text{S}(g) + 9\text{Fe}_2\text{O}_3 = 6\text{Fe}_3\text{O}_4 + \text{SO}_2(g) + \text{H}_2\text{O}(g) \quad \text{(R1)}
\]

\[
\text{H}_2\text{S}(g) + 3\text{Fe}_2\text{O}_3 = 9\text{FeO} + \text{SO}_2(g) + \text{H}_2\text{O}(g) \quad \text{(R2)}
\]

\[
\text{H}_2\text{S}(g) + 3\text{FeO} = 3\text{Fe} + \text{SO}_2(g) + \text{H}_2\text{O}(g) \quad \text{(R3)}
\]

\[
\text{H}_2\text{S}(g) + 1/3\text{Fe}_2\text{O}_3 = 1/3\text{Fe}_2\text{S}_3 + \text{H}_2\text{O}(g) \quad \text{(R4)}
\]

\[
\text{H}_2\text{S}(g) + \text{FeO} = \text{FeS} + \text{H}_2\text{O}(g) \quad \text{(R5)}
\]

\[
\text{H}_2\text{S}(g) + \text{Fe} = \text{FeS} + \text{H}_2(g) \quad \text{(R6)}
\]

A thermodynamic simulation was conducted by using HSC Chemistry version 6.0, based on the minimization of Gibbs free energy, to understand the sulfur migration behavior during the CLC of in situ coal pyrolysis process. The thermodynamic equilibrium constants of the reaction between the iron and iron oxides (\( \text{FeO}_y \), \( \text{Fe}_2\text{O}_3 \), \( \text{Fe}_3\text{O}_4 \), \( \text{FeO} \), and \( \text{Fe} \)) and \( \text{H}_2\text{S} \) to form sulfurous gases (mainly \( \text{SO}_2 \)) and ferric sulfides (\( \text{FeS} \) and \( \text{Fe}_2\text{S}_3 \)) were first calculated within the temperature range of 700–1100 °C, as shown in Figure 2. It was noted that R1 was most thermodynamically favorable, which showed the highest
reactivity of Fe$_2$O$_3$ with H$_2$S. The elevated temperature also posed a positive effect on R1. It was speculated from these equilibrium constants $K$ that the possibility of the formation of iron sulfide (R4−R6) was lower than that of formation of SO$_2$ (R1), and these equilibrium constants showed a decreased trend with the increased temperature. Thus, the formation of iron sulfide will decrease at higher temperature theoretically. A value of log $K < 0$ for R2 and R3 indicated that these reactions were difficult to proceed. The results showed that the reaction between Fe$_3$O$_4$/FeO and H$_2$S impossibly occurred.\(^{11}\)

The equilibrium compositions were simulated on the basis of 1000 mol syngas gas with 371.35 mol CO, 491.85 mol CO$_2$, 113.99 mol CH$_4$, 22.75 mol H$_2$, and 5.06 mol H$_2$S, which was determined according to the coal pyrolysis products at 950 °C (as shown in Figures 4a and 6a). A value of 1.0 of the fuel to oxygen carrier ratio is defined as stoichiometric mole of synthesis gas needed to reduce Fe$_2$O$_3$ to Fe$_3$O$_4$. All of the chemical species considered in this calculation system are listed in Table 2.

Figure 3 shows the evolution of the sulfurous species, iron species and conventional gas at different fuel to oxygen carrier ratios at 950 °C. CO and H$_2$ were almost completely oxidized by the oxygen carrier when the fuel to oxygen carrier ratio was less than 1.0 (as shown in Figure 3a) due to the relatively excessive of lattice oxygen provided by Fe$_2$O$_3$. The concentration of CH$_4$ was always approximate to zero due to the fully decomposition of CH$_4$ under any conditions of the fuel to oxygen carrier ratio (as shown in Figure 3a). With respect to the sulfurous gases (as shown in Figure 3b), there was only SO$_2$ generated when the fuel to oxygen carrier ratio was less than 1.0, which indicated that H$_2$S could be completely oxidized by Fe$_2$O$_3$ to generate SO$_2$ via R1 at 950 °C in theory. When the fuel to oxygen carrier ratio was higher than 1.2, S$_2$ was generated from the decomposition of H$_2$S (R7), and COS was generated by the reaction of S$_2$ and CO as R8. However, S$_2$ was decreased to zero when the H$_2$ concentration increased to 0.05 vol % at the fuel to oxygen carrier ratio of 1.8. Thus, the H$_2$ was able to inhibit the decomposition of H$_2$S in real CLC processes.\(^{5,6,17}\) The concentration of CS$_2$ was always close to zero at any fuel to oxygen carrier ratio.

$$H_2S(g) = H_2(g) + 1/2S_2(g)$$ \hspace{1cm} (R7)

$$CO(g) + 1/2S_2(g) = COS(g)$$ \hspace{1cm} (R8)

As shown in Figure 3c, Fe$_3$O$_4$ was the main reduction form of Fe$_2$O$_3$ when the fuel to oxygen carrier ratio was less than 1.0. Moreover, solid sulfur compound of FeS and Fe$_{0.877}$S were generated when the fuel to oxygen carrier ratio was higher than 1.3, which was the product of reaction between FeO and H$_2$S (R5) (shown in Figure 2). There was no Fe$_2$S$_3$ generated (R4; shown in Figure 3c), which could also be explained by the lower thermodynamic equilibrium constants of R4 than that of R5. During the CLC process, there was usually no reduction form of Fe due to the thermodynamic limitation.\(^{18}\) Thus, there was no possibility of R6 taking place in CLC even though the equilibrium constant of R6 was high.

### 3.2. Conventional Gases Distribution.

The carbonaceous gases and H$_2$ distribution during the blank experiment (loaded with silica sand in the CLC reactor) are shown in Figure 4a, and the comparative experiment was conducted to investigate the conversion of the in situ XLT coal volatile products (including the carbonaceous gases, H$_2$, and sulfurous gases, Table 2. Chemical Species Considered in the HSC Calculation for Fe-Based Oxygen Carrier

<table>
<thead>
<tr>
<th>Species</th>
<th>g</th>
<th>solid oxide species</th>
<th>solid sulfur species</th>
<th>simple substance species</th>
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</thead>
<tbody>
<tr>
<td>H$_2$(g), H$_2$O(g), CO(g), CO$_2$(g), CH$_4$(g), C(g), C$_2$(g), C$_3$(g), C$_4$(g), C$_5$(g), C$_6$(g), C$_7$(g), C$_8$(g), S$_2$(g), S$_3$(g), S$_4$(g), S$_5$(g), S$_6$(g)</td>
<td>FeCO$_3$, FeO, Fe$_2$O$_3$, Fe$_3$O$_4$, Fe$_5$O$_7$, Fe$_7$O$_9$</td>
<td>FeS, FeS$_2$, FeS$_3$, FeS$_4$</td>
<td>Fe$_7$C, Fe$_7$C(B)</td>
<td>C$_7$C(A), C$_7$(C(D), Fe, S</td>
</tr>
</tbody>
</table>

$^a$g is the gaseous state; C(A) and C(D) are amorphous and diamond carbon, respectively; Fe$_7$C(B) is β-iron carbide, and FeS$_3$(M) is marcasite.
which was generated in the pyrolysis reactor and carried into the second CLC fuel reactor without cooling down process) by oxygen carrier, as shown in Figure 4b. In each experiment, either 40 g of silica sand or 40 g of oxygen carrier was loaded in the CLC fuel reactor, and 0.232 g of XLT coal was fed to the pyrolysis reactor, corresponding to the fuel to OC ratio of 0.5 (i.e., the OC to fuel ratio of 2.0). All the experiments were repeated three times at a typical CLC operational temperature, 950 °C.

As shown in Figure 4, the conventional gases during the pyrolysis process were H2, CO, CH4, and CO2, and the CO2 yield was 0.501 in the blank experiment, while for the CLC experiment of in situ pyrolysis gases, the detected carbonaceous species were CO2 and a little unconverted CO, which indicated that most of combustible gases (CO, CH4, and H2) was converted by oxygen carrier. A very high CO2 yield (0.963) in the CLC experiment can be explained by the well-mixing of pyrolysis gas and OC at the second CLC reactor as well as high-pressure resistance of the little porous distributor, resulting in the even distribution of pyrolysis gases (small or even no bubbles, thereby avoiding the bypassing of combustible gases as possible) through the bed inventory in the CLC fuel reactor. The carbon conversion reached 0.514 during the CLC experiment, which was slightly higher than that in the blank experiment. This is because some light hydrocarbons in tar were converted by the OC to detectable carbonaceous gases. The similar carbon conversion attained in the two experiments indicated that the pyrolysis process of coal was not affected by the oxygen carrier loaded at the second stage CLC reactor, which demonstrated the comparability of blank experiment and CLC experiment.

3.3. Sulfurous Gases Distribution. Figure 5 shows the evolution of sulfurous gases from the CLC fuel reactor. In the blank experiment of silica sand, the H2S was rapidly released and the peak of 280 ppmv was reached at ca. 30 s. The CS2 was subsequently increased to 34 ppmv, which can be ascribed to the decomposition of the pyrite (FeS2) or the reaction of pyrite and hydrocarbons and shown in R9. A small amount of COS was detected with a peak of 4 ppmv in the CO atmosphere, which was generated by the combination of S2 and pyrite with CO.19 There was very low concentration of SO2 in range of 0–0.6 ppmv, which was far below the detection accuracy of FTIR (5 ppmv). Generally, the released SO2 was from the decomposition of sulfates in coal.19

FeS2 + C = Fe + CS2(g) \hspace{1cm} (R9)

FeS2 + CH4(g) = Fe + 2H2(g) + CS2(g) \hspace{1cm} (R10)

In the iG-CLC of in situ coal volatile, the concentration of sulfurous gases from the fuel reactor was significantly changed. The peak of H2S was decreased to 93 ppmv. Meanwhile, a large amount of SO2 was quickly produced, which was mainly due to the oxidation of H2S in the volatile with oxygen carrier. As concluded from the HSC simulation, H2S could be totally oxidized by Fe2O3 to generate SO2 as shown in Figure 3b, with the highest equilibrium constant K. In addition, there was no COS and CS2 detected, which were also oxidized by the oxygen carrier, as in R11 and R12. In the HSC simulation, there was no H2S in the outlet gas, and the SO2 was close to 100 vol %, which was calculated based on the ideal thermodynamic equilibrium condition. The presence of a small amount of H2S could be explained as follows. (1) In an actual reaction process, the release of volatiles in coal was rather fast at high temperatures. Thus, the limited residence time of volatile matters may lead to incomplete reaction between H2S and oxygen carrier. (2) The reaction between H2S and oxygen carrier was after the reactions between CO, CH4 and H2 with oxygen carrier, as revealed in previous work.11 As indicated by the HSC results shown in Figure 2, the reaction between the partially reduced oxygen carrier (mainly consisting of Fe3O4) and H2S (R2) could probably not take place thermodynamically.

CS2(g) + 18Fe2O3 = 12Fe3O4 + CO2(g) + 2SO2(g) \hspace{1cm} (R11)

COS(g) + 9Fe2O3 = CO2(g) + 6Fe3O4 + SO2(g) \hspace{1cm} (R12)
Figure 6 shows the total volume of sulfurous gases (H₂S, SO₂, CS₂, and COS) from the fuel reactor during the coal pyrolysis process at blank experiment and CLC experiment. The results showed that SO₂ in the blank experiment was 0.93 ± 0.43 μL, which was below the lower limit of detection of FTIR as mentioned above. Thus, the generation of SO₂ could be neglected. The amounts of H₂S and CS₂ were 350.2 ± 7.8 and 32.6 ± 2.3 μL at the average value of three repeated experiments, respectively. The amount of COS was 3.8 ± 0.8 μL. The amounts of the sulfurous gases released were related to the type of coal used. When the coal volatile was constantly carried into the fuel reactor to react with oxygen carrier, CS₂ and COS were decreased to zero, indicating that CS₂ and COS was totally converted by oxygen carrier as R10 and R11. To be more specific, 62.8 wt % of H₂S was converted to SO₂ based on the increased amount of SO₂ and no sulfides (Fe₂S₃, Fe₀.₈₇₇S, or FeS) formation was observed (proved by SEM + EDX analysis in section 3.6). This result was consistent with the thermodynamic simulation of HSC chemistry: R1 was more thermodynamically favorable than R8 and R12, especially at high operational temperature. Similar results have also been found by Gu et al.¹ and Wang et al.¹. No sulfide was generated due to the high oxygen carrier to fuel ratio. Actually, during the reoxidization process of the OC (step 3 of the CLC experiment), no SO₂ was detected.

3.4. Sulfurous Gases Conversion. Figure 7 shows the carbon conversation rate (dX_C/dt) as a function of carbon conversion for the two comparative experiments. Based on the definition of carbon conversion, eq 7, it was related to the carbonaceous gases (CO₂, CO, and CH₄) to the coal carbon ratio. Thus, the yield and amount of pyrolysis products should be the same under the blank experiment and CLC experiment (in which the mixing of coal and OC was avoided) with the same mass of coal fed. The carbon conversion should also be the same. As shown in Figure 7, the carbon conversions of blank experiment and the CLC experiment were 0.507 and 0.514, respectively, when the coal pyrolysis process was completely finished. The slight difference could be attributed to the different fate of tar at the CLC experiment and the blank experiment. At the blank experiment with silica sand loaded, the tar was still in the gaseous phase without conversion. Subsequently, the gaseous tar was cooled at the down-tail tube and then removed by the tar-removing unit. That is, the component in tar is not detectable by the online gas analyzer. However, in the CLC experiment, the gaseous tar could be converted by OC to carbonaceous gases, which could be detected by the online gas analyzer. Thus, the carbon conversion of CLC experiment was slightly higher than that of the blank experiment. Additionally, when the carbon conversion was lower than 0.24, the maximum carbon conversion rate of CLC experiment was higher than that of the blank experiment. The peak carbon conversion rates were also different, which were 0.017 s⁻¹ at the carbon conversion of 0.16 (CLC experiment) and the 0.016 s⁻¹ at that of 0.23 (blank experiment), respectively, due to the same reason as mentioned above. The result also indicated that the tar could be easily converted into gaseous phases, resulting in the maximum peak of carbon conversion rate at earlier stage under the CLC experiment. When the carbon conversion exceeded 0.24, the carbon conversion rates were almost equal because that the effect of carbon in tar was reduced.

During the coal pyrolysis process (the first reactor), the sulfur compounds decomposed gradually with the increased temperature and then the sulfur immigrated to the pyrolysis products, char and tar. The sulfur releasing rate was quite fast at 950 °C. Figure 8 shows the sulfur conversion rate as a function of sulfur conversion. In the blank experiment, the sulfur conversion rate was shown a similar trend but lower than the carbon conversion rate. However, for the CLC experiment, the sulfur conversion rate was higher than the carbon conversion rate when the carbon conversion was lower than 0.08. It was because that the sulfur in tar was converted by OC to detectable sulfurous gases rather than being removed by the tar.
removing unit. Therefore, the sulfur conversion rate in CLC experiment was higher than that in blank experiment. When the carbon conversion exceeded 0.37, the sulfur conversion rates were almost the same in two comparison experiments. It was explained by that the release of tar was nearly finished and the CS$_2$ was not formed at the end of coal pyrolysis process, as shown in Figure 5. In addition, the conversion of H$_2$S to SO$_2$ had no effect on the sulfur conversion rate based on the definition of sulfur conversion rate (eq 4). The sulfur conversion reached 0.46 after the pyrolysis gas went through the oxygen carrier, compared to the value of 0.32 attained in the blank experiment, as shown in Figure 8. Once more, the higher sulfurous gases conversion rate of CLC experiment was explained by that the sulfur-containing species in tar was converted and oxidized into gaseous sulfur contents by the oxygen carrier.

3.5. Sulfur Balance. A “rough” sulfur balance was calculated based on the sulfur in volatile (m$_{s-v}$), as shown in eq 3. The sulfur balance of blank experiment was 84.1% because of some sulfur (such as the thiophene sulfide) remained in pyrolytic semichar and tar, and the tar was removed before the gas being introduced into FTIR. Thus, the sulfur in tar was not detected by FTIR, and resulted in the lower sulfur balance in the blank experiment. The mass fraction of H$_2$S, COS, CS$_2$, and SO$_2$ was 70.1, 0.8, 13.1, and 0.2 wt %, respectively. The sulfur balance of CLC experiment was 94.2 wt %, and the mass percentage of SO$_2$ was 68.2 wt %. There was 26.0 wt % of residual H$_2$S in the outlet gas because of the limited oxidization activity of Fe-based OC with H$_2$S$_2$ and the fast releasing rate of H$_2$S, as shown in Figure 9.

3.6. Characterization of the Oxygen Carrier. The surface morphology and element distribution of both the fresh and used oxygen carrier were characterized by environmental scanning electron microscope (ESEM, FEI Quanta 200) coupled with energy dispersive X-ray spectroscopy (EDX, FEI Quanta 200). As shown in Figure 10, the structure of the oxygen carrier was maintained well without sintering or agglomeration. This result is consistent with that obtained in our previous publications. The EDX results show that S element was not detected on the surface of both the fresh and used oxygen carrier, implying that the S-containing species generated by coal pyrolysis can mostly be oxidized by the oxygen carrier into sulfur oxides (SO$_2$) as R1. The obtained results from the EDX analysis agreed well with the simulation results shown in Figure 3.

4. DISCUSSION

Figure 11 presents the sulfur migration paths during coal pyrolysis process in chemical looping combustion environment.

The sulfur contents in the coal could migrate to the gaseous sulfur in volatile, tar as well as solid sulfur in char. At the operation temperature of CLC (950 °C), the organic sulfur and pyrite of inorganic sulfur were the main pyrolysis species during the coal pyrolysis process, which released as the gaseous products (H$_2$S, CS$_2$, and COS). The sulfate was difficult to decompose; thus, it belongs to stable noncombustible sulfur. The reducible sulphurous gases (H$_2$S, CS$_2$, and COS) could be converted into SO$_2$ by the oxygen carrier. During the coal pyrolysis process, the migration path of the sulfur in tar could be in two paths: on the one side, the tar could be desulfurized under the H$_2$/CO/CH$_4$ atmosphere, which was similar to the hydro-desulfurization process of coal tar, and then the sulphurous gases were oxidized by the OC; on the other side, the tar was directly reacted with OC and then the sulfur was released due to the C−S bond fission. The detailed migration paths of the sulfur in tar should be further investigated. Solid sulfur remained in char also needs further investigation afterward.

5. CONCLUSIONS

The sulfur distribution and evolution during the CLC of in situ coal pyrolysis products were investigated in the two-stage fluidized bed reactor, which was used to evaluate the direct reaction between oxygen carrier and in situ coal pyrolysis gases without a cooling process and avoiding the contact between...
coal and OC to eliminate the effect of OC on the coal pyrolysis process. The sulfur distribution was effected by the Fe-based OC when compared with the blank experiment. The main conclusions were drawn as detailed below:

(1) The sulfurous gases can be oxidized by the OC in the CLC environment, resulting in a quite different distribution compared to the blank experiment. In the absence of OC, H2S is the main sulfurous pyrolysis product of XLT lignite, accounting for 70.1 wt % of all sulphurous gases, and the rest are 0.8 wt % of COS, 0.2 wt % of SO2 and 13.1 wt % of CS2. However, the fraction of these sulfurous gases in the CLC environment were changed to 26.0 and 68.2 wt % for H2S and SO2, respectively.

(2) The sulfurous gas conversion rates in the blank experiment and CLC experiment were different when the carbon conversion was lower than 0.08. The difference could be attributed to the conversion of sulfur in tar by the OC in the CLC experiment, which accelerated the “phenomenological” sulfur conversion rate. The sulfur balance was up to 94.2% at the CLC experiment because of the detectable sulfurous gases converted from tar.

(3) In the presence of OC, 63% of H2S in lignite pyrolysis gases was oxidized by the active phase of OC (Fe2O3) to generate SO2 via the main reaction H2S(g) + 9Fe2O3 = 6Fe3O4 + H2O(g) + SO2(g). COS and CS2 were nearly completely oxidized by Fe2O3.

(4) The sulfur migration paths during coal pyrolysis process in CLC environment can be concluded as: gaseous sulfur species (H2S, CS2 and COS) and the sulfur content in tar were first released and then oxidized by the oxygen carrier to generate SO2. There was also a part of unconverted H2S released in the fuel reactor.

Author Contributions
‡J.M. and C.W. contributed equally.

Notes
The authors declare no competing financial interest.

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References
(22) Ma, J.; Zhao, H.; Tian, X.; Wei, Y.; Rajendran, S.; Zhang, Y.; Bhattacharya, S.; Zheng, C. Chemical looping combustion of coal in a
