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Research Article

Chemical Looping Combustion of Petroleum Coke with CuFe₂O₄ as Oxygen Carrier*

Utilizing petroleum coke as fuel in an efficient and environmentally friendly way is a great challenge. Within the technological framework of chemical looping combustion, the reaction of the oxygen carrier CuFe₂O₄ with a typical high-sulfur petroleum coke (designated as JS) was performed, focusing on the conversion of the JS coke, the oxygen transfer from CuFe₂O₄, and the reaction characteristics involved. Simultaneously, the evolution of sulfur and minerals present in JS was also considered. Thermogravimetric analysis of the reaction of CuFe₂O₄ with JS demonstrated the reaction superiority of CuFe₂O₄, with its reactivity being close to that of CuO. The preferred CuFe₂O₄ oxygen excess number Φ for JS conversion was determined as unity. Furthermore, both the experimental means, including Fourier transform infrared spectroscopy, field scanning electron microscopy/ energy-dispersive X-ray spectrometry and X-ray diffraction analysis, and the thermodynamic simulation of the reaction of CuFe₂O₄ with JS indicated that the main reduced counterparts of CuFe₂O₄ were Cu and Fe₃O₄. Most of the organic sulfur dominant in JS coke reacted with the reduced CuFe2O4 to form Cu2S, and the side product Fe₂SiO₄ should also be noted for its detrimental effect on the reactivity of CuFe₂O₄.

Keywords: Chemical looping combustion, Oxygen carrier, Petroleum coke, Thermogravimetric analysis

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1 Introduction

Petroleum coke is a solid byproduct of the oil refinery process. It is reported that on average 3.1 % of oil is refined into petroleum coke. Over the past decades, the output of petroleum coke increased greatly with the abrupt increase in oil consumption across the world. Although petroleum coke has the potential to be used as fuel for combustion [1] or gasification [2], its low reactivity and the serious environmental problems involved deterred its use, and most of it is still being stockpiled without utilization [3].

Chemical looping combustion (CLC) has gained great attention as a novel combustion technology for its great potential to solve energy and environmental problems [4, 5]. Recently, the feasibility of direct use of petroleum coke as fuel for CLC applications has been verified [6]. But the oxygen carriers (OC) used were mainly confined to single OC, such as Fe_2O_3 based [7,8] or CuO-based ones [9,10]. In relation to such single OC, the CuFe₂O₄ OC was found not only to overcome the disadvantages of the single CuO or Fe_2O_3 OC but also to display beneficial synergistic effects on the reactivity of the OC, as shown in our previous research works [11,12]. Therefore, it is worthwhile to explore the reaction characteristics of the CuFe₂O₄ OC with petroleum coke.

Furthermore, both the sulfur and mineral evolution during the reaction of petroleum coke with $CuFe_2O_4$ as OC should be given attention, although the content of ash in petroleum coke is generally low. But the sulfur content in petroleum coke is very high, which, without countermeasures, would bring about serious environmental pollution [13]. In addition, the interaction between the evolved sulfur species or minerals in the petroleum coke and the reduced OC would deteriorate the reactivity of the OC as well [14].

Here, $CuFe_2O_4$ was synthesized using a novel sol-gel combustion synthesis (SGCS) method, and its reaction with a Chinese petroleum coke was investigated using thermogravimetric analysis (TGA), to explore the reaction characteristics. The evolved gases were on-line detected by Fourier transform infrared (FTIR) spectroscopy. After reaction for the TGA, the

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morphology and the chemical components of the reduced solid products were characterized by field scanning electron microscopy/energy-dispersive X-ray spectrometry (FSEM-EDX), and their phases were further identified by X-ray diffraction (XRD) analysis. Finally, a thermodynamic simulation of the reduction of $CuFe_2O_4$ with this selected petroleum coke was conducted in order to gain a comprehensive understanding of the reaction mechanism involved.

2 Experimental Procedures

2.1 Materials and Characterization

The CuFe₂O₄ OC used in this research was synthesized by SGCS method with hydrated metal nitrates and urea as the precursors. A series of operation processes were involved, such as gel preparation, preheating, and sintering. The detailed preparation procedure is described in a previous report [15]. Finally, after grinding and sieving, the as-prepared CuFe₂O₄ within 63–106 μ m was collected for use.

As to the fuel, a typical Chinese petroleum coke was obtained from Shanghai Jinshan Petrochemical Corp. and is designated as JS hereafter. After similar procedures of drying, grinding and sieving, the JS coke sample in the size range of 63-106 µm was collected for use. The basic composition data of the sieved coke obtained from the proximate and ultimate analyses as well as the ash composition analysis are provided in Tab. 1, indicating that the sieved coke has typical characteristics such as high sulfur, high fixed carbon, and high heating values. The sulfur content present in JS coke was found to be as high as 5.25 wt %, typical of high-sulfur coke [16]. Further analysis by the Chinese national standard GB/T215-2003 indicated that, with a sulfur content larger than 90 %, the JS coke was organic sulfur dominated. Meanwhile, its carbon content was very high and fell within the carbon content range of high-rank coal such as anthracites [2]; thus, the reactivity of JS was very low [17]. As a result, the overall reaction characteristics are expected to differ greatly from those of coal [18] and a thorough investigation was needed.

Finally, after the OC synthesis and coke preparation, both the synthesized $CuFe_2O_4$ and the as-prepared JS coke sample were evenly mixed in a laboratory mortar at the designated mass ratio, using the developed mass balance method de-

Table 1. Properties of the JS coke studied.

Proximate analysis [wt %]				Ultim	LHV						
M _{ad}	$V_{\rm ad}$	$A_{\rm ad}$	FC _{ad}	С	Н	Ν	S	O ^{b)}	-[MJ/kg]		
2.11	15.15	2.04	80.97	80.45	3.47	1.27	5.25	5.41	35.46		
Ash analysis of JS coke [wt %]											
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO3	CaO	${\rm TiO}_2$	Co ₃ O ₄	K ₂ O	MgO	Na ₂ O		
55.33	17.98	11.32	2.59	3.65	1.08	2.47	1.28	0.80	0.50		

M, Moisture content; V, volatile matter; A, ash content; FC, fixed carbon; ad, air-dried basis; LHV, lower heating value. ^{a)} Dry basis. ^{b)} The oxygen content was determined by difference.

scribed in our previous reports [11, 19, 20]. Based on the properties of the JS coke as shown in Tab. 1, the relative chemical formula of 1 kg JS coke can be represented as $C_{65.6}H_{33.7}N_{0.89}S_{1.60}O_{3.31}$. When the CuFe₂O₄ oxygen excess number Φ was 1, i.e., the CuFe₂O₄ supplied theoretically just met the oxygen consumption for the full conversion of JS coke, the mass ratio of CuFe₂O₄ to JS coke was determined as 26.2. Similarly, at $\Phi = 0.5$ and 1.5, the relative mass ratios were determined as 13.1 and 39.2, respectively.

2.2 Experimental Methods

The reaction characteristics of the synthesized CuFe_2O_4 with JS at different oxygen excess numbers were investigated using a simultaneous thermal analyzer (Netzsch STA 409 PC, Germany). The mixture of JS with CuFe_2O_4 was heated from ambient temperature to 850 °C at 25 °C/min, and held for 20 min at this temperature to ensure sufficient conversion of the JS coke. An N₂ atmosphere was used, and several pre-screening experiments were performed to ensure the reproducibility of the experimental results. The flow rate of N₂ and the total mass for the mixture of JS and OC were determined at 80 mL min⁻¹ and ~ 15 mg, respectively.

After the TGA tests, the evolved gases from the reaction of JS coke with $CuFe_2O_4$ in the TGA were first dried in a portable tubular gas desiccator and then in situ detected with an FTIR spectrometer (EQUINOX 55; Bruker, Germany). The IR scanning range was 4000–500 cm⁻¹.

Finally, the surface morphology and chemical elements present in the solid residues from the reaction of JS with $CuFe_2O_4$ were studied using a field scanning electron microscope (Sirion 200, The Netherlands) coupled with an energy-dispersive X-ray spectrometer (Genesis, USA). The formed phases were further identified by XRD (X'Pert PRO, The Netherlands) with 40 kV and 40 mA CuKa radiation and in the step-scanned range of $2\theta = 10-90^\circ$.

2.3 Thermodynamic Simulation of the Reaction of CuFe₂O₄ OC with JS Coke

Although the thermodynamic equilibrium analysis has some limitations without consideration of the kinetic constraints in the real process, such as turbulent mixing and temperature gradients [21], the equilibrium calculation would benefit a better understanding of the lattice oxygen transfer involved in the OC studied and the JS coke transformation. Based on the minimization of the total Gibbs free energy, the reaction of CuFe₂O₄ with JS coke was further simulated using the HSC-Chemistry software 4.1.

According to the properties of JS coke given in Tab. 1, a complex reaction system was established for JS coke, which was considered to consist of the main matrix elements (such as C, H, N, S, and O), seven categories of potential minerals, and their possible intermediates present in JS, similar to our previous studies for coal representation [11, 19].

3 Results and Discussion

3.1 TGA-FTIR Investigation of the Reaction of CuFe₂O₄ with JS Coke

3.1.1 TGA Investigation of the Reaction of CuFe₂O₄ with JS Coke

The reaction of JS coke with the synthesized $CuFe_2O_4$ at the oxygen excess number $\Phi = 1$ under N_2 atmosphere was performed and assessed by TGA. The results of the TG and DTG analyses are shown in Fig. 1 a–d, with both JS pyrolysis and its reaction with the single reference oxides CuO and Fe₂O₃ included as well.

Firstly, as to JS pyrolysis shown in Fig. 1 a, b, based on the DTG curve in Fig. 1 b, above 200 °C JS pyrolysis was observed to experience only one discernible stage. Accompanied by devolatilization, the coke graphitization occurred with crystallite realignment [22], as described later. The characteristic temperature $T_{\rm m}$, i.e., the peak temperature relative to the DTG maximum, was found to reside at 643.9 °C, falling within the typical temperature range for devolatilization of various petroleum cokes [23]. Although the fixed carbon content of petroleum coke was generally similar to that of anthracite [2], as compared to our previous research on anthracite [19], the pyrolysis described by Furimsky [2] differed greatly. Therefore, further research on the reaction of JS with CuFe₂O₄ was performed.

The reaction of JS with $CuFe_2O_4$ was further investigated, as shown in Fig. 1 a, d. Both the reactions of JS with the reference oxides CuO or Fe_2O_3 were included in Fig. 1 a, c for comparison. From Fig. 1 a, it can be seen that the final weight after the reaction of JS with $CuFe_2O_4$ reached 80.2 %, falling within the respective final weights of JS with CuO and Fe_2O_3 , but its final



weight loss was much closer to that of JS with CuO. This means that the reactivity of $CuFe_2O_4$ with JS was greatly improved and far superior to Fe_2O_3 , although the dopant fraction of CuO involved in $CuFe_2O_4$ was theoretically deduced as only ~33 wt % by the chemical formula of $CuFe_2O_4$. Correspondingly, the maximal weight loss rate of $CuFe_2O_4$ with JS reached 0.3204 wt % min⁻¹, nearly surpassing that of JS with CuO, which clearly reflected the beneficial synergistic effect of $CuFe_2O_4$ OC compared to the single reference oxides. So, $CuFe_2O_4$ OC was desired to be adopted as OC in the realistic CLC system.

3.1.2 FTIR Analysis of Gas Evolution during the Reaction of CuFe₂O₄ with JS Coke

In order to obtain deeper insights into the reaction of $CuFe_2O_4$ with JS coke, the evolved gaseous products were on-line detected using FTIR coupled with TGA. The three-dimensional IR contours related to the gaseous products from the reaction of JS coke with $CuFe_2O_4$ are presented in Fig. 2. Meanwhile, the gaseous products evolved from the pyrolysis of JS coke were also recorded, for comparison.

Firstly, as a reference for JS coke pyrolysis, from Fig. 2 a it could be observed that, except for H₂O, the main gas products evolved were CO₂, CO, CH₄, of which CO₂ was ascribed to the cracking and reforming of functional groups such as carboxyl (C=O) and COOH, but the CO release was mainly related to the cracking of carbonyl (C–O–C) and carboxyl (C=O) groups [24]. According to the direct relationship of different IR peak heights with the variation tendency of the concentration for the relative gas [25], the CO concentration evolved was much less than that of CO₂ during the pyrolysis of JS coke. CH₄ was produced above 400 °C, arising from the disintegration of the side

> chains attached to the unstable macromolecules of JS coke [22, 23]. Furthermore, although the realistic distribution of various solid organic sulfur species was very complex in the JS coke sample and determined by different factors [26], during its pyrolysis, most of the organic sulfur involved was converted to SO₂ and COS (Fig. 2 a), among which SO₂ mainly resulted from the pyrolysis of organic sulfones [27, 28] and subsequently COS was formed through the reaction of SO₂ $+ 3CO \rightarrow COS + 2CO_2$, as proposed by Shen et al [29].

> Then, from Fig. 2 b it can be seen that in the reaction of JS coke with $CuFe_2O_4$ OC, below 450 °C, the presence of CO_2 , CO, CH_4 , and SO_2 mainly resulted from the JS pyrolysis, as discussed above. With further increasing reaction temperature, reaction of the gaseous products from the JS coke pyrolysis

Figure 1. Reaction of JS coke with $CuFe_2O_4$ OC. (a) Weight variation, (b) weight loss rate of JS coke pyrolysis under N_2 atmosphere, (c) weight loss rate of JS coke with the single reference oxides Fe_2O_3 or CuO, (d) weight loss rate of JS coke with $CuFe_2O_4$ combined OC.



769.9 °C at $\Phi = 0.5$ or of 789.0 °C at $\Phi = 1.5$. On the contrary, the weight loss rate of CuFe2O4 with JS at $\Phi = 1$ reached the highest value of 0.3204 wt % min⁻¹, far higher than the relative values at $\Phi = 0.5$ or 1.5, which is consistent with the experimental observation of Sun et al. [30]. Furthermore, the main mechanism in effect for the maximal weight loss rate at $\Phi = 1$ was explored and should be attributed to the more effective contact of CuFe₂O₄ with JS particles at $\Phi = 1$, similar to the conclusion reached by Siriwardane et al. [31] and Piekiel et al [32].

3.2 Chemical and Microstructure Analysis

To further clarify the reaction of JS with CuFe2O4 and to better understand the evolution of both the solid sulfur and mineral distribution in JS, the morphology of the solid products from the reaction of JS with CuFe2O4 was characterized using FSEM, as shown in Fig.4. The JS pyrolysis residue was also included as reference. The elemental compositions for the optionally selected spots on the FSEM figures were calculated using the ZAF correction method and are listed in Tab.2. In addition, the detailed phases involved in the reaction of

Figure 2. FTIR spectra for the evolution of gaseous species. (a) Pyrolysis of JS coke, (b) reaction of CuFe₂O₄ with JS coke at $\Phi = 1$.

with $CuFe_2O_4$ occurred, and thus the main products were observed as CO_2 and H_2O . In addition, a little CO was also formed, mainly due to the insufficient supply of $CuFe_2O_4$ OC, through the formation of side compounds between the reduced $CuFe_2O_4$ and the minerals contained in JS coke, as illuminated later.

3.1.3 Effect of the CuFe₂O₄ Oxygen Excess Number on Its Reaction with JS Coke

A suitable oxygen excess number of CuFe₂O₄ is very important to promote the full conversion of JS coke [6]. Therefore, the reaction characteristics of CuFe₂O₄ with JS at the different mass ratios, i.e. different CuFe₂O₄ oxygen excess numbers Φ , including $\Phi = 0.5$, 1 and 1.5, were further investigated, as presented in Fig. 3. This figure shows that the characteristic temperature of CuFe₂O₄ with JS at $\Phi = 1$ was 732.3 °C, lower than the two characteristic temperatures for CuFe₂O₄ with JS of $CuFe_2O_4$ with JS were identified using XRD analysis, and the results are provided in Fig. 5.



Figure 3. Effect of the $CuFe_2O_4$ OC excess number on its reaction with JS coke.



Figure 4. FSEM-EDX analysis of the solid products of the reaction between JS coke and $CuFe_2O_4$. (a) JS coke pyrolysis, (b) reaction of JS coke with $CuFe_2O_4$, (c) oxidization of the reduced $CuFe_2O_4$ with air.

In Fig. 4 a, for the pyrolysis of JS, the solid residues of JS in the SEM pattern are observed to mainly consist of the relatively dark bulk in spot 1 and a little fragmentary discrete particle in spot 2. By EDX analysis, the atomic fraction of C in spot 1 was 96.03 %, higher than that in spot 2, resulting from the main carbon matrix having not completely disintegrated during JS pyrolysis, while spot 2 was identified as minerals dispersed over the carbon matrix, mainly composed of Si and Al by EDX analysis. As shown in Fig. 5 for JS pyrolysis, the XRD results indicate that the main mineral observed was SiO_2 , while the crystallite of the graphitized carbon was more intense compared to the original coke itself (not shown). Especially at the (002) band, its diffraction intensity reached 781.2.

Table 2. Elemental analysis (atomic %) of the reaction of JS coke with $CuFe_2O_4$ OC by FSEM-EDX, applying the ZAF correction method.

Sample		С	0	Si	Fe	Al	S	Са	Cu
JS pyrolysis	Spot 1	96.03	0.57	0.04	0.04	0.03	3.19	0.00	0.00
	Spot 2	86.31	7.01	1.16	0.10	1.29	3.76	0.07	0.00
JS + CuFe ₂ O ₄ (Red)	Spot 1	13.94	1.58	0.37	0.88	0.14	0.11	0.33	81.96
	Spot 2	15.13	1.33	0.25	1.04	0.36	0.25	1.04	80.84
JS + CuFe ₂ O ₄ (Ox)	Spot 1	0.78	46.87	0.31	11.98	0.14	0.18	0.09	49.09
	Spot 2	0.45	49.11	0.17	11.76	0.09	0.13	0.17	44.87



Figure 5. XRD analysis of the solid products of the reaction between JS coke and CuFe₂O₄. (1) Quartz (SiO₂), (2) copper (Cu), (3) copper sulfide (CuS₂), (4) aluminum silicate (Al₂SiO₅), (5) magnetite (Fe₃O₄), (6) iron oxide (Fe₂O₃), (7) ferrosite (FeSiO₃), (8) copper oxide (CuO), (9) copper ferrite (CuFe₂O₄), and (10) fayalite (Fe₂SiO₄).

Furthermore, the SEM pattern in Fig. 4 b for the reaction of JS with $CuFe_2O_4$ shows that the bulky carbon matrix of JS was nearly consumed, with only ~14% of carbon left (Tab. 2). Oxygen was almost completely consumed to oxidize the petroleum coke. In addition, although no obvious indication of agglomeration or sintering was observed from Fig. 4 b for the reduced $CuFe_2O_4$, the distribution of Cu and Fe was not even in spots 1 and 2. As shown in Tab. 2, the contents of Cu on the two optionally selected points were around 80–81%, but the Fe content was found to be much less at only ~1%. This is possibly due to the preferential mobility of Cu because of its low melting point (~1085 °C) and thus its segregation from Fe₃O₄, another reduced counterpart of CuFe₂O₄.

In addition, it should be noted that some side products formed during the reaction of JS with $CuFe_2O_4$. Some of the organic sulfur forms contained in JS were found to react with the reduced $CuFe_2O_4$ and formed Cu_2S , which could be

further reoxidized with air to CuO in the air reactor (AR), as observed by Kyotani et al. [33]. However, some silicates such as Fe₂SiO₄ or Fe₂SiO₃ were produced through the reduced CuFe₂O₄ with SiO₂ present in JS, as observed in Fig. 5 a. Based on the XRD diffraction intensity of the respective species, although these side products formed were much less abundant than the main reduced counterparts of CuFe₂O₄, including Cu and Fe₃O₄, the detrimental effect was significant. Complete regeneration of the reduced CuFe2O4 could not be reached because the formed FeSiO₃ in the fuel reactor (FR) was entrained to the AR and further oxidized to the inert Fe₂SiO₄ therein and could not further react with CuO to form CuFe2O4 [34]. Thus, as shown in Fig. 4 c, the surface of the regenerated CuFe₂O₄ was covered with CuO, as can be deduced from Tab. 2 by the atomic ratio of Cu to O, which was further verified by the XRD analysis shown in Fig. 5 c.

3.3 Thermodynamic Investigation of the Reaction of CuFe₂O₄ with JS Coke

Finally, in order to better understand JS coke conversion and the evolution of sulfur and minerals present in JS coke, a thermodynamic simulation of the JS reaction with $CuFe_2O_4$ was conducted.

From Fig. 6 a, it can be observed that carbon contained in JS coke was mainly converted to CO_2 and that an enhanced reaction temperature benefited to convert more petroleum coke into CO_2 , which is in agreement with the findings of other researchers [1]. However, some CO was found to occur above 500 °C, meaning that the conversion of petroleum coke was incomplete, mainly due to the inert compounds formed between the reduced $CuFe_2O_4$ and the minerals contained in JS coke, as discussed above.

Furthermore, Fig. 6 b, c shows that the reduced counterparts of $CuFe_2O_4$ were Cu and Fe_3O_4 , consistent with the XRD analysis in Fig. 5 b. However, although the sulfur content was high enough in JS, more than 90% of it was converted into solid Cu_2S instead of gaseous sulfur species (Fig. 6 d), in agreement with the FTIR observation in Fig. 2 b for the reaction of JS coke with $CuFe_2O_4$, except for a little SO₂. During their reaction, no discernible gaseous sulfur species were formed. In contrast, besides Cu_2S , both Fe_2SiO_4 and $FeSiO_3$ were observed to form (Fig. 6 c). All of these side products should be responsible for the incomplete conversion of petroleum coke, as observed above.

4 Conclusions

The reaction of $CuFe_2O_4$ with JS, a typical high-sulfur petroleum coke, was performed in combination with TGA. A systematic investigation was done using both different experimental means (FSEM-EDX and XRD) and thermodynamic simulation. The following conclusions were reached:

- The TGA analysis of the reaction of CuFe₂O₄ with JS demonstrated its reaction superiority over Fe₂O₃. The reactivity of CuFe₂O₄ was found to be much closer to that of CuO during the reaction with JS. And the preferred CuFe₂O₄ OC excess number Φ was found as unity.



Figure 6. Equilibrium distribution of various species for the reaction of JS coke with $CuFe_2O_4$. (a) Various C-containing species, (b) Cu-containing species, (c) Fe-containing species, and (d) various sulfur species.

- FSEM-EDX and XRD analysis indicated that the main reduced counterparts of CuFe₂O₄ were Cu and Fe₃O₄, which was also verified by the thermodynamic simulation of the reaction of CuFe₂O₄ with JS.
- The side products Cu₂S and Fe₂SiO₄ should be noted as well. They were not only detrimental to the reactivity of CuFe₂O₄ OC but also prevented the reduced CuFe₂O₄ from being fully regenerated.

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