Thermodynamic Investigation of Carbon Deposition and Sulfur Evolution in Chemical Looping Combustion with Syngas

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Chemical looping combustion (CLC) with syngas, a synthesized gas mixture of CO, H_2, CO_2, H_2O(g), N_2, and H_2S, was investigated using thermodynamic simulation, with focus on carbon deposition and sulfur evolution in CLC. Five metal oxides, such as NiO, CuO, Fe_2O_3, Mn_3O_4, and CoO, were selected as oxygen carriers for CLC application. Different influencing factors on the formation of carbon deposits were investigated, including pressure, fuel reactor (FR) temperature, oxygen excess number Φ (denoting the availability of lattice oxygen in the oxygen carrier to the fuel), and fuel gas composition. Higher temperature and larger oxygen excess number Φ inhibited the formation of carbon deposits while the pressurized condition caused the opposite. The increase of H_2O(g) and CO_2 fraction in syngas reduced carbon deposition while, in contrast, a larger H_2S occurrence in syngas led to more carbon deposits to be formed. A sensitivity analysis to the different factors revealed that carbon deposition was mainly determined by the FR temperature and the oxygen carriers provided while other factors played a minor role. In addition, the predominant C-bearing species and their distributions at different temperatures were thermodynamically investigated. At low FR temperature and oxygen-deficient condition (i.e., oxygen excess number $\Phi < 1$), the predominant carbon species as solid deposits were mainly elemental carbon or carbonates for NiO, CuO, Fe_2O_3, and CoO while MnC_2 and $MnCO_3$ were the main species for Mn_3O_4. In terms of the evolution of sulfur in CLC with syngas containing a basic composition of CO, N_2, H_2, and H_2S, the low pressure, high temperature, and adequate lattice oxygen would make more sulfur species form in the gas phase. After that, CO_2 and H_2O(g) were introduced into the syngas, and they were found to possibly serve as additional oxidizers to convert H_2S into SO_2. The oxidation function of CO_2 was slightly stronger than that of steam. Again, the evolution and distribution of various sulfur species was studied. For four metal oxides (NiO, Fe_2O_3, Mn_3O_4, and CoO), the most possible solid sulfur compounds were Ni_3S_2, $Fe_{0.84}S$, $MnSO_4$, and $Co_{0.89}S$, respectively. But for CuO, at $\Phi < 1$, Cu_2S was the main solid sulfur compound while at $\Phi > 1$ $CuSO_4$ and Cu_2SO_4 dominated.

1. Introduction

Public increasing concern over global warming and the severe problems related to climate change necessitate the control of CO_2 emission from fossil fuels, especially coal.[1] Currently, the major technologies for CO_2 abatement are classified into postcombustion, precombustion decarbonization, and oxy-fuel combustion technologies. However, all of these technologies generally require gas separation and therefore much energy consumption. Fundamentally different to them, chemical looping combustion (CLC), a novel method, addresses the CO_2 capture by completely avoiding any gas separation.[2] The CLC system is composed of two reactors, an air reactor (AR) and a fuel reactor (FR), as shown in Figure 1, where the air and fuel are never mixed together. In the FR, the fuel is oxidized with metal oxides M_xO_y instead of air in the normal combustion. At the full conversion of fuel, the exit gas stream from the FR mainly consists of CO_2 and steam. Pure CO_2 will be readily recovered by condensing the steam. The reduced metal oxide M_xO_{y-1} is then transferred from the FR to the AR, where it is reoxidized by air. Compared to the normal combustion, because CO_2 in CLC is not diluted with N_2 in the air, it can easily be separated without much energy consumption. Another two verified advantages for CLC are, first, to thoroughly eradicate the formation of NO_x, as a result of the introduction of fuel and air into different reactors and of the moderate AR operating

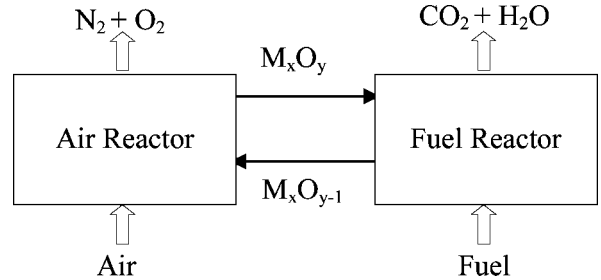

Figure 1. Scheme of CLC. M_xO_y/M_xO_{y-1} denotes the oxidized and reduced oxygen carriers, respectively.

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temperature,[3] and, then, to improve the thermal efficiency of fuel combustion as a result of the lesser irreversibility of fuel oxidation.[4] Therefore, using CLC can simultaneously solve energy and environmental problems.[5]

In CLC-related research, the oxygen carrier development and further optimization of their performances attract the most interest.[6–9] Currently, the main oxygen carriers considered are Ni, Cu, Fe, Mn, or Co based oxides.[10] To attain an optimal performance of oxygen carriers in CLC, special attention should be paid to side reactions, mainly involving the deposition of carbon from carbonaceous fuel and the evolution of sulfur species in gas fuel. Otherwise, several disadvantages would be caused from these side reactions. First, carbon deposition causes potentially the deactivation of oxygen carriers in the FR. When the carbon deposits on the oxygen carrier are transported from the FR back to the AR, CO_2 will be generated there thus causing a reduced CO_2 capture efficiency of the CLC system. Second, gas sulfur components in the syngas could possibly react with oxygen carriers and form various sulfur compounds that might be poisonous to oxygen carriers. Therefore, it is essential to understand the pathways of carbon deposition and sulfur evolution in CLC so as to eliminate the negative effects of these side reactions.

Carbon deposition is a complex phenomenon which is believed to be influenced by several factors, such as pressure, temperature, availability of lattice oxygen in the oxygen carriers, contents of $H_2O(g)$ and CO_2 in the fuel gas, and so forth. Different measures have been investigated to inhibit the generation of solid carbon species, such as injection into the FR of a certain amount of steam, CO_2, and so on.[11–13] The evolution of gas sulfur components was previously studied via thermodynamic analysis,[14,15] with the predominant sulfur species in gas and solid phases predicted. It was also postulated that besides oxygen carriers, the steam and CO_2 might also be oxidizers to convert the fuel sulfur component (H_2S) to SO_2 and other gas sulfur species (such as $S_2(g)$ and COS). Jerndal et al.[14] also analyzed the different amounts of sulfur in gas phase needed to form various sulfides or sulfates for different metal oxides. Nevertheless, research on carbon deposition and sulfur evolution in CLC is still very limited. There exist many unknowns associated with the formation of carbon deposition and the evolution of sulfur components in an FR; thus, further investigations are needed to understand both phenomena better.

As we know, coal is much more abundant than other fossil fuels and, also, more CO_2 is generated from coal utilization. It would be highly advantageous and meaningful if the gas fuel derived from coal is adopted for CLC. The feasibility of integrating coal gasification and CLC with lower energy penalties in power generation has been validated.[9] Simulations performed by Anheden and Svedberg[16] and Jin and Ishida[17] indicated that CLC integrated with coal gasification had the potential to achieve a higher efficiency than a similar combined cycle using conventional CO_2 capture technology. Therefore, the syngas derived from coal gasification will be considered as the fuel gas in CLC simulation in this study. In fact, the gas components in syngas generated from coal gasification varied greatly.[18] The variation range was reported for H_2 25–30%, CO 30–60%, CO_2 5–15%, H_2O 2–30%, H_2S 0.2–1%, and N_2 0.2–1%. Nevertheless, in previous studies, the syngas, simply simulated as 50% CO and 50% H_2 in their volumetric fraction, was mostly adopted as the fuel for CLC simulation and experiment investigations.[8,19] Jin and Ishida[17] even used H_2, CO, $H_2O(g)$, CO_2, and Ar to represent the syngas in their experimental study on CLC. But none of thermodynamic simulations on CLC have been conducted with a complex syngas composition as that of the fuel. Furthermore, the effect of different fuel gas compositions, particularly the occurrence of $H_2O(g)$, CO_2, and H_2S in syngas, on the formation of carbon deposits and sulfur evolution has never been systematically studied before. It is now worthy to perform a comprehensive thermodynamic simulation with a complicated CLC system to investigate the two phenomena.

In this study, the syngas containing a mixture of gas components (CO, H_2, $H_2O(g)$, CO_2, H_2S, N_2) was considered as a fuel in CLC for thermodynamic simulation using the HSC-Chemistry software 4.0. The reduction reactions of oxygen carriers with syngas in an FR were investigated considering five metal oxides (NiO, CuO, Fe_2O_3, Mn_3O_4, CoO). The influence of pressure, temperature, and amount of oxygen carrier was briefly investigated and followed by a detail analysis of the effect of the fuel gas composition on carbon deposition. Particularly, the occurrence of $H_2O(g)$, CO_2, and H_2S in syngas on carbon deposition was iterated. A sensitivity analysis of the effect of these factors on carbon deposition was performed to quantita-

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Table 1. Composition of Syngas (vol %)

H_2	CO	CO_2	$H_2O(g)$[a]	H_2S	N_2
25	35	10	20	3	balance

[a] g: denotes the component in its gas phase.

tively evaluate their different influencing degrees. Furthermore, the effects of different factors (temperature, pressure, air excess number) and the occurrences of $H_2O(g)$ and CO_2 in syngas on sulfur species evolution were also clarified. Finally, the predominant carbon and sulfur species in a wide temperature range were both thermodynamically predicted. This study provides much essential information for a better understanding of carbon deposition and sulfur evaluation occurring in the CLC process.

2. Method and Calculation Procedure

2.1. Design of Reaction System. The representative syngas composition used in this simulation is listed in Table 1, and its relative atomic composition could be represented as $C_\alpha H_\beta S_\gamma O_\delta (CO_2)_\lambda (H_2O)(N_2)_\nu$, where the atom numbers were determined by Table 1. The reduction reaction of oxygen carriers with syngas in the FR and the reoxidation of the reduced oxygen carriers in the AR could be depicted, respectively, as follows

$$C_\alpha H_\beta S_\gamma O_\delta (CO_2)_\lambda (H_2O)_\mu (N_2)_\nu (g) + (2\alpha + \beta/2 + 2\gamma - \delta) M_x O_y \rightarrow (2\alpha + \beta/2 + 2\gamma - \delta) M_x O_{y-1} + (\alpha + \lambda) CO_2(g) + (\beta/2 + \mu) H_2O(g) + \gamma SO_2(g) + \nu N_2(g) \quad (1)$$

$$2M_x O_{y-1} + (O_2 + 3.76N_2)(g) \rightarrow 2M_x O_y + 3.76N_2(g) \quad (2)$$

According to previous literature,[10] five metal oxides (NiO, CuO, Fe_2O_3, Mn_3O_4, and CoO) were selected as oxygen carriers in the CLC simulation system of this study. Generally, reduced counterparts of the selected metal oxides are in elemental form, such as NiO−Ni. However, special attention should be paid to Fe, Cu, Mn, and Co oxides because of their different oxidation states. For iron, it could have several forms such as Fe_2O_3−Fe_3O_4−FeO−Fe, but in the FR of a real CLC system, because of the low conversion rate of Fe_2O_3 to other lower valence states of Fe than to Fe_3O_4, the conversion of Fe_2O_3 to Fe_3O_4 will be the predominant path.[20] CuO may decompose into Cu_2O in a N_2 atmosphere around 800 °C despite its stability in the air atmosphere at the same temperature but at a low decomposition rate,[21] so the CuO−Cu pair was considered in this study with Cu_2O just included in the system as the transition form of copper oxides (as shown in Table 2). Mn_3O_4 was selected as the Mn-bearing oxygen carrier because its higher valence forms (MnO_2 and Mn_2O_3) are not stable and decompose in air at around 500 and 820 °C,[22] respectively. Thus, the Mn_3O_4−MnO pair was considered as the FR temperature of interest was mainly fixed at around 950 °C.

In addition, although metal oxides are necessary to combine with various supports (such as SiO_2, Al_2O_3, TiO_2, etc.) as oxygen carriers for CLC application, as a first step this study investigated the reduction reaction of metal oxides alone with syngas for a better understanding of their reaction characteristics. The potential effect of supports on carbon deposition and sulfur evolution in CLC will be investigated in our future study. All the chemical species considered in this calculation system for different metal oxides are shown in Table 2, including the metal oxides pairs, common gas species, deposited carbon species, and sulfur species. Almost all the related solid phase C- and S-bearing species available in the HSC database have been included to investigate the predominant carbon species that might lead to carbon deposition and the predominant sulfur species that could influence the performance of oxygen carriers in the FR of CLC.

2.2. Determination of Oxygen Excess Number Φ. The availability of oxygen present in metal oxides is one of the most important factors to determine the full conversion of fuel in the FR. Furthermore, carbon deposition and the evolution of gas sulfur components are also closely associated with the amount of oxygen carriers supplied. The theoretic stoichiometric oxygen needed for the full conversion of syngas shown in eq 1 was $(2\alpha + \beta/2 + 2\gamma - \delta)$, and supposing the realistic oxygen contained in oxygen carriers was $Y(O)$, then the oxygen excess number Φ was defined as follows

$$\Phi = Y(O)/(2\alpha + \beta/2 + 2\gamma - \delta) \quad (3)$$

In eq 3, $\Phi < 1$ denoted that the oxidation of syngas with oxygen carriers was initiated under an oxygen-deficient condition; $\Phi > 1$ meant that the reaction was occurring in an oxygen-rich environment; and $\Phi = 1$ referred to that the oxygen supplied theoretically just met the requirement of a full conversion of fuel.

2.3. Calculation Method. The reduction reaction of various metal oxides with syngas in the FR was investigated using the HSC-Chemistry software 4.0 and based on the minimization of the total Gibbs free energy. The predominant equilibrium compositions in the FR were simulated, with focus on the carbon- and sulfur-bearing species, at various pressures (1, 10, 15, and 30 bar), temperatures (mainly 100−1400 °C for all metal oxides except for CuO at a relatively lower temperature, because of the much lower melting point of the reduced element Cu, i.e., ∼1085 °C), and oxygen excess numbers Φ (including $\Phi < 1$, $\Phi = 1$, and $\Phi > 1$, respectively). It was noteworthy that the thermodynamic equilibrium analysis did not consider any kinetic constraints, such as, mixing and/or temperature gradients occurring in the real process; thus, experimental works were needed to verify the simulations. Nevertheless, the equilibrium calculation provides a useful guide for predicting major species in the system, allowing a better understanding of the complex reactions to happen in the CLC system, including those associated with carbon deposition and sulfur evolution.

In view of carbon deposition, first, a simple syngas system (containing only CO, N_2, and H_2) was considered to investigate the effect of temperature, pressure, and Φ. Then, the fuel gas composition was changed by introducing $H_2O(g)$, CO_2, and H_2S separately into the simple system, aiming to understand their different effects on carbon deposition. Furthermore, to compare the degree of influence of these factors on carbon deposition, a sensitivity analysis was performed, and the relative linear sensitivity coefficient ω_i of carbon deposition amount m toward various factors χ_i (including temperature, pressure, Φ, the

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Table 2. Species Considered in the HSC Calculation for Various Metal Oxides[a]

metal oxides	NiO−Ni	Fe_2O_3−Fe_3O_4	CuO−(Cu_2O)−Cu	Mn_3O_4−MnO	CoO−Co
common species	H_2(g), H_2O(g) CO(g), CO_2(g), CH_4(g), C(g), C_2(g), C_3(g), C_4(g), C_5(g), C, C(A), C(D) H_2S(g), SO_2(g), SO_3(g), COS(g), S(g), S_2(g), S_3(g), S_4(g), S_5(g), S_6(g), S_7(g), S_8(g), CS(g), CS_2(g), S N_2(g), NO(g), NO_2(g), NO_3(g), N_2O(g), N_2O_2(g), N_2O_3(g), N_2O_4(g), N_2O_5(g)				
deposited carbon species	Ni_3C	Fe_3C Fe_3C(B)		MnC_2, Mn_3C Mn_7C_3 $Mn_{15}C_4$ $Mn_{23}C_6$	Co_2C
	$NiCO_3$	$FeCO_3$	$CuCO_3$ $Cu_2(OH)_2CO_3$ $Cu_3(OH)_2(CO_3)_2$	$MnCO_3$	$CoCO_3$
deposited sulfur species	$NiS_{0.84}$ NiS, NiS(A) Ni_3S_2, Ni_3S_4	$Fe_{0.877}S$ FeS, FeS_2 FeS_2(M) Fe_2S_3, Fe_7S_8	CuS Cu_2S	MnS MnS_2	$CoS_{0.89}$, CoS $CoS_{1.333}$ CoS_2, Co_3S_4 Co_9S_8
	$NiSO_4$ $NiSO_4 \cdot H_2O$ $NiSO_4 \cdot 4H_2O$ $NiSO_4 \cdot 6H_2O$ $NiSO_4 \cdot 7H_2O$	$FeSO_4$ $Fe_2(SO_4)_3$ $FeSO_4 \cdot H_2O$ $FeSO_4 \cdot 4H_2O$ $FeSO_4 \cdot 7H_2O$	$CuSO_4$ Cu_2SO_4 $CuSO_4 \cdot H_2O$ $CuSO_4 \cdot 3H_2O$ $CuSO_4 \cdot 4H_2O$ $CuO \cdot CuSO_4$	$MnSO_4$ $MnSO_4 \cdot H_2O$ $MnSO_4 \cdot 4H_2O$ $MnSO_4 \cdot 5H_2O$ $MnSO_4 \cdot 7H_2O$	$CoSO_4$ $CoSO_4 \cdot 6H_2O$ $CoSO_4 \cdot 7H_2O$

[a] g is the gaseous state; C(A) and C(D) are amorphous and diamond carbon, respectively; Fe_3C(B) is β-iron carbide and FeS_2(M) is marcasite; NiS(A) is α-nickel sulfide.

content of H_2O(g), CO_2, and H_2S in the syngas) was calculated by the finite difference method.[23]

$$\omega_i = \frac{\Delta m/m}{\Delta \chi_i / \chi_i} \tag{4}$$

where i denotes the various factors mentioned above. The parameters of these factors adopted as the base case were the FR temperature 600 °C (the same as Jin et al. used[12]), pressure 1 bar, $\Phi = 0.5$, and the volume of H_2O(g) 20%, of CO_2 10%, and of H_2S 3%, respectively. After five calculations were performed for each factor changing the factor value from the base case while keeping other parameters constant, it was found that the results of the sensitivity analysis showed the same tendency for the same factor. Therefore, only one representative case was reported. Finally, the distribution of various carbon-bearing species was analyzed considering the complicated syngas system containing all the gas species as shown in Table 1, under different pressures, FR temperatures, and oxygen excess numbers Φ.

Furthermore, the sulfur evolution in CLC was simulated first in a simple system of syngas (CO, N_2, H_2, and H_2S). After that, H_2O(g) and CO_2 were introduced separately into the system, and the influence of their presence on sulfur distribution was evaluated. Finally, various sulfur species were predicted in the FR of the CLC system with the complete syngas as fuel and under different conditions as shown in Table 1.

3. Results and Discussion

3.1. Carbon Deposition. *3.1.1. Effect of Various Factors on Carbon Deposition.* The occurrence of carbon deposition in the FR was predicted under various conditions, and the results are depicted in Figure 2. The conditions for forming carbon deposits (i.e., various carbon species in the solid phase) in a simple syngas (CO, N_2, H_2) system are summarized in Figure 2a, with varying temperature, pressure, and Φ. The three solid lines denote the equilibrium boundary of free carbon deposition at three pressures (1, 10, and 30 bar) and at various oxygen excess numbers Φ (0−0.9) and FR temperatures (400−1300 °C). The area below each boundary indicates the carbon deposition region while the area above denotes no solid carbon formation under the related condition. At the beginning, it was found that at a fixed pressure and Φ the area of carbon deposition decreased with FR temperature increase. Meanwhile, at a fixed FR temperature and atmospheric pressure, a larger Φ (i.e., more oxygen carrier) was needed to reach the area of "no carbon deposition". Also, the pressurized condition caused the area of carbon deposition to increase. Overall, high temperature, low pressure, and sufficient oxygen carriers were beneficial to reduce the carbon deposition. This simulation result was similar to that of Jerndal et al.,[14] though the fuel used in this study was syngas instead of methane.

Furthermore, the effect of H_2O(g) content in syngas on carbon deposition was investigated by introducing steam at different concentrations into the simple syngas as the fuel of CLC. The simulated results are presented in Figure 2b. First, it was found that at a fixed FR temperature and Φ, the area of carbon deposition decreased with H_2O(g) content in the syngas. A higher FR temperature produced less deposited carbon on the oxygen carrier, similar to the findings in Figure 2a. In terms of the inhibition mechanism of carbon deposition with the addition of H_2O(g), Jerndal et al.[14] reported that the H_2O(g) acted as the additional lattice oxygen source, similar to the oxygen provided by the oxygen carrier, to enhance the conversion of carbon deposit to CO_2 while Ishida et al.[12] believed that the H_2O(g) addition initiated the shifting reaction of CO in syngas and thus reduced the conversion of CO to carbon via the Boudouard reaction. Similarly, the CO_2 and H_2S were introduced separately into the system (data not shown here). CO_2 behaved quite similarly as H_2O(g) in inhibiting carbon deposition through possibly different mechanisms while the addition of H_2S led to more solid carbon deposition. Nevertheless, further research is needed to obtain a better understanding of the different effects of steam, CO_2, and H_2S on carbon deposition. In the complicated

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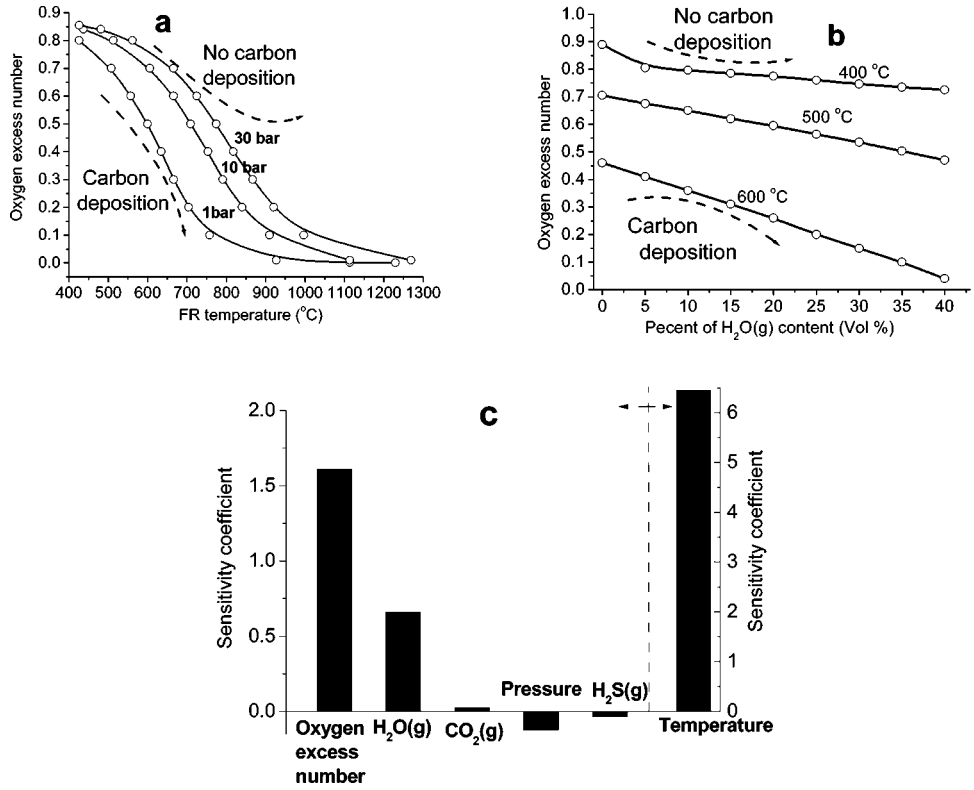

Figure 2. Effects of different factors on carbon deposition: (a) effect of temperature, pressure, and oxygen excess number Φ in a simple syngas system; (b) effect of H_2O(g) content on carbon deposition; and (c) sensitivity coefficient of various factors on carbon deposition.

syngas system (see Table 1), the influence of changing temperature and pressure demonstrated almost the same tendency of effects as those observed in the simple system (Figure 2a). The only difference found was that, at the same FR temperature and pressure, the area of free carbon deposition for the complicated syngas system was far enlarged compared to that for the simple system, most likely because of the synergistic effect of H_2O(g), H_2S, and CO_2 on carbon deposition.

A sensitivity analysis was conducted to understand the different extents of the considered factors on carbon deposition. The sensitivity coefficient values of various factors on carbon deposition are shown in Figure 2c, which were generated by changing the parameters from the base case to temperature 500 °C, pressure 10 bar, and Φ = 0.6 and the volume of H_2O(g) to 10%, of CO_2 to 20%, and of H_2S to 0%, respectively. First, the sensitivity values of temperature, Φ, and the contents of H_2O(g) and CO_2 toward the variation of carbon deposition were positive, which meant that increase of these parameters would eliminate carbon deposition. Nevertheless, the sensitivity values of pressure and content of H_2S were negative, which implied that increase of these parameters would cause more deposited carbon, similar to the finding reported by Jerndal et al.[14] Furthermore, the influence of temperature on eliminating carbon deposition was the most significant with the sensitivity coefficient over 6 as indicated by the right-side *Y*-axis. Following it, Φ and the content of steam showed their sensitivity coefficients respectively at ∼1.5 and 0.5, as indicated by the left-side *Y*-axis. The content of CO_2 demonstrated the minimal eliminating effect on carbon deposition. On the contrary, the pressure showed a higher potential than the content of H_2S in causing carbon deposition. Furthermore, the effect of H_2O(g) on the inhibition of carbon deposition was greater than that of CO_2 (Figure 2c), which was the same as the previous finding.[12] This indicated that, at the same reaction condition, the addition of H_2O(g) was more effective than that of CO_2 to inhibit solid carbon formation.

3.1.2. Predominant Carbon-Bearing Species for the Studied Metal Oxides. The equilibrium distributions of various C-bearing species in CLC at different pressures (1 bar, "solid line"; 15 bar, "dashed line") and fixed Φ (0.5) for different metal oxides (NiO, Fe_2O_3, CuO, Mn_3O_4, and CoO) are shown in Figure 3a,c,d,e,f, respectively. In addition, the predominant C-bearing species for NiO were simulated at different oxygen excess numbers (Φ = 0.8 and 1.2) at 1 bar, and the result is given in Figure 3b. The discussions on Figure 3 are given below.

(i) Effect of Temperature. In Figure 3a,d,e,f with temperature increasing from 100 to 1400 °C as well as in Figure 3c for CuO with the FR temperature to 1085 °C, CO_2 was found as the predominant carbon species in the whole temperature range for almost all the metal oxides studied. The percentages of CO became significant from 600 °C onward for the four metal oxides, except for Mn_3O_4. Various carbon deposits (mostly carbon and metal–carbonates) were found generally at low temperature while at high temperature (>1000 °C) only CO_2 and CO are thermodynamically stable carbon species. It is noteworthy that, for Mn_3O_4, the deposited carbon species were mainly $MnCO_3$ and MnC_2, different from other metal oxides.

In Figure 3, $CH_4$was always generated and mainly occurred at low temperature (below 700 °C) for most of the metal oxides studied except for Mn_3O_4. This basically agreed with the previous findings[24] where a laboratory fluidized bed reactor was used to test different oxygen carriers. Although there was no CH_4 present in the syngas supplied (50% H_2 and 50% CO), CH_4 was found to form through the methanation reaction of CO and H_2, especially at low FR temperature (generally below 600 °C). Furthermore, in this

(24) Mattisson, T.; Johansson, M.; Lyngfelt, A. CO_2 capture from coal combustion using chemical-looping combustion -reactivity investigation of Fe, Ni and Mn based oxygen carriers using syngas. Presented at the 2006 Clearwater Coal Conference, Clearwater, FL, U.S.A., 2006.

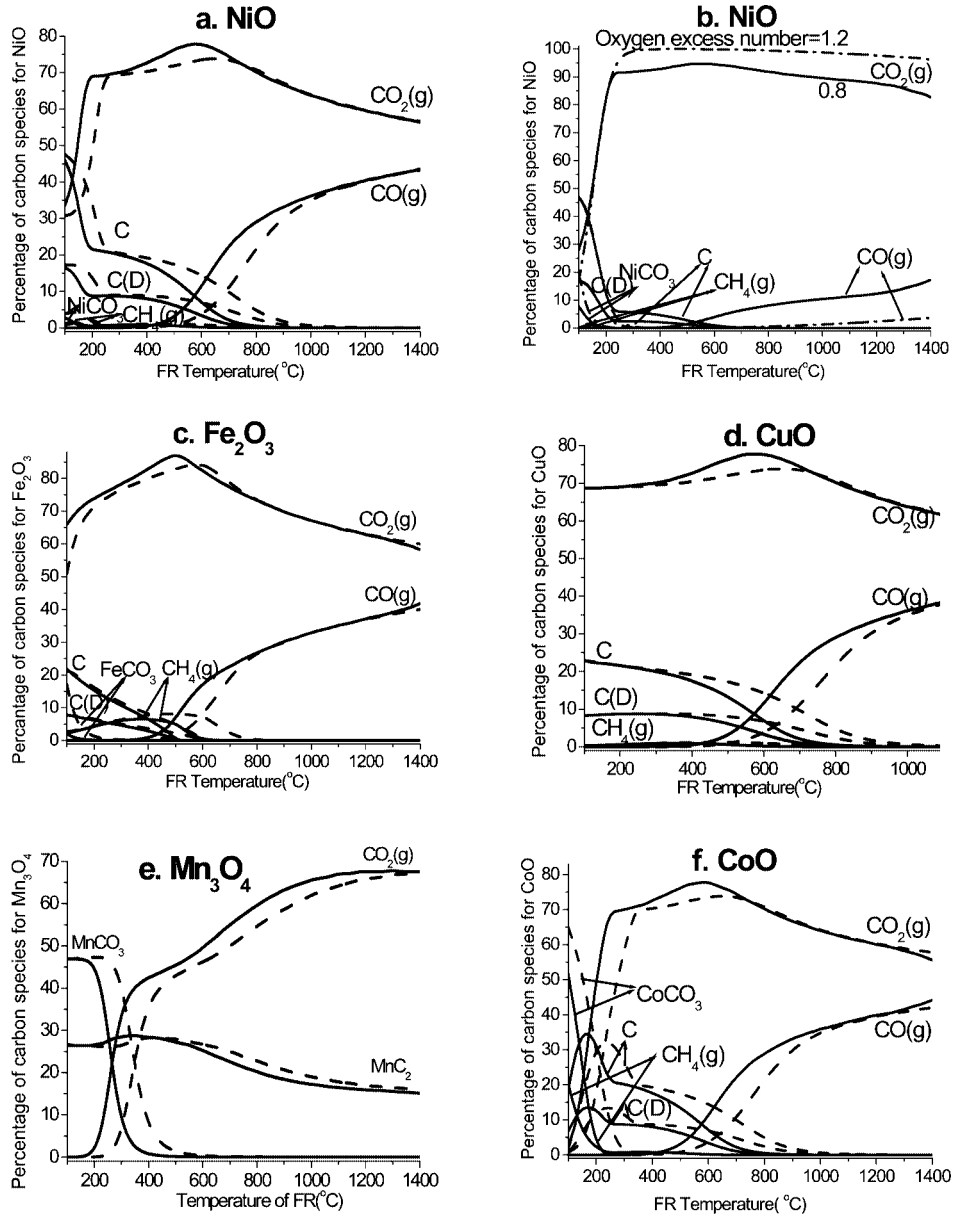

Figure 3. Equilibrium distribution of various carbon species for different metal oxides, (a, b) NiO, (c) Fe_2O_3, (d) CuO, (e) Mn_3O_4, and (f) CoO. The simulated conditions are oxygen excess number $\Phi = 0.5$, pressure $P = 1$ bar (solid line), $\Phi = 0.5$, $P = 15$ bar (dash line) for parts a, c, d, e, and f, respectively, but for part b, $\Phi = 0.8$, $P = 1$ bar (solid line) and $\Phi = 1.2$, $P = 1$ bar (dashed-dotted line) were used.

study it was found that the percentages of CH_4 diminished with increasing pressure and Φ.

(ii) Effect of Pressure. When pressure was increased from 1 to 15 bar for various metal oxides studied, the equilibrium percentages of CO_2 and CO somewhat declined at the studied temperature range; thus, the percentages of various solid carbon species increased. Especially at low FR temperature (mainly at 100−600 °C), the percentages of elemental carbons and relative carbonates of the studied metal oxides were strikingly increased.

(iii) Effect of Φ. In Figure 3b, with Φ changing from 0.8 to 1.2, the CO_2 equilibrium percentage increased obviously to nearly 100% from a very low temperature (around 200 °C), corresponding to a decrease of CO equilibrium percentage. The percentages of various deposited carbon species declined to a large degree from $\Phi = 0.5$ (see Figure 3a) to $\Phi = 0.8$ and 1.2 (see Figure 3b), most likely because of the enhanced conversion of elemental carbon to CO_2 with more oxygen supplied.

(iv) Predominant C-Bearing Species. In Figure 3, the deposited carbon species were mainly elemental carbons and their carbonates for NiO, Fe_2O_3, and CoO while for CuO only elemental carbon was predicted as its main carbon deposits. Different to others, the deposited carbon species for Mn_3O_4 were $MnCO_3$ and MnC_2.

3.1.3. Carbon Deposition Pathway in CLC with Syngas. As reported by different researchers,[11–13] there are two possible routes to form carbon deposition in CLC: catalytic methane decomposition (eq 5) and the Boudouard reaction (eq 6).

$$CH_4(g) \rightarrow C + 2H_2(g) \quad (5)$$

$$2CO(g) \rightarrow C + CO_2(g) \quad (6)$$

Both reactions are known to be slow, but with the presence of catalysts such as Ni, these reactions can be readily catalyzed to occur. It was found that at high reaction temperature (above 617 °C), the deposited carbon mainly arose from the decomposition of CH_4, that is, eq 5, while at low reaction temperature (397 °C), the Boudouard reaction, that is, eq 6, was favored.

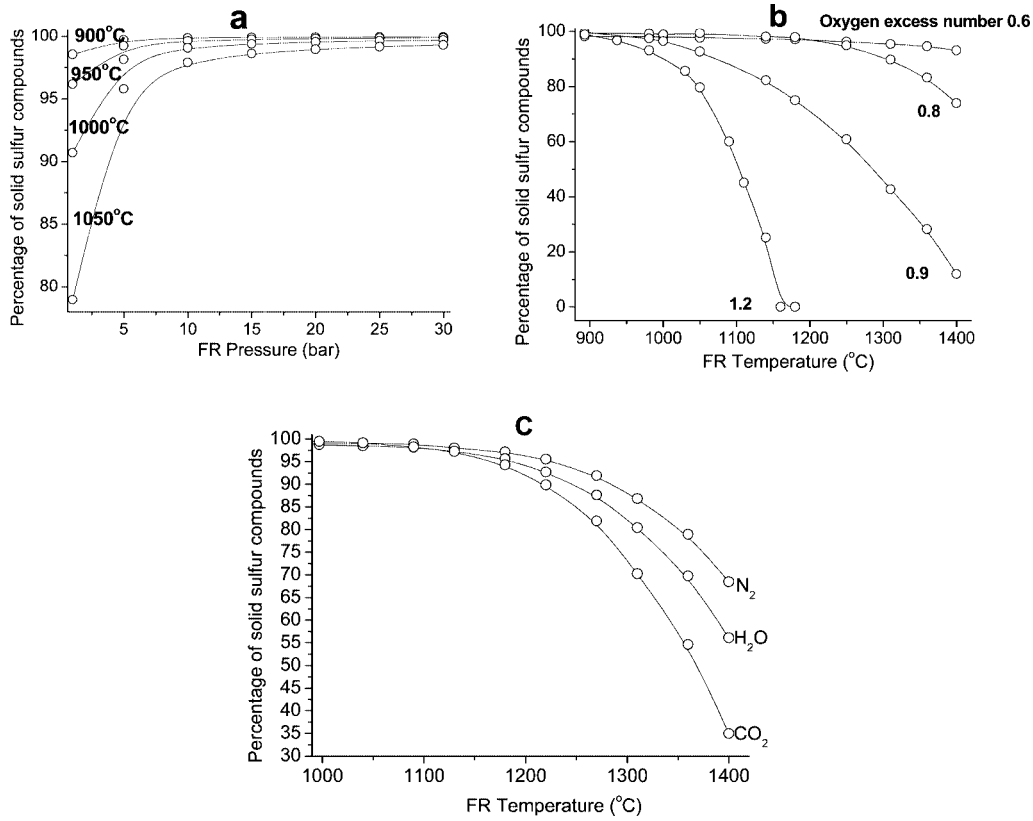

Figure 4. Effects of different factors on the percentage of solid sulfur compounds: (a) effect of pressure and temperature in the simple syngas without $H_2O(g)$ and CO_2, pressure 1 bar, and oxygen excess number $\Phi = 1.2$; (b) effect of oxygen excess number Φ in the simple syngas, pressure 1 bar; and (c) effect of $H_2O(g)$ and CO_2, pressure 1 bar, oxygen excess number $\Phi = 0.8$, and 30% of $H_2O(g)$, CO_2, or N_2 was separately introduced into the simple syngas.

According to the thermodynamic simulation results (Figure 3), the formation of CH_4 was inevitable, especially at low FR temperature (below 600 °C). Because methane decomposition occurs at relatively high temperature (>617 °C) and only trace amounts of methane formed at relatively low temperature (<600 °C), it was unlikely for carbon deposition to happen via catalytic methane decomposition. Therefore, the Boudouard reaction, that is, eq 6, was most possibly the main pathway of carbon deposition in CLC of syngas.

3.2. Evolution of Sulfur in CLC of Syngas. *3.2.1. Effect of Various Factors on Sulfur Species Distribution.* The formation of solid sulfur species and their potential depositions on oxygen carriers are also a big concern to CLC. The effects of various factors (including temperature, pressure, and Φ) on the percentage of solid sulfur compounds in CLC were investigated at first with the simple syngas (CO, N_2, H_2, and H_2S) as the fuel and NiO as oxygen carrier. Following that, 30% $H_2O(g)$ and CO_2 each were introduced separately into the syngas, and the effects of their occurrences on solid sulfur percentages were also explored. The simulated results are shown in Figure 4. Concerning the effect of temperature and pressure, it was found that the percentage of solid sulfur compounds obviously increased with pressure rising from 1 to 10 bar while it remained almost unchanged with a further increase of pressure to 30 bar. Furthermore, with the FR temperature increasing from 900 to 1050 °C and at a FR pressure of 1−10 bar, the percentage of solid sulfur compounds correspondingly decreased.

The effect of oxygen excess number Φ on the percentage of solid sulfur compounds is shown in Figure 4b. With Φ increasing, the percentage of solid sulfur compounds sharply decreased, which implied that more solid sulfur compounds were converted into gas sulfur species. Particularly, all these changes happened at FR temperature above 1000 °C.

Figure 4c shows the effects of introducing $H_2O(g)$, CO_2, or N_2 (taken as the reference case) on the percentage of solid sulfur compounds. In this case, the simulated condition was set as $\Phi = 0.8$, pressure 1 bar. At 1150−1400 °C of FR temperature, when 30% of CO_2, $H_2O(g)$, or N_2 were separately introduced into the simple syngas system, the percentage of solid sulfur compounds steeply declined with FR temperature. The effect of CO_2 was the most significant, followed by $H_2O(g)$ and N_2. The change caused by introducing N_2 (inert gas) into the system (as a reference case) reflected actually the sole effect of increasing temperature on the percentage of solid sulfur in the system. It implied that with the same amount of CO_2 or $H_2O(g)$ included in the simple syngas, more solid sulfur was converted into gas species, most likely because of chemical interactions. Furthermore, in the studied condition ($\Phi = 0.8$, 1150−1400 °C, 1 bar), SO_2 will be the predominant gas species (to be confirmed with thermodynamic simulations shown in the subsequent text). This indicated that the oxidation capacity of CO_2 in converting solid sulfur or H_2S into SO_2 was greater than that of $H_2O(g)$, especially at the studied condition. This result was consistent with the earlier reports which indicated CO_2 and $H_2O(g)$ were possible oxidizers to convert H_2S to mainly SO_2,[14,15] especially under oxygen-deficient conditions. In addition, similar conclusions could also be reached from simulations with other metal oxides besides NiO, though the details (not shown here) somewhat differed. Further investigations are needed to understand the mechanisms related to the oxidation effects of CO_2 and $H_2O(g)$ in syngas, as observed from this simulation.

3.2.2. Predominant Sulfur Compounds. The equilibrium distributions of various sulfur species at atmospheric pressure

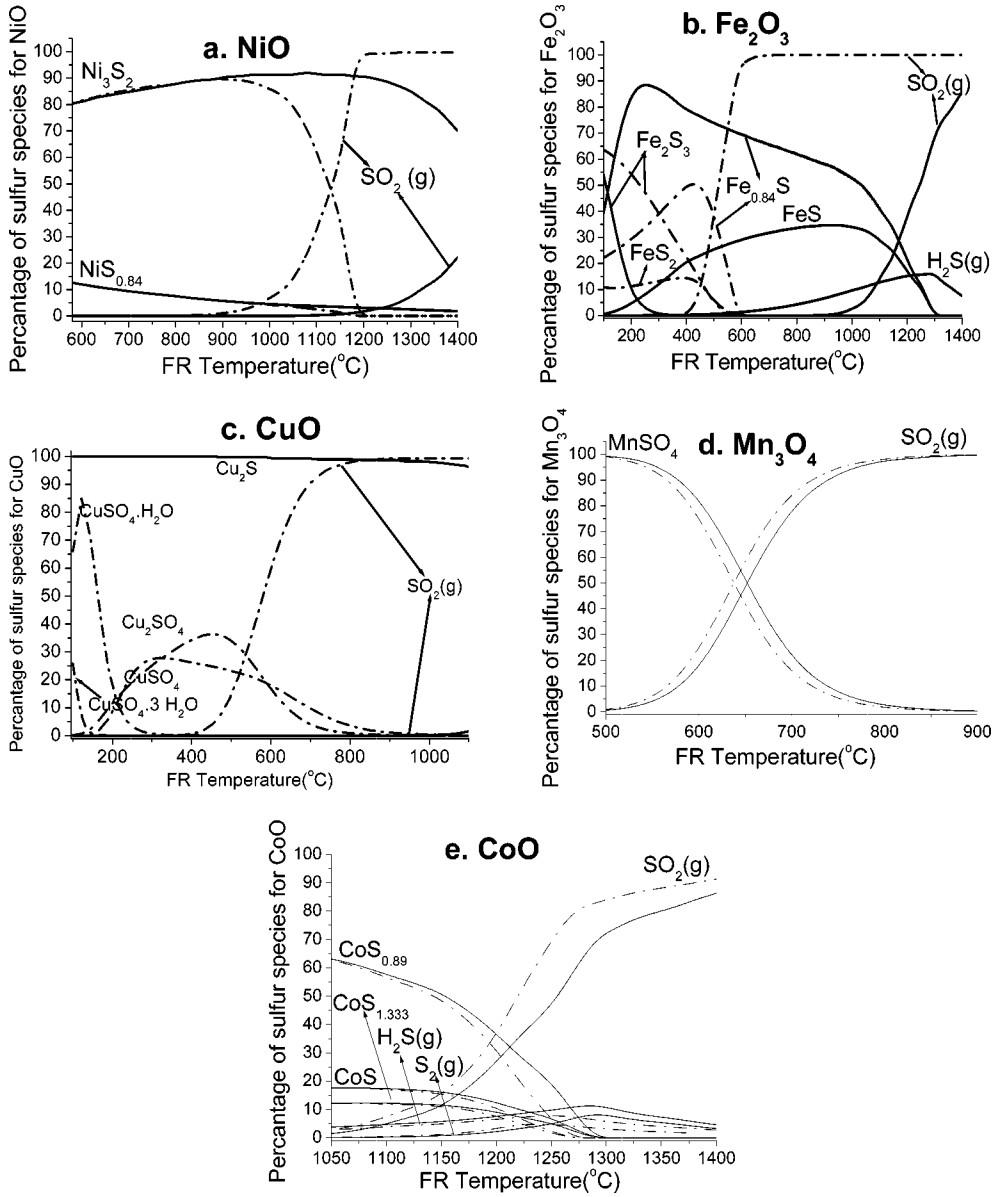

Figure 5. Equilibrium distribution of various sulfur species for different metal oxides, (a) NiO, (b) Fe_2O_3, (c) CuO, (d) Mn_3O_4, and (e) CoO, respectively. The simulated condition is $\Phi = 0.8$ (solid line) and 1.2 (dashed-dotted line), pressure 1 bar.

and $\Phi = 0.8$ and 1.2, respectively, for different metal oxides, NiO, Fe_2O_3, CuO, Mn_3O_4, and CoO, are shown in Figure 5. From these figures, two main findings could be attained.

(i) Effect of Oxygen Excess Number Φ *and Temperature.* The oxygen excess number Φ influenced the evolution of the sulfur species greatly. With Φ increasing from 0.8 to 1.2, the percentages of sulfur species with low valences (such as H_2S and sulfides) were decreased, accompanied by the increase of SO_2 percentage at high temperature. H_2S was only found at $\Phi = 0.8$ for Fe_2O_3 and CoO as oxygen carriers. In contrast, SO_2 was thermodynamically not stable at $\Phi = 0.8$ for NiO and CuO while it was mainly produced at oxidizing conditions ($\Phi = 1.2$). It indicated that more sulfur deposition might form at oxygen-deficient conditions. This agreed with the finding obtained from Figure 4b.

The equilibrium percentage of SO_2 was also increased with the FR temperature, similar to the conclusion of Jerndal et al.[14] At whatever oxygen excess number Φ, the deposited solid sulfur species were always present at relatively low temperature. Furthermore, the temperature of nearly full conversion of sulfur (mostly H_2S and sulfides) into SO_2 in the FR was above 1100 °C for NiO (at $\Phi = 1.2$), Fe_2O_3 (at $\Phi = 0.8$), and CoO (both $\Phi = 0.8$ and 1.2), which was far bigger than that for Fe_2O_3 (at $\Phi = 1.2$), CuO (at $\Phi = 1.2$), and Mn_3O_4. It implied that more gas sulfur species (correspondingly less sulfur solid deposits) were possibly generated for the latter three cases at the real FR temperature (800−1000 °C) in the CLC system.

(ii) Predominant Sulfur Compounds Distribution. The solid sulfur species with the largest percentages, which meant the most possible sulfur compounds deposited on oxygen carriers at low temperature, were mostly various sulfides (such as Ni_3S_2, $Fe_{0.84}S$, $CoS_{0.89}$) for three oxygen carriers (NiO, Fe_2O_3, and CoO). $MnSO_4$, instead of sulfides, was found as the predominant solid species for Mn_3O_4 as the oxygen carrier in CLC, at both oxidizing and reducing conditions. For CuO, at $\Phi < 1$, the sulfide (Cu_2S) was the most thermodynamically possible solid sulfur compound while for $\Phi > 1$ various solid copper sulfates dominated at low temperature.

4. Conclusions

A full conversion of gas fuel in the FR is crucial to enhance the CO_2 separation efficiency of the CLC system. Side reactions,

including carbon deposition and sulfur evaluation from trace H_2S contained in the gas fuel, are detrimental to the performance of oxygen carriers and thus inhibit the conversion of gas fuel. These side reactions were studied through thermodynamic simulation in considering five metal oxides (i.e., NiO, CuO, Fe_2O_3, Mn_3O_4, and CoO) as the oxygen carriers and syngas as the fuel. The effects of various factors (including temperature, pressure, oxygen excess number Φ, and the contents of $H_2O(g)$ and CO_2 in the syngas) on these side reactions were considered. On the basis of the simulation results, the following conclusions were reached.

(i) Carbon deposition and the evolution of sulfur in CLC were influenced largely by various factors. At whatever conditions considered, the pressurized condition led to more solid carbon and sulfur species deposited on oxygen carriers. A higher FR temperature favorably enhanced full conversion of syngas as evidenced by the significant decrease of carbon deposits and the conversion of most sulfur compounds into SO_2 at high temperature. A bigger Φ decreased the tendency of carbon deposition and led to more gas sulfur species formed, mainly SO_2.

(ii) The effects of $H_2O(g)$ and CO_2 in the syngas on both side reactions were further clarified. Through sensitivity analysis of various influencing factors on carbon deposition, the increase of H_2O and CO_2 contents in syngas could inhibit carbon formation, and the inhibition degree of $H_2O(g)$ was greater than that of CO_2 while the increase of the H_2S fraction in syngas led to more carbon deposition. In terms of the effect of $H_2O(g)$ and CO_2 in syngas on the conversion of sulfur compounds into SO_2, the oxidation effect of CO_2 was found to be stronger than that of $H_2O(g)$, especially at oxygen-deficient conditions.

(iii) The carbon and sulfur compounds that potentially deposit on the oxygen carrier were speciated. At low FR temperature and oxygen-deficient conditions, the main carbon deposited species for NiO, Fe_2O_3, CuO, and CoO were C and C(D), while for Mn_3O_4, $MnCO_3$, and MnC_2 were mainly deposited carbon species. Meanwhile, the most possible solid sulfur compounds deposited on oxygen carriers were Ni_3S_2, $Fe_{0.84}S$, $MnSO_4$, and $CoS_{0.89}$ for NiO, Fe_2O_3, Mn_3O_4, and CoO. But for CuO, under oxygen-deficient conditions, that is, $\Phi < 1$, the sulfur deposited compound was Cu_2S; in contrast to this, at $\Phi > 1$, $CuSO_4 \cdot H_2O$ was formed at 100−200 °C, and at 200−500 °C, the deposited sulfur compounds were mainly $CuSO_4$ and Cu_2SO_4.

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