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Thermodynamics on Sulfur Migration in $CaSO_4$ Oxygen Carrier Reduction by CO

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Abstract $CaSO_4$ is an attractive oxygen carrier for chemical looping combustion(CLC) because of its high oxygen capacity and low price. The utilization of a $CaSO_4$ oxygen carrier suffers the problems of sulfur release, and deactivation caused by sulfur loss. With respect to the fact that partial sulfur release could be recaptured and then recycled to $CaSO_4$ by CaO sorbent, the mixture of $CaSO_4$-CaO can be treated as an oxygen carrier. Thermodynamics of $CaSO_4$ and $CaSO_4$-CaO reduction by CO have been investigated in this study. The sulfur migrations, including the sulfur migration from $CaSO_4$ to gas phase, mutual transformation of sulfur-derived gases and sulfur migration from gas phase to solid phase, were focused and elucidated. The results show that the releases of S_2, S_8, COS and CS_2 from $CaSO_4$ oxygen carrier are spontaneous, while SO_2 can be released at high reaction temperatures above 884 °C. SO_2 is the major emission source of sulfur at low CO/$CaSO_4$ molar ratios, and COS is the major part of the byproducts as soon as the ratio exceeds 4 at 900 °C. Under CO atmosphere, all the sulfur-derived gases, SO_2, S_2, S_8 and CS_2, involved are thermodynamically favored to be converted into COS substance, and are spontaneously absorbed and solidified by CaO additive just into CaS species, which may be recycled to $CaSO_4$ as oxygen carrier in the air reactor. But high reaction temperatures and high CO_2 concentrations are adverse to sulfur capture.

Keywords Chemical looping combustion; CO_2 separation; $CaSO_4$ oxygen carrier; Sulfur migration; Sulfur capture

1 Introduction

CO_2 is the major greenhouse gas that affects the climate of the earth. In a conventional combustion system, fossil fuel is directly mixed with air and burnt. The concentration of CO_2 in the flue gas, diluted by the nitrogen of air, is merely 10%—14%. When the diluted CO_2 is disposed, a large amount of energy will be consumed in CO_2 separation and compression.

Chemical looping combustion(CLC) has been suggested as a promising combustion technology to control the greenhouse gas emission because CO_2 is inherently separated in the process[1,2]. The chemical looping combustion typically consists of two separate reactors: an air reactor and a fuel reactor. An oxygen carrier, which circulates between the two reactors, transfers oxygen from air to fuel. Thus, the air and the fuel will never be mixed, and the flue gas is a concentrated CO_2 stream without the dilution of N_2 from air[3—10].

The metal oxides Fe_2O_3[11—16], NiO[12—15], CuO[12,13], Mn_2O_3[12,14,16] and CoO[3] are the main focuses due to their high reactivities. However, the utilization of the metal oxygen carriers may be limited because of the high cost and sulfur poisoning.

$CaSO_4$ is an attractive oxygen carrier for the commercial application of CLC because of its easy availability and low price[17]. Fig.1 shows a schematic of the CLC process based on $CaSO_4$ oxygen carrier with CO. In the fuel reactor, $CaSO_4$ is reduced to CaS by CO:

$$\frac{1}{4}CaSO_4 + CO \longrightarrow \frac{1}{4}CaS + CO_2 \qquad (1)$$
$$\Delta H^{\ominus}_{298.15} = -42.76 \text{ kJ/mol}$$

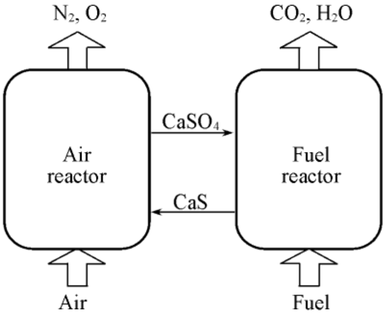

Fig.1 Schematic illustration of a chemical looping combustion of coal with a dual fluidized bed

And then the reduced oxygen carrier CaS is oxidized by air to $CaSO_4$ in the air reactor, where the oxygen is transferred

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from air to $CaSO_4$:

$$CaS+2O_2 \longrightarrow CaSO_4,\ \Delta H^{\theta}_{298.15}=-960.89\ \text{kJ/mol} \tag{2}$$

In this way, the stream from the air reactor is composed of atmospheric N_2 and residual O_2, and the stream from the fuel reactor almost consists of CO_2 without the dilution of N_2 from the air. Previous investigations[17—28] have been performed on a CLC of gaseous and solid fuels with a $CaSO_4$ oxygen carrier, involving the natural ore and nano material, and many promising results have been obtained. The $CaSO_4$ oxygen carrier had high reduction reactivity and stability in a long-time reduction-oxidation test by using the gaseous fuels in a laboratory fixed/fluidized bed reactor[20]. The reaction rates of the nanosized $CaSO_4$ oxygen carriers supported by Al_2O_3 binder are significantly increased, because the fresh samples have higher surface areas. The nanosized $CaSO_4$ oxygen carriers have excellent thermal stability, which may be due to the formation of $CaAl_2O_4$ substance[26]. Thus, $CaSO_4$ oxygen carrier may be a low-cost alternative oxygen carrier with high oxygen capacity even though the sulfur release problem exists.

The sulfur release could be recycled to $CaSO_4$ by adding lime or limestone sorbent. The method of adding lime or limestone to $CaSO_4$ oxygen carrier was proposed in our previous studies[18]. The sorbent reacts with sulfur-derived gases to form CaS, $CaSO_4$ and $CaSO_3$ in the fuel reactor. Then the sulfidation product is expected to be oxidized to $CaSO_4$ in the air reactor, and can be used as oxygen carrier in the following cycle of CLC system. Thus, the advantage of the approach is *in situ* sulfur capture in the reactor, without the introduction of extra reactant and reaction. However, no publication on the sulfur capture by CaO sorbent in CLC with $CaSO_4$ oxygen carrier can be found. The role of CaO-based sorbent is examined and validated in this study.

Lime and limestone are typical sorbents and extensively used for sulfur capture in both conversional coal-fired combustion systems and coal gasification systems[29,30]. For a conversional coal combustion process, SO_2 species is the main sulfur-derived gas and the desulfurization with CaO sorbent is carried out in the presence of O_2, with the formation of $CaSO_4$ ($CaO+SO_2+1/2O_2 \longrightarrow CaSO_4$). During the process of a coal gasification, H_2S species is the main sulfur-derived gas, and it can be trapped by CaO or $CaCO_3$($CaO+H_2S \longrightarrow CaS+H_2O$, $CaCO_3+H_2S \longrightarrow CaS+CO_2+H_2O$).

The sulfur captures in the present work differ from those sulfur-derived gas captures either in coal gasification systems or in conversional coal combustion systems. For the $CaSO_4$ oxygen carrier reduction by CO in the fuel reactor, SO_2 is the main sulfur-derived gas[18,25]. However, the desulfurization environment used in a fuel reactor of a CLC system is different from that for coal combustion. The sulfur capture in a fuel reactor is undertaken under a reductive atmosphere, which is composed of CO and CO_2 rather than O_2.

With respect to sulfur release that could be recaptured and then recycled to $CaSO_4$ by lime or limestone, the mixture of $CaSO_4$ and lime or $CaSO_4$ and limestone can be treated as an oxygen carrier. Thermodynamics study on the sulfur migration in $CaSO_4$ and $CaSO_4$-CaO reduction by CO was undertaken in this paper. The sulfur migrations, including the sulfur migration from $CaSO_4$ to gas phase, mutual transformation of sulfur-derived gases, and sulfur migration from gas phase to solid phase, are focused. The effects of reaction temperature, CO concentration, CO_2 concentration and molar ratio of CaO to $CaSO_4$ on sulfur emission and CO_2 generation are taken into account.

2 Gibbs Free Energy Analysis on Sulfur Migrations in $CaSO_4$ Reduction by CO

The Gibbs free energy changes of a system, represented as ΔG, can be used for predicting the direction of a reaction or process. The ΔG of a system is the change in the enthalpy(ΔH) of the system minus the product of the Kelvin temperature and the change in the entropy(ΔS) of the system. Thus, the Gibbs free energy changes of a system are a state function that depends only on the current, equilibrium state of the system. It obviously varies with the partial pressures of any gas involved in the reaction system. However, it is difficult to calculate the ΔG value for a chemical reaction because the partial pressure of gaseous product is usually unclear for most of reaction system. For reactions under the condition of constant pressure and temperature, a general assessment can be made on the direction of a reaction with the standard-state Gibbs free energy changes according to the method of ref. [31]. The standard-state Gibbs free energy change, represented as ΔG^{θ}, is the Gibbs free energy change under standard-state conditions, where the partial pressures of all gas involved are 101.325 kPa respectively. If $\Delta G^{\theta}<0$, the reaction will be spontaneous at any temperature. If $0<\Delta G^{\theta}<40$ kJ/mol, the direction of reaction is in doubt, and more efforts should be done to determine whether the reaction is spontaneous or not. If $\Delta G^{\theta}>40$ kJ/mol, the reaction is very unfavorable under the reaction conditions.

2.1 Sulfur Migration from $CaSO_4$ to Gas Phase

The reduction of $CaSO_4$ to CaS by CO is a complicated process because a series of side reactions with sulfur release involved therein, including $CaSO_4$ decompositions reactions *via* reactions (3)—(5)[Eqs.(3)—(5)], and CaS decomposition with CO_2 *via* reaction (6)[Eq.(6)][24]. The sulfur emits *via* various paths, leaving CaO as well as $CaCO_3$ byproduct in the solid residual.

Besides SO_2 formation, other sulfur species may be generated *via* Eqs.(7)—(14):

$$CaSO_4+CO \longrightarrow CaO+CO_2+SO_2,\ \Delta H^{\theta}_{298.15}=219.19\ \text{kJ/mol} \tag{3}$$

$$CaSO_4+CO \longrightarrow CaCO_3+SO_2,\ \Delta H^{\theta}_{298.15}=40.39\ \text{kJ/mol} \tag{4}$$

$$\frac{3}{4}CaSO_4+\frac{1}{4}CaS \longrightarrow CaO+SO_2,\ \Delta H^{\theta}_{298.15}=261.94\ \text{kJ/mol} \tag{5}$$

$$\mathrm{CaS{+}3CO_2 \longrightarrow CaO{+}3CO{+}SO_2},\ \Delta H^{\theta}_{298.15}=390.22\ \mathrm{kJ/mol} \tag{6}$$

$$\frac{1}{3}\mathrm{CaSO_4{+}CO \longrightarrow \frac{1}{3}CaO{+}CO_2{+}\frac{1}{24}S_8},\ \Delta H^{\theta}_{298.15}=-12.46\ \mathrm{kJ/mol} \tag{7}$$

$$\frac{1}{3}\mathrm{CaSO_4{+}CO \longrightarrow \frac{1}{3}CaCO_3{+}\frac{2}{3}CO_2{+}\frac{1}{24}S_8},\ \Delta H^{\theta}_{298.15}=-72.06\ \mathrm{kJ/mol} \tag{8}$$

$$\frac{1}{3}\mathrm{CaSO_4{+}CO \longrightarrow \frac{1}{3}CaO{+}CO_2{+}\frac{1}{6}S_2},\ \Delta H^{\theta}_{298.15}=4.79\ \mathrm{kJ/mol} \tag{9}$$

$$\frac{1}{3}\mathrm{CaSO_4{+}CO \longrightarrow \frac{1}{3}CaCO_3{+}\frac{2}{3}CO_2{+}\frac{1}{6}S_2},\ \Delta H^{\theta}_{298.15}=-54.81\ \mathrm{kJ/mol} \tag{10}$$

$$\frac{1}{4}\mathrm{CaSO_4{+}CO \longrightarrow \frac{1}{4}CaO{+}\frac{3}{4}CO_2{+}\frac{1}{4}COS},\ \Delta H^{\theta}_{298.15}=-20.35\ \mathrm{kJ/mol} \tag{11}$$

$$\frac{1}{4}\mathrm{CaSO_4{+}CO \longrightarrow \frac{1}{4}CaCO_3{+}\frac{1}{2}CO_2{+}\frac{1}{4}COS},\ \Delta H^{\theta}_{298.15}=-65.05\ \mathrm{kJ/mol} \tag{12}$$

$$\frac{1}{4}\mathrm{CaSO_4{+}CO \longrightarrow \frac{1}{4}CaO{+}7/8CO_2{+}\frac{1}{8}CS_2},\ \Delta H^{\theta}_{298.15}=-19.43\ \mathrm{kJ/mol} \tag{13}$$

$$\frac{1}{4}\mathrm{CaSO_4{+}CO \rightarrow \frac{1}{4}CaCO_3{+}\frac{5}{8}CO_2{+}\frac{1}{8}CS_2},\ \Delta H^{\theta}_{298.15}=-64.13\ \mathrm{kJ/mol} \tag{14}$$

Fig.2 shows the standard-state Gibbs free energy changes for sulfur migration from $CaSO_4$-based oxygen carrier to gas phase within the reaction temperature range of 0—1000 °C. For reaction (6)[Eq.(6)] with SO_2 release, the ΔG^{θ} is about positive 340—157 kJ/mol, which means the reaction is rather unfavorable under the reaction condition. SO_2 emissions *via* reactions (3)—(5)[Eqs.(3)—(5)] are spontaneous at high reaction temperatures. S_2, S8, COS, and CS_2 emissions can happen spontaneously, and low reaction temperatures favor both COS and CS_2 formations.

It is interesting that the ΔG^{θ} for reactions (8), (10), (12) and (14)[Eqs.(8), (10), (12), (14)] with S_8, S_2, COS and CS_2 emissions and $CaCO_3$ formation are going close to zero with the change of reaction temperature. It indicates that reactions (8), (10), (12) and (14)[Eqs.(8), (10), (12), (14)] become less spontaneous, closer to equilibrium. An opposite tendency is demonstrated for reactions (7), (9), (11), (13)[Eqs.(7), (9), (11), (13)] with S_8, S_2, COS and CS_2 emissions and CaO formation, indicating these reactions are favored at high reaction temperatures. In all, high reaction temperatures favor reactions with SO_2 emission, and also favor reactions with S_2, S_8, COS, and CS_2 emissions and CaO formation as well.

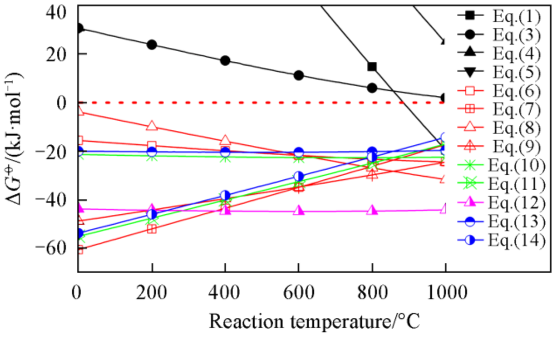

Fig.2 Standard-state Gibbs free energy changes for reactions of sulfur migration from $CaSO_4$-based oxygen carrier to gas phase as well as to CaS species

2.2 Sulfur Migration Among Sulfur-derived Gases

According to the Mattisson and Lyngfelt's study[32] and our study with TGA-FTIR tool[18], when SO_2 releases from the process of $CaSO_4$ reduction, the SO_2 reacts with CO and is converted to COS. A slight amount of CS_2 and S_2(sulfur vapor) is formed during the reduction of spent gypsum by CO according to the Okumura's study[33]. Thus, mutual transformation among the sulfur-derived gases such as SO_2, S_2, S_8, COS, and CS_2 may occur during the $CaSO_4$ reduction process, but no publication can be found on sulfur migration. A detailed description of sulfur migration under CO or CO/CO_2 atmosphere will be presented in this study. Reactions of sulfur transformations in gas phase involved are as follows:

$$\mathrm{SO_2{+}2CO \longleftrightarrow \frac{1}{8}S_8{+}2CO_2},\ \Delta H^{\theta}_{298.15}=-256.57\ \mathrm{kJ/mol} \tag{15}$$

$$\mathrm{SO_2{+}2CO \longleftrightarrow \frac{1}{2}S_2{+}2CO_2},\ \Delta H^{\theta}_{298.15}=-204.82\ \mathrm{kJ/mol} \tag{16}$$

$$\mathrm{S_8{+}8CO \longleftrightarrow 8COS},\ \Delta H^{\theta}_{298.15}=-352.18\ \mathrm{kJ/mol} \tag{17}$$

$$\mathrm{S_2{+}2CO \longleftrightarrow 2COS},\ \Delta H^{\theta}_{298.15}=-191.54\ \mathrm{kJ/mol} \tag{18}$$

$$\mathrm{SO_2{+}3CO \longleftrightarrow COS{+}2CO},\ \Delta H^{\theta}_{298.15}=-300.59\ \mathrm{kJ/mol} \tag{19}$$

$$\mathrm{SO_2{+}3CO \longleftrightarrow \frac{1}{2}CS_2{+}\frac{5}{2}CO_2},\ \Delta H^{\theta}_{298.15}=-296.90\ \mathrm{kJ/mol} \tag{20}$$

$$\mathrm{CS_2{+}CO_2 \longleftrightarrow 2COS},\ \Delta H^{\theta}_{298.15}=-7.39\ \mathrm{kJ/mol} \tag{21}$$

$$\mathrm{S_8 \longleftrightarrow 4S_2},\ \Delta H^{\theta}_{298.15}=413.98\ \mathrm{kJ/mol} \tag{22}$$

Fig.3 shows the standard-state Gibbs free energy changes for sulfur migration among sulfur-derived gases. The sulfur migrations of SO_2 to S_2, S_8, COS, and CS_2, S_2 to COS, S_8 to COS, and CS_2 to COS can happen spontaneously within the temperature range of 0—1000 °C. It manifests that under CO or CO/CO_2 atmosphere, all the sulfur-derived gases involved, namely SO_2, S_2, S_8 and CS_2, are thermodynamically favored to be converted into COS. The reactions of sulfur migration in gas phase become less spontaneous with the increaring reaction temperature, except for shifts of CS_2 to COS and S_8 to S_2.

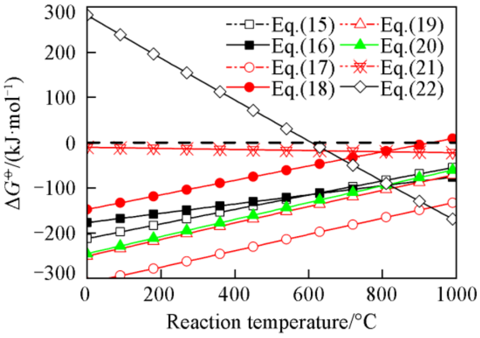

Fig.3 Standard-state Gibbs free energy changes for reactions of sulfur migration in gas phase

2.3 Sulfur Migration from Gas Phase to CaS Phase

The sulfur release accounts for a small fraction of the total amount of the oxygen carrier, and can be recycled to $CaSO_4$ by adding CaO sorbent. The sorbent may react with sulfur-derived gases SO_2, S_2, S_8, COS, and CS_2 to form CaS and $CaSO_3$ in the fuel reactor *via* the following reactions:

$$\mathrm{CaO+SO_2}\longrightarrow\mathrm{CaSO_3},\ \Delta H^{\theta}_{298.15}=931.93\ \mathrm{kJ/mol} \tag{23}$$

$$\mathrm{CaO+SO_2+3CO}\longrightarrow\mathrm{CaS+3CO},\ \Delta H^{\theta}_{298.15}=396.80\ \mathrm{kJ/mol} \tag{24}$$

$$\mathrm{2CaO+S_2+2CO}\longrightarrow\mathrm{2CaS+2CO_2},\ \Delta H^{\theta}_{298.15}=-370.80\ \mathrm{kJ/mol} \tag{25}$$

$$\mathrm{8CaO+S_8+8CO}\longrightarrow\mathrm{8CaS+8CO_2},\ \Delta H^{\theta}_{298.15}=-1069.22\ \mathrm{kJ/mol} \tag{26}$$

$$\mathrm{CaO+COS}\longrightarrow\mathrm{CaS+CO_2},\ \Delta H^{\theta}_{298.15}=-562.84\ \mathrm{kJ/mol} \tag{27}$$

$$\mathrm{2CaO+CS_2}\longrightarrow\mathrm{2CaS+CO_2},\ \Delta H^{\theta}_{298.15}=-186.65\ \mathrm{kJ/mol} \tag{28}$$

Fig.4 shows the standard-state Gibbs free energy changes for sulfur migration from gas phase to CaO sorbent. All gaseous sulfur species involved such as SO_2, S_2, S_8, COS, and CS_2 can be spontaneously absorbed and solidified just into CaS species, while SO_2 retention *via* reaction (23)[Eq.(23)] in the form of $CaSO_3$ is not a spontaneous process. Thus, the sulfidation product is expected to be only CaS, which may be recycled to $CaSO_4$ in the air reactor, and can be used as oxygen carrier in the following cycle of CLC system. Besides, all the reactions with SO_2, COS, CS_2, S_2, and S_8 capture become less spontaneous with rising reaction temperature, especially with SO_2 and S_2 capture. It manifests that high reaction temperature is adverse to sulfur-derived gas capture.

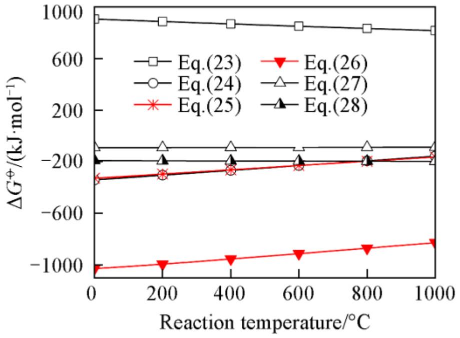

Fig.4 Standard-state Gibbs free energy changes for reactions of sulfur migration from gas phase to CaS species and to $CaSO_3$ species

3 Discussion

3.1 Main Route for Sulfur Migration

The following equation relates the standard-state Gibbs free energy of reaction to the Gibbs free energy of reaction during a reaction process: $\Delta G=\Delta G^{\theta}+RT\ln Q$, where Q is the reaction quotient, which is the function of the partial pressures and the stoichiometric numbers of gaseous products of a reaction, the partial pressures and the stoichiometric numbers of gaseous reactants of a reaction during a reaction process.

Simplified analysis for sulfur migration is carried out on the assumption that the composition in the gas phase only includes a sulfur-derived gas, CO and CO_2, and the concentration of sulfur-derived gas in the gas phase is 1%, and the CO and CO_2 concentration, referred as c_{CO} and c_{CO_2}, are varying from 99% to 0 and 0 to 99% respectively. The effects of CO and CO_2 concentration on the directions of chemical reactions at 900 °C are taken into account. $CaCO_3$ is thermodynamically favored to decomposition below 900 °C, and the reactions involving $CaCO_3$ formation are not taken into consideration. Based on the Gibbs free energy change ΔG, main route for sulfur migration and sulfur migration direction during the $CaSO_4$-CaO oxygen carrier reduction by CO can be obtained and summarized in Fig.5.

According to Le Chatelier's principle, high CO_2 concentrations are adverse to sulfur capture. Indeed, SO_2 capture cannot occur when CO_2 concentration in gas phase exceeds 98%, and CO concentration is below 1%. However, S_2, S_8, COS, and CS_2 absorptions are spontaneous under the hypothetical reaction condition. Since all the sulfur-derived gases involved, namely SO_2, S_2, S_8, and CS_2, are thermodynamically favored to be converted into COS, proper reaction conditions can be selected to enhance COS formation for effective solidification.

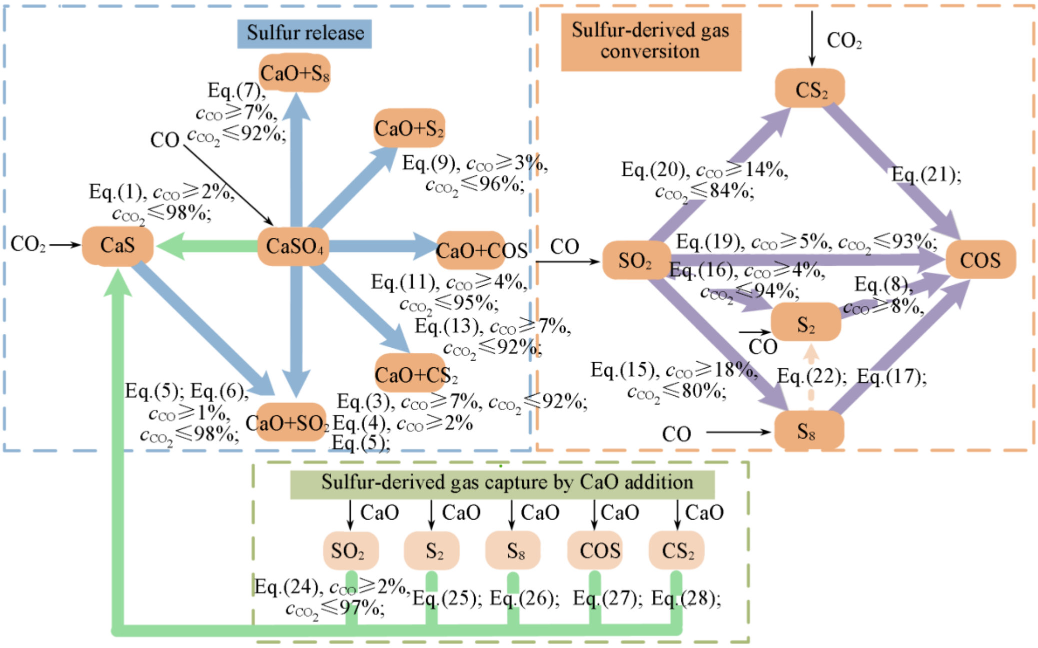

Fig.5 Main routes for sulfur migration at 900 °C

The analysis on a sulfur-derived gas migration is carried out on the assumption that the composition in the gas phase only includes the sulfur-derived gas, CO and CO_2, the concentration of sulfur-derived gas in the gas phase is 1%, and the CO and CO_2 concentration, referred as c_{CO} and c_{CO_2}, are varying from 99% to 0 and 0 to 99%, respectively.

3.2 Equilibrium Compositions of $CaSO_4$ Reduction by CO with the Consideration of SO_2, COS, CS_2 and S_2 Releases

Actually, the equilibrium compositions of $CaSO_4$ reduction by 100% CO at the stoichiometric molar ratio of $CaSO_4$/CO(0.25) and different reaction temperatures were studied based on the principle of the Gibbs free energy minimization in the literature[25]. The gaseous phases were assumed as CO, CO_2, SO_2, COS, CS_2 and S_2. The solid phases were assumed to be $CaSO_4$, CaS and CaO($CaCO_3$)[25]. We also made a calculation on the process with respect to reaction temperature and CO concentration, and the effect of reaction temperature on the distribution of gas products is shown in Fig.6, which agrees with the result in the literature[25]. It shows that within the temperature range of 900—950 °C, CO_2 is the main product, with the concentration over 97%. There are thermodynamic limitations that cause the incomplete conversion of CO to CO_2. The CO concentration in the flue gas remains about 1.04%. The byproducts SO_2, COS, S_2 as well as CS_2 are thermodynamically formed; thereinto, SO_2 is the major source of sulfur emissions, and other sulfur-containing gas are negligible.

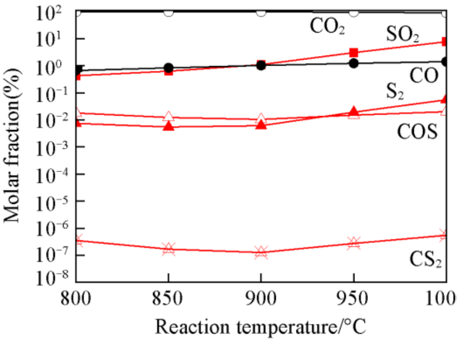

Fig.6 Gas phase equilibrium compositions of $CaSO_4$ reduction with CO at the CO/$CaSO_4$ molar ratio of 1 and different reaction temperatures

CO concentration has significant influences on the distribution of the sulfur-derived gases, as presented in Fig.7. When the CO/$CaSO_4$ molar ratio is over 4, excessive CO remarkably suppresses the sulfides release. The concentrations of both SO_2 and S_2 decrease remarkably with the increasing Co/$CaSO_4$ molar ratio, while the concentrations of COS and CS_2 decrease somewhat. Instead of SO_2 substance, COS is the major part of the byproducts as soon as the Co/$CaSO_4$ molar ratio exceeds 4.

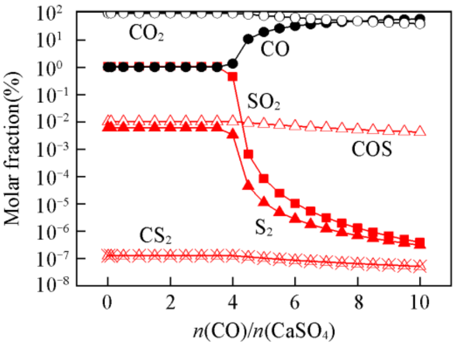

Fig.7 Gas phase equilibrium compositions of $CaSO_4$ reduction with CO at 900 °C and different CO/$CaSO_4$ molar ratios

Moreover, reaction temperature and CO_2 concentration also have significant influences on the distribution of the sulfur-derived gases. The equilibrium reactions between CaO and sulfur-derived gas and CO at the stoichiometric molar ratio, at different reaction temperatures and with different CO_2 concentrations are further studied, and the results are presented in Fig.8 and Fig.9. The absorptions of sulfur-derived gases by CaO addition are thermodynamically favored. Without the presence of CO_2 in the gas phase, the equilibrium capture ratios for SO_2 and S_2 substances drop with rising reaction temperature, while it is almost constant for COS and CS_2 substances, which denotes that COS and CS_2 substances are more promisingly trapped by CaO under CO or CO/CO_2 atmosphere even at high reaction temperatures. However, CO_2 substance in gas phase does not favor the captures of sulfur-derived gases(SO_2, COS, S_2, S_8 and CS_2).

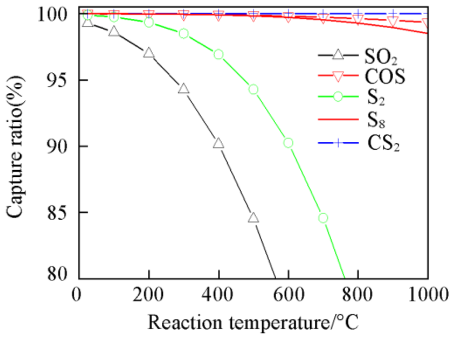

Fig.8 Sulfur capture ratio at different reaction temperatures and without CO_2 in gas phase when the stoichiometric reaction between a sulfur-derived gas and CaO addition achieves chemical equilibrium state

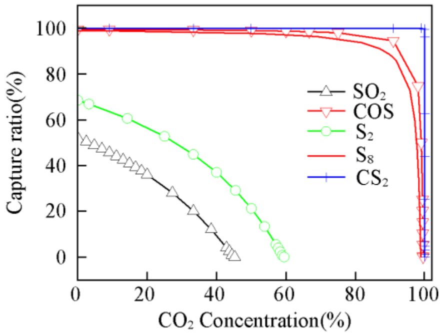

Fig.9 Sulfur capture ratio at 900 °C and with different CO_2 concentrations in gas phase when the stoichiometric reaction between a sulfur-derived gas and CaO addition achieves chemical equilibrium state

When the CO_2 concentration in gas phase exceeds 42.85%, 99.35%, 57.29%, 98.72% and 99.98% respectively, the capture ratios for sulfur-derived gases SO_2, COS, S_2, S_8 and CS_2 are below 5%. The degree of difficulty in sulfur capture by CaO addition is ordered from being difficult to easy: SO_2, S_2, S_8, COS and CS_2. Thus, during the $CaSO_4$ reduction by CO(the $CaSO_4$/CO molar ratio is below 0.25), the equilibrium distributions of sulfur-derived gases almost remain unchanged with the introduction of CaO additive. When the reaction system achieved chemical equilibrium state, the high equilibrium CO_2 concentration(up to 97.84%) limits sulfur capture. On a whole, high reaction temperatures and high CO_2 concentrations are detrimental to sulfur-derived gas capture by CaO sorbent under CO or CO/CO_2 atmosphere, and the negative impacts are relatively smaller on COS and CS_2 captures as well as S_8 capture.

Considering the plenty of CO_2 that are formed during the reduction of $CaSO_4$ by CO, the sulfur-derived gas captures are thermodynamically limited. However, during an actual reaction process, CO_2 concentration in gas phase is far away from the equilibrium concentration because of the migration of gas product from the fuel reactor to the bulk phase. The capture of sulfur-derived gases by CaO additive is thermodynamically favored during a real reaction process, and it is better to remove the CO_2 liberation from the reactor to the bulk phase as soon as possible for better sulfur capture performance.

4 Conclusions

Thermodynamics of $CaSO_4$ reduction and $CaSO_4$-CaO reduction by CO during the chemical reaction process have been investigated in the present work. Sulfur migration from $CaSO_4$ to gas phase, mutual transformation of sulfur-derived gases and sulfur migration from gas phase to solid phase are focused. The effects of reaction temperature, CO concentration, CO_2 concentration, CaO/$CaSO_4$ molar ratio on sulfur migration and CO_2 generation are discussed. Some results are achieved as follows. S_2, S_8, COS and CS_2 emission from $CaSO_4$ oxygen carrier are spontaneous, while SO_2 can be released spontaneously at high reaction temperatures above 884 °C. All the sulfur-derived gases are spontaneously absorbed and solidified by CaO additive into CaS species, which may be recycled to $CaSO_4$ as oxygen carrier in the air reactor. The degree of difficulty in sulfur capture by CaO addition is ordered from being difficult to easy: SO_2, S_2, S_8, COS and CS_2.

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