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RESEARCH PAPER

Simulated investigation of chemical looping combustion with coal-derived syngas and $CaSO_4$ oxygen carrier

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Abstract: Compared to metal oxides, $CaSO_4$ adopted as oxygen carrier (OC) in chemical looping combustion (CLC) presents several advantages such as low cost, easy availability and superior oxygen transfer capacity, whilst the SO_2 emission and solid sulfur deposit in the process could be a big concern. In this study, thermodynamic simulations were conducted to investigate the sulfur distribution in a CLC system with $CaSO_4$ as OC and syngas derived from coal as the fuel. Several findings were attained: (i) On the main products and reaction pathways in the fuel reactor (FR), at the low temperature of 100°C–400°C, the main sulfur species and carbon deposit were H_2S and $CaCO_3$ via the methanation of CO with H_2 coupled with both the shift reaction of CO with $H_2O(g)$ and the ensuing thermochemical sulfate reduction (TSR). Then at 400°C–915°C, CaS and CO_2 were the main products through the reaction of $CaSO_4$ with H_2 or CO, and both products increased with increasing FR temperature. Furthermore, at the FR temperature higher than 915°C, due to the initiation of the solid side reaction between CaS and $CaSO_4$, the percentage of CaS declined. In contrary, the percentages of CaO, H_2 and CO increased possibly due to the consumption of part of $CaSO_4$ in the side reaction and thus not enough lattice oxygen available. In the air reactor (AR), the oxidization of CaS by air into $CaSO_4$ was always dominant. Besides at Φ_{AR} below 0.8, both the solid side reaction of $CaSO_4$ with CaS and the oxidization of CaS into CaO were simultaneously in effect. (ii) In the FR, the optimized condition was suggested as at around 915°C, atmospheric condition and carefully controlled Φ_{FR} around unity. (iii) In the AR, sufficient supply of air was important for the oxidization of CaS, and $\Phi_{AR} \geq 1$ would ensure the full oxidization of CaS into $CaSO_4$ and prevent the emission of SO_2 and formation of CaO as well. Overall, this study provided the most suitable conditions of using $CaSO_4$ as OC in CLC of syngas with minimal SO_2 emissions and CaO formation.

Keywords: chemical looping combustion (CLC); coal-derived syngas; oxygen carriers; $CaSO_4$; thermodynamic simulation

Control and stabilization of the CO_2 concentration level in the atmosphere is of great necessity. Compared to a variety of CO_2 control technologies with high energy consumption, chemical looping combustion (CLC) has gained great attention across the world for its verified advantages, such as the inherent separation of CO_2 without any energy consumption, the improvement in the thermal efficiency of fuel combustion, and a thorough eradication of the formation of NO_X[1].

Currently, most researchers are developing various metal oxides OCs, such as those of Ni, Cu, Fe, Mn, Co, etc. However, certain drawbacks are associated with these costly metal OCs[2]. In contrast, some sulfates, especially $CaSO_4$, have attracted increasing interest, as sulfates demonstrate more prominently economical advantage over those metal oxides and are easily accessible from desulfurization process. Furthermore, if $CaSO_4$ is used as OC, its oxygen ratio is 0.47, more than twice of the oxygen ratios for all the metal oxide pairs.

Though the reduction of $CaSO_4$ in the SO_2 capture process has been widely investigated[3–7], researches on adopting $CaSO_4$ as a potential OC in CLC system so far are not sufficient enough. Zheng et al[8] validated the feasibility of using sulfates (including $CaSO_4$, $BaSO_4$ and $SrSO_4$) as potential OCs via thermodynamic analysis. Shen et al[9] thermodynamically simulated the reduction of $CaSO_4$ with coal in an interconnected fluidized beds system. Wang[10] evaluated the feasibility of integrating a gasifier into CLC system using the ASPEN Plus software-package. Furthermore, the reduction reaction of $CaSO_4$ with different gases (including CH_4, H_2 or CO) in the FR has also been experimentally studied[11,12]. However, attention is still not sufficient enough

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to pay to the evolution of various sulfur species and solid sulfur deposits during the reduction reaction of $CaSO_4$ in the FR[13], the reaction pathways in the FR involving $CaSO_4$ as OC, and the effects of various factors, such as pressure, temperature and oxygen excess numbers on the distribution of various sulfur species. Further investigations are thus needed to understand these aspects.

Coal is much more abundant than other fossil fuels, but more CO_2 is also generated from coal utilization. It would be thus highly advantageous to use coal as fuel for CLC. And there exist two routes for CLC of coal, i.e., the direct route with coal itself as fuel[14], and the indirect route with the syngas derived from coal gasification as fuel. Considering such great limitations for the direct route as the low rate of coal gasification and the difficult separation of reduced OC from coal ash, the focus of this research is concentrated on the indirect route of coal, i.e., syngas from coal gasification will be considered as the fuel for the CLC simulation. In fact, the gas components in syngas generated from coal gasification varies greatly. Nevertheless, syngas, simply simulated as 50% CO and 50% H_2 in their volumetric fraction, was mostly adopted as the fuel for the CLC simulation and experimental investigations in previous studies. Song et al[13] further adopted the gas mixtures of H_2,CO and CO_2 to simulate syngas from coal gasification. Jin[15] ever used H_2, CO, H_2O (g), CO_2 and Ar to represent the syngas in their experimental study. But none of thermodynamic simulations has been conducted on the CLC with a complex syngas composition as the fuel. In addition, the use of a pressurized CLC system would have several advantages[16]. Therefore, the effect of pressure on the distribution of various sulfur species in the FR is further investigated.

In this study, syngas containing a mixture of gas components (CO, H_2, H_2O(g), CO_2, H_2S, N_2) was considered as fuel in the CLC. Based on the thermodynamic simulation, the reduction reaction of $CaSO_4$ with syngas in the FR and the oxidization of the reduced CaS with air in the AR were investigated. Due to the complexity of the redox reaction of $CaSO_4$ with syngas and air, their reaction products were determined and the apparent conversion of reducing $CaSO_4$ into CaS in the FR was calculated. Then possible reaction pathways initiated in the FR and AR at different reaction conditions were identified. Finally, the effect of different factors on the distribution of various sulfur species was also investigated and the optimized reaction conditions were proposed.

1 Method and calculation procedure

1.1 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 $C_\alpha H_\beta S_\gamma O_\delta (CO_2)_\lambda (H_2O)_\mu (N_2)_\nu$. After supplying sufficient $CaSO_4$ and air in the FR and AR, the reduction reaction of $CaSO_4$ with syngas in the FR and the oxidation of the reduced CaS in the AR could be depicted as follows:

$$C_\alpha H_\beta S_\gamma O_\delta (CO_2)_\lambda (H_2O)_\mu (N_2)_\nu (g) + (2\alpha+\beta/2+2\gamma-\delta)\ CaSO_4 \rightarrow (2\alpha+\beta/2+2\gamma-\delta)CaS+(\alpha+\lambda)CO_2(g)+(\beta/2+\mu)H_2O(g)+\gamma SO_2(g)+\nu N_2(g) \quad (1)$$

$$CaS+2(O_2+3.76N_2) \rightarrow CaSO_4+7.52N_2(g) \quad (2)$$

1.2 Determination of lattice oxygen number of $CaSO_4$ Φ_{FR} and air excess number Φ_{AR}

The availability of lattice oxygen present in $CaSO_4$ was one of the most important factors to determine the full conversion of fuel in the FR. The theoretic stoichiometric lattice oxygen needed for the complete conversion of syngas as shown in Eq. (1) was $(2\alpha+\beta/2+2\gamma-\delta)$. Supposing the realistic oxygen contained in $CaSO_4$ was X(O), then the lattice oxygen excess number of $CaSO_4$ Φ_{FR} was defined as follows:

$$\Phi_{FR} = x(O)/\ (2\alpha+\beta/2+2\gamma-\delta) \quad (3)$$

Similarly, in AR, based on Eq. (2), the air excess number Φ_{AR} could be also defined below.

$$\Phi_{AR}=y(O_2)/2 \quad (4)$$

Overall, Φ_{FR} or Φ_{AR} <1 denoted that the oxidation of syngas with $CaSO_4$ in the FR or the oxidization of the reduced CaS in the AR was initiated under oxygen-deficient condition. Φ_{FR} or Φ_{AR}>1 meant the reaction occurred in an oxygen-rich environment; and Φ_{FR} or Φ_{AR}=1 referred to the oxygen supplied theoretically met the complete conversion of the fuel or the reduced CaS.

1.3 Calculation method

The HSC-Chemistry software 4.0 was used based on the minimization of the total Gibbs free energy. The predominant equilibrium compositions in the FR were calculated with focuses on the distribution of various sulfur species at varied pressures ($1\sim30\times10^5$ Pa), temperature (100°C–1400°C) and different oxygen excess number Φ_{FR}. Owing to the complexity of the reduction of $CaSO_4$ with syngas under different reaction conditions[11], the most possible reaction pathways involved were further identified mainly via comparing the equilibrium constant K_p of different reactions, which was related to the Gibbs free energy ΔGr and absolute temperatures. Here, only the reactions with positive equilibrium constants can be spontaneously initiated and the bigger equilibrium constant K_p signified the higher affinity of the involved reactants.

Table 1 Composition of syngas (vol%)

H_2	CO	CO_2	H_2O (g)	H_2S	N_2
25	35	10	20	3	Balance

Finally, based on the equilibrium products obtained from the reduction reaction of $CaSO_4$ with syngas, the apparent conversions were defined in Eq. (5) as x_i for the oxidization of CO and H_2 into CO_2 and H_2O, and in Eq. (6) as x_{CaSO4} for the reduction of $CaSO_4$ into CaS, though the evolution of CO and H_2 with the FR temperature was complex and possibly influenced by related side reactions.

$$x_i = (N_{i(initial)} - N_{i(final)})/N_{i(initial)} \quad (5)$$

$$x_{CaSO4} = N_{CaS(final)}/N_{CaSO4(initial)} \quad (6)$$

where i in Eq. (5) represents H_2 or CO, N in both Eq. (5) and Eq. (6) denotes the mole numbers, and the subscript of "initial" and "final" are the initial input mole numbers and the final equilibrium mole numbers of the involved species.

2 Results and discussion

2.1 Equilibrium products distribution of the reduction of $CaSO_4$ with syngas in the FR

With the minimization of ΔGr for the reduction of $CaSO_4$ with syngas at Φ_{FR}=1, FR total pressure of 10^5 Pa and the FR temperature of 100°C–1400°C, the equilibrium distribution of various calcium-bearing, sulfur-bearing and carbon-bearing species are depicted in Figs. 1(a)–1(c), respectively.

At low FR temperature (100°C–400°C), $CaSO_4$ was mostly converted to the thermodynamically more stable $CaCO_3$ with nearly 10% $CaSO_4$ left. The main sulfur-bearing species were H_2S and $CaSO_4$ with the percentage of H_2S up to ~90%. The main carbon-bearing species were CO_2 and $CaCO_3$, and $CaCO_3$ was the sole carbon deposit other than various elemental carbons found for the cases of metal oxides as OCs[28]. At medium FR temperature (400°C–915°C), the percentage of CaS sharply increased from zero to its peak value. In contrast, the percentages of $CaCO_3$ and H_2S declined markedly, especially for H_2S, which demonstrated an exponential curve as reported by Shen et al[9], though the fuels used were differed in the two studies. The percentage of CO_2 firstly increased from ~65% to above 90% at ~500°C, then it diminished with increasing FR temperature. Finally, when the FR temperature was higher than 915°C, the percentage of CaS decreased accompanied by the formation of CaO in Fig. 1(a) and SO_2 , S_2(g) in Fig. 1(b). The percentage of CO_2 further decreased with the presence of CO at FR temperature higher than 1000°C.

Furthermore, using Eqs. (5) and (6), the apparent conversions of CO into CO_2, H_2 into H_2O, and $CaSO_4$ into CaS were calculated as shown in Fig. 2 and denoted as $X_{CO\text{-}CO2}$, $X_{H2\text{-}H2O}$ and $X_{CaSO4\text{-}CaS}$, respectively. It was found that at the FR temperature of 500°C–1300°C, the apparent conversions of CO, H_2 and $CaSO_4$ were all above 90%. The conversions of the former two decreased with increasing FR temperature while that of $CaSO_4$ into CaS firstly increased with an increase in the FR temperature and reached 96% at 915°C, and then it decreased with a further increase in the FR temperature. Furthermore, during 500°C–950°C, the conversion of CO to CO_2 was higher than that of H_2 to H_2O(g), which was however inverse at the FR temperature above 950°C, similar to the observation of Song in their experimental test with $CaSO_4$ as OC[7].

2.2 Possible reaction pathways for the reduction of $CaSO_4$ with syngas

The reduction reaction of $CaSO_4$ with syngas was very complex, and the analysis of the possible reaction pathways involved would be favorable to understand the redox reaction of $CaSO_4$ in the CLC system. The equilibrium constant K_p in combination with the distribution of various species from the thermodynamic simulation was adopted as the evaluation index (Fig. 1). And thus the possible reaction pathways at different FR temperatures were supposed as follows.

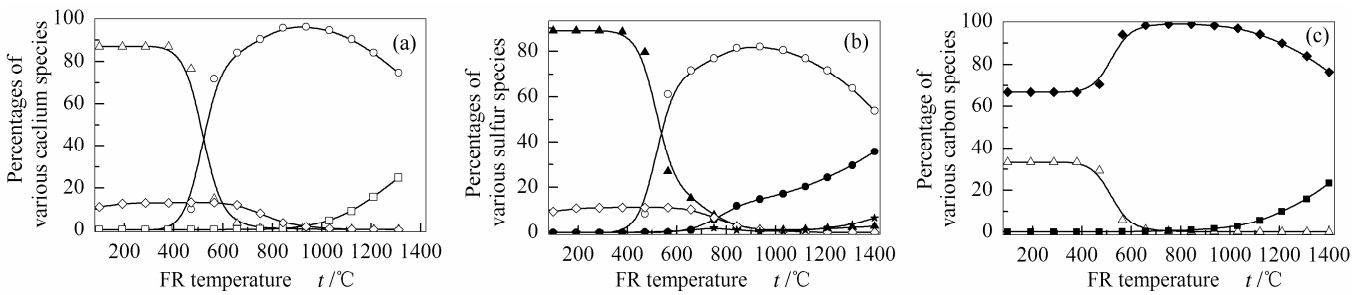

Fig. 1 Equilibrium distribution of various species

(a): calcium species; (b): sulfur species; (c): carbon species.

The simulated condition: Φ_{FR} =1, p =1×10^5 Pa

△: $CaCO_3$; ○: CaS; ◇: $CaSO_4$; □: CaO; ▲: H_2S; ●: SO_2; ◆: CO_2; ■: CO; ★: S_2

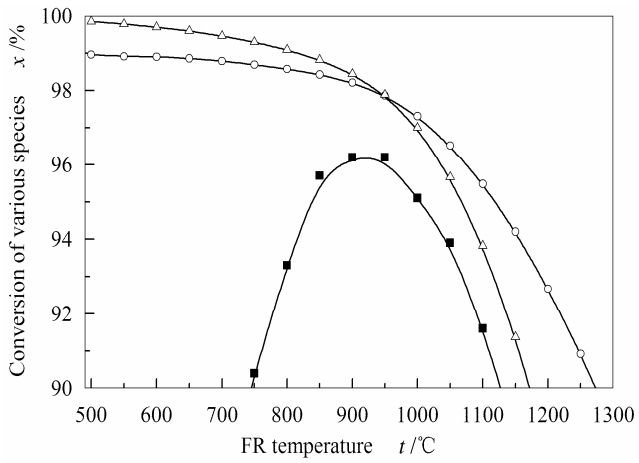

Fig. 2 Conversion of H_2, CO and $CaSO_4$

The simulated condition: Φ_{FR} =1, p =1×10^5 Pa

△: $x_{CO\text{-}CO2}$; ○: $x_{H2\text{-}H2O}$; ■: $x_{CaSO4\text{-}CaS}$

(i) Low FR temperature (100°C–400°C)

At Φ_{FR} =1, FR pressure of 1×10^5 Pa and 100°C–400°C, since CO and H_2 were the main composition in the syngas, both the methanation reaction of CO with H_2 and the shift reaction of CO with H_2O(g) were simultaneously presented as listed in Eqs. (7) and (8), respectively:

$$CO + 3H_2 = CH_4 + H_2O \quad (7)$$

$$CO + H_2O(g) = CO_2 + H_2 \quad (8)$$

Generally, the volume ratio of H_2 to CO in syngas is less than three[22,24,29], and the amount of H_2 was not enough to completely convert CO to CH_4 only through Eq. (7), so the H_2 produced through Eq. (8) could be also used as the additional H_2 source. Meanwhile, the H_2O(g) produced in Eq. (7) would be conducive to the shift reaction of CO in Eq. (8). And thus, both Eqs. (7) and (8) were simultaneously initiated and complementary to each other. The feasibility of Eqs. (7) and (8) at low temperature has been proved thermodynamically and experimentally.

Following Eqs. (7) and (8), the reduction reaction of $CaSO_4$ with CH_4, i.e., thermochemical sulfate reduction (TSR) as shown in Eq. (9), was also evidenced in geochemistry, though this process had to experience over a long time at such a low temperature[18] , and thus is not the temperature range of interest for the application of CLC.

$$CaSO_4 + CH_4 = CaCO_3 + H_2S + H_2O(g) \quad (9)$$

(ii) Medium FR temperature (400°C–915°C)

Due to the sharp decrease of equilibrium constants for Eqs. (7) and Eq.(8) with increasing FR temperature, the reduction reactions of $CaSO_4$ with CO or H_2 (as shown in Eqs. (10) and (11) below) began to dominate with increasing FR temperature from 400 to 915°C as indicated by the increase of percentages of CaS (Fig. 1(a)) and CO_2 (Fig. 1(c)). On the contrary, the Eqs. (7) – (9) were weakened, and the percentages of $CaCO_3$ (Fig. 1(a)) and H_2S(Fig. 1(b)) were declined.

$$CaSO_4 + 4CO = CaS + 4CO_2 \quad (10)$$

$$CaSO_4 + 4H_2 = CaS + H_2O \quad (11)$$

In addition, from Fig. 1(b), when the FR temperature was higher than ~700°C, SO_2 was produced and its percentage increased with increasing FR temperature. From the equilibrium constants of various potential reactions and the stoichometric relations of the main products predicted from thermodynamic simulation, SO_2 was supposed to most likely come from the oxidization of H_2S with $CaSO_4$ as shown in Eq. (12):

$$CaSO_4 + 4/3H_2S = CaS + 4/3SO_2 + 4/3H_2O(g) \quad (12)$$

(iii) High FR temperature (915°C–1400°C)

When the FR temperature was further increased from 915°C upwards, from Figs. 1(a)–1(c), the percentages of CaS and CO_2 sharply diminished with increasing FR temperature, though they were still the predominant products. Meanwhile, CaO was produced and its percentage increased with increasing FR temperature as well (Fig. 1(a)). Here, though Eqs. (10) –(12) were still the main pathways for the conversion of $CaSO_4$ with syngas, some other side reactions might become increasingly important as well[11] and CaO was supposed to generate over 880°C mainly from the solid reaction between CaS and $CaSO_4$ as shown in Eq. (13)[6].

$$3CaSO_4 + CaS = 4CaO + 4SO_2 \quad (13)$$

Considering CaS was the desirable product to be transported to AR, Eq. (13) was the undesirable side reaction of Eqs. (10) and (11). Thus, attention should be paid to inhibit this reaction in the FR of CLC system. Of course, the presence of CaO produced in Eq. (13) could initiate the neutralization of CaO with H_2S (in syngas) as shown in Eq. (14),

$$CaO + H_2S = CaS + H_2O(g) \quad (14)$$

In addition, above 1200°C (in Fig.1b), the formation of S_2(g) was found instead of COS in the result of Zheng et al[19], because the fuel used in both researches was different. And S_2(g) formed in this research perhaps was arisen from another solid reaction between CaS and $CaSO_4$[7] as shown below:

$$3CaSO_4 + CaS = 4CaO + 2S_2(g) \quad (15)$$

The presence of CO at high FR temperature (in Fig. 1(c)) was supposed to be resulted from the existence of side reaction (Eq. (12)), which was competing with Eqs. (10) and (11), and thus $CaSO_4$ became insufficient to fully oxidize CO and H_2 to CO_2 and H_2O(g).

Overall, the reduction reactions of $CaSO_4$ with syngas were preferred at medium temperature, especially at around 900°C, so that the TSR reaction at the low temperature of the FR and several side reactions of $CaSO_4$ with CaS at high FR temperature could be avoided.

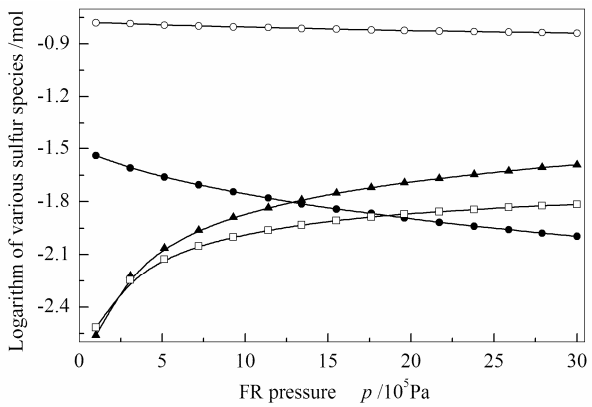

Fig. 3 Effect of FR pressure on the distribution of sulfur species

The simulated condition: Φ_{FR} =1, t_{FR}=915°C

○: CaS; □: $CaSO_4$; ▲: H_2S; ●: SO_2

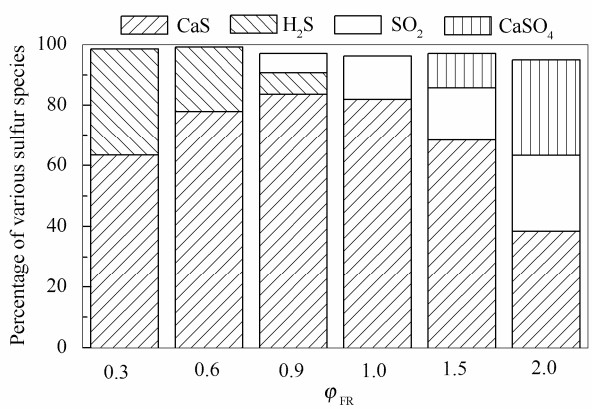

Fig. 4 Effect of Φ_{FR} on the distribution of various sulfur species

The simulated condition: p =1×10^5 Pa, t_{FR}=915°C

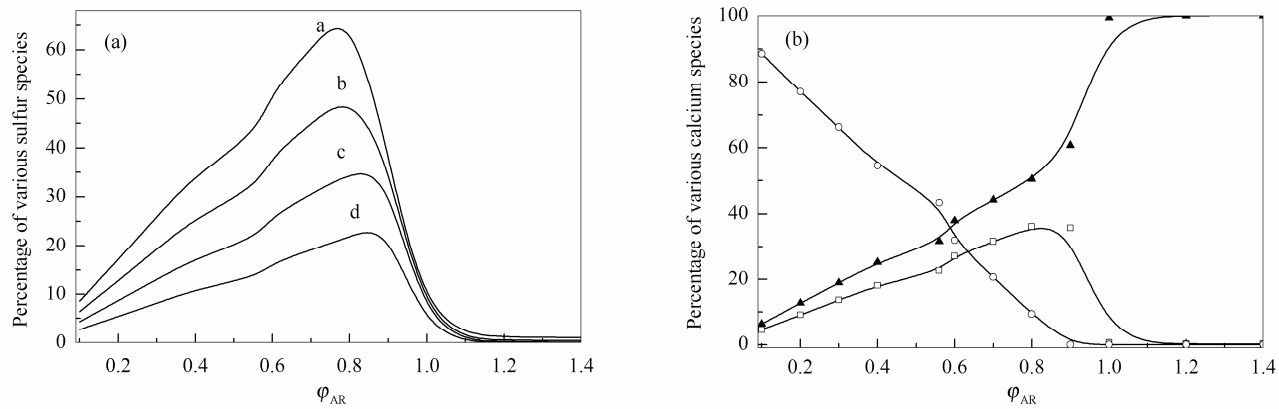

Fig. 5 Effect of Φ_{AR} on the oxidization of CaS

(a): SO_2 distribution with Φ_{AR}; (b): distribution of various calcium species with Φ_{AR} at 950°C

a: 1050°C; b: 1000°C; c: 950°C; d: 900°C

The simulated condition: p =1×10^5 Pa

○: CaS; ▲: $CaSO_4$; □: CaO

2.3 Effects of various factors on the reduction of $CaSO_4$ with syngas in the FR

Effects of the FR total pressure and lattice oxygen present in $CaSO_4$ on the distribution of various sulfur species were further investigated as depicted in Figs. 3 and 4, respectively.

In Fig. 3, Φ_{FR} was fixed as 1 and the FR temperature was selected as 915°C, where the highest conversion of $CaSO_4$ into CaS occurred (as shown in Fig. 2). The mole numbers of formed CaS and SO_2 decreased with increasing total pressure in the FR, which was contrary to the behaviors of H_2S and $CaSO_4$. Such results were possibly arisen from the existence of certain side reactions to the reduction reactions of $CaSO_4$ with CO (Eq. (10)) or H_2 (Eq. (11)). Owing to both the consumption of part of the H_2 and CO through the methanation reaction (Eq. (7)) and the shift reaction of CO (Eq. (8)) with increasing FR pressure, the amount of CaS produced via Eqs. (10) and (11) was slightly diminished, but the mole numbers of $CaCO_3$ and H_2S were increased via Eq. (9). Overall, in terms of $CaSO_4$ conversion to CaS, pressurized condition was not beneficial at the optimized temperature for CLC application.

Additionally, the effect of Φ_{FR} on the distribution of various sulfur species is presented in Fig. 4. At low Φ_{FR} (such as 0.3 and 0.6), CaS and H_2S were the main sulfur-bearing species, but when Φ_{FR} increased to 0.9, besides CaS and H_2S, SO_2 became one main species possibly due to the solid reaction between CaS and $CaSO_4$ (Eq. (13)). Furthermore, when Φ_{FR} was larger than unity, no H_2S was existed. The decrease in the percentage of CaS and the increase in the percentage of SO_2 indicated that Eq. (13) was fully initiated. Therefore, in order to maintain the high conversion of $CaSO_4$ to CaS and avoid the formation of SO_2, a sufficient but not an excess of $CaSO_4$ was suggested to introduce into the FR.

2.4 Oxidization of the reduced CaS in the AR

Although the oxidization of CaS has also been widely studied in the desulfurization process for coal combustion, both the atmosphere and temperature involved were greatly different from those used in AR of CLC system. In the realistic CLC system, sufficient oxidization of the reduced CaS by air in the AR into $CaSO_4$ is very important to sustain many cycles of the reaction of $CaSO_4$ with syngas. During CaS oxidization, the amount of air supply determined the CaS conversion into $CaSO_4$, and influenced both the SO_2 emission and the formation of CaO greatly[20]. Therefore, the effect of air supply on both the SO_2 emission at different temperatures and the distribution of various calcium species at 950°C was calculated and presented in Figs. 5(a) and (b), respectively.

From Fig. 5(a), it could be observed that at Φ_{AR} below ~ 0.8, the SO_2 emission was increased with increasing Φ_{AR} and temperature. Especially, the higher temperatures, the bigger amount of SO_2 emission, which was in accordance with the experimental results of different authors[20]. Meanwhile, when Φ_{AR} was higher than 0.8 at all the temperatures studied (900°C–1050°C), the emission of SO_2 sharply declined towards zero with Φ_{AR} increasing to unity. Furthermore, from Fig. 5(b), it could be found that among various calcium species with the increase of Φ_{AR} at 950°C, the percentage of CaS nearly decreased linearly, but the percentage of CaO increased until Φ_{AR} reached 0.9, and then quickly decreased towards zero, while the percentage of $CaSO_4$ increased to 100% in a sigmoidal mode until Φ_{AR} reached unity. Overall, during CaS oxidization, sufficient supply of air (i.e., $\Phi_{AR} \geq 1$) could ensure the full conversion of CaS into $CaSO_4$, and simultaneously prevent the emission of SO_2 and formation of CaO.

Finally, based on the various species of CaS oxidization from the thermodynamic simulation, possible reaction pathways could be also deduced. At all the temperature and Φ_{AR} investigated, Eq. (2) was always dominant; but when Φ_{AR} was below 0.8 coupled with Eq. (2), both the reaction as expressed in Eq. (12) and the reaction as shown in Eq. (16) would be in effect.

$$CaS+3/2O_2(g)= CaO+ SO_2(g) \quad (16)$$

3 Conclusions

In this study, $CaSO_4$ was adopted as OC for CLC system, and its reduction with syngas in the FR and the oxidization of the reduced CaS in AR was thermodynamically investigated. The following conclusions were reached.

The reduction of $CaSO_4$ with syngas in the FR generated various products at different ranges of temperature. The main reaction pathways involved were proposed. At low FR temperature (100°C–400°C), $CaCO_3$ and H_2S were mainly produced through the methanation of CO and H_2 and the ensuing TSR reaction. At medium FR temperature (400°C–915°C), the reductions of $CaSO_4$ with CO or H_2 began to dominate. Furthermore, at high FR temperature (915°C–1400°C), SO_2 and $S_2(g)$ were mainly produced through the two solid reaction between CaS and $CaSO_4$.

Pressure, temperature and Φ_{FR} in the FR were demonstrated to show important influences on the distribution of various sulfur species. At 915°C of FR temperature, Φ_{FR}=1 and atmospheric pressure, a satisfactory conversion of H_2 and CO in the reaction with $CaSO_4$ was attained, but pressurized condition caused not only a decrease of the percentages of CaS, $CaSO_4$ and H_2S, but also an increase in the percentage of SO_2. Meanwhile, the optimized reaction condition for the reduction of $CaSO_4$ with syngas in the FR was 915°C, atmospheric pressure and carefully controlled Φ_{FR} around unity.

During CaS oxidization in the AR, the oxidization of CaS by air into $CaSO_4$ was always dominant, and $\Phi_{AR} \geq 1$ would ensure the full conversion of CaS into $CaSO_4$ and prevent the emission of SO_2 and formation of CaO as well.

References

[1] Ishida M, Jin H. A novel chemical-looping combustor without NO_x formation. Ind Eng Chem Res, 1996, 35(7): 2469–2472.

[2] Mattision T, Garcia-Labiano F, Kronberger B, Lyngfelt A, Adanez J, Hofbauer H. Chemical-looping combustion using syngas as fuel. Int J Greenhouse Gas Control, 2007, 1(1): 158–169.

[3] Lyngfelt A, Leckner B. Sulphur capture in circulating fluidized-bed boilers: Can the efficiency be predicted? Chem Eng Sci, 1999, 54(2): 5573–5584.

[4] Swift W M, Wheelock T D. Decomposition of calcium sulfate in a two-zone reactor. Ind Eng Chem Process Des Dev, 1975, 14(3): 323–327.

[5] Diaz-Bossio L M, Squier S E, Pulsifer A H. Reductive decomposition of calcium sulfate utilizing carbon monoxide and hydrogen. Chem Eng Sci, 1985, 40(3): 319–324.

[6] Lyngfelt A, Leckner B. Sulfur capture in fluidized bed combustors: The effect of reductive decomposition of $CaSO_4$. Chem Eng J, 1989, 40(2): 59–69.

[7] Sohn H Y, Kim B-S. A novel cyclic reaction system involving CaS and $CaSO_4$ for converting sulfur dioxide to elemental sulfur without generating secondary pollutants: 1 Determination of process feasibility. Ind Eng Chem Res, 2002, 41(13): 3081–3086.

[8] Zheng Y, Wang B W, Song K, Zheng C G. The performance research on new oxygen carrier $CaSO_4$ used in chemical-looping combustion. Journal of Engineering Thermophysics, 2006, 27(3): 531–533.

[9] Shen L H, Xiao J, Xiao R, Zhang H. Chemical looping combustion of coal in interconnected fluidized beds of $CaSO_4$ oxygen carrier. Proceedings of the CSEE, 2007, 27(2): 69–74.

[10] Wang J, Anthony E J. Clean combustion of solid fuels. Appl Energy, 2008, 85(2/3): 73–79.

[11] Shen L, Zheng M, Xiao J, Xiao R. A mechanistic investigation of a calcium-based oxygen carrier for chemical looping combustion. Combust Flame, 2008, 154(3): 489–506.

[12] Tian H, Guo Q, Yue X, Liu Y. Investigation into sulfur release in reductive decomposition of calcium sulfate oxygen carrier by hydrogen and carbon monoxide. Fuel Process Technol, 2010, 91(11): 1640-1649.

[13] Song Q, Xiao R, Deng Z, Zheng W,Shen L,Xiao J. Multicycle study on chemical-looping combustion of simulated coal gas with a $CaSO_4$ oxygen carrier in a fluidized bed reactor. Energy Fuels, 2008, 22 (6): 3661–3672.

[14] Zheng M, Shen L, Xiao J. Reduction of $CaSO_4$ oxygen carrier with coal in chemical looping combustion: Effects of temperature and gasification intermediate. Int J Greenhouse Gas Control, 2010, 4(6): 716–728.

[15] Jin H, Ishida M. A new type of coal gas fueled chemical-looping combustion. Fuel, 2004, 83(17/18): 2411–2417.

[16] Xiao R, Song Q, Song M, Lu Z, Zhang S, Shen L. Pressurized chemical-looping combustion of coal with an iron-based oxygen carrier. Combust Flame, 2010, 157(16): 1140–1153.

[17] Cho P, Mattisson T, Lyngfelt A. Carbon formation on nickel and iron oxide-containing oxygen carriers for chemical-looping combustion. Ind Eng Chem Res, 2005, 44(4): 668–676.

[18] Cross M M, Manning D A C, Bottrell S H, Worden R H. Thermochemical sulphate reduction (TSR): Experimental determination of reaction kinetics and implications of the observed reaction rates for petroleum reservoirs. Org Geochem, 2004, 35(4): 393–404.

[19] Zheng M, Shen L H, Xiao J. Reduction of $CaSO_4$ oxygen carrier with CO in chemical-looping combustion. Journal of Chemical Industry and Engineering, 2008, 59 (11): 2812–2818.

[20] Zheng M, Shen L H, Gao Z P, Xiao J. Oxidization of CaS with O_2 for oxygen carrier regeneration in chemical-looping combustion. Acta Sceientiae Circumstantiae, 2009, 29(2): 330–338.