



Investigation into sulfur release in reductive decomposition of calcium sulfate oxygen carrier by hydrogen and carbon monoxide

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ABSTRACT

Chemical looping combustion (CLC) is a promising technology with the inherent property of separating CO₂ from flue gas. For calcium sulfate (CaSO₄) oxygen carrier, the inhibition of the produced sulfurous gases in the reduction of CaSO₄, including sulfur dioxide (SO₂), hydrogen sulfide (H₂S) and carbonyl sulfide (COS), is the key for a CLC system. In this paper, the sensitivities of reacting temperature, oxygen ratio number (defined in this paper) and the mole fraction of both carbon monoxide (CO) and hydrogen (H₂) in the syngas to the sum of the amounts of released SO₂, H₂S and COS are discussed respectively. Thermo-gravimetric analysis (TGA) tests demonstrated that the amount of the produced sulfurous gases is greatly dependent on the partial pressure of H₂ or CO in the reduction of CaSO₄. When the partial pressure of H₂ or CO is higher than 40 kPa, the production of sulfurous gases, indicating the deterioration of the recyclability of CaSO₄, can be prevented completely even if the reacting temperature is as high as 1000 °C. A new kind of CaSO₄/CaCO₃ oxygen carrier is prepared using a mechanical mixing method. The addition of CaCO₃ nanoparticles largely improves the recyclability of the oxygen carrier in comparison with the fresh CaSO₄ oxygen carrier, without CaCO₃ nanoparticles, in a multi-cycle TGA test.

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1. Introduction

Presently, we must face a serious problem concerning the increasing emissions of greenhouse gases. Carbon dioxide (CO₂) is a well-known greenhouse gas, and a major part of CO₂ is released from the expanding use of coal for the generation of electricity. In recent years, the increased frequency of El Niño event, multiplication of severe storms and accelerating melting of glaciers may all be related to large emissions of the manmade greenhouse gases [1–3]. However, most of the current processes for sequestering CO₂ are associated with a significant penalty to the efficiency of power plants because of the considerable energy utilized to separate CO₂ from the flue gas.

Chemical looping combustion (CLC) technology has the inherent feature of CO₂ capture. It is a flameless combustion technology where the direct contact between fuel and oxygen is avoided. A basic CLC system consists of two interconnected reactors, one for fuel and one for air. Oxygen is utilized for fuel combustion in the CLC process by means of the intermediate oxygen carrier, which is alternately reduced and oxidized while circulating in the reactor system. Therefore, after condensing the water, pure CO₂ is obtained from the fuel reactor exhaust gas stream without nitrogen dilution. Accordingly, the additional equipment and energy for separation of CO₂ can be avoided.

The majority of previous studies on the CLC system are mainly concentrated on those metal oxide oxygen carriers. The reactivity behavior and recycled performance of Ni-based [4–15], Cu-based [4,7,16–18], Co-based [7,9,19], Fe-based [4,7,11,14,20–22], Mn-based [4,7,20] oxides and the bimetallic oxides [4,17–19] were all studied. However, they all have the disadvantages of low capacity of carrying oxygen and high cost. In addition, the high endothermic enthalpy in the reduction of Fe-based oxygen carriers by methane and the potential pollution to the environment of Co-based, Mn-based and Ni-based oxygen carriers are all negative to their large use in CLC system. Therefore, it is important to develop some materials of the oxygen carrier with low cost, high oxygen transfer capability and friendliness to the environment.

In recent years, CaSO₄ is believed as an alternative to the metal oxide oxygen carriers. It has some obvious advantages. Firstly, CaSO₄ has an oxygen transport capacity greater than the metal oxide oxygen carriers. The oxygen transport ratio, R_0 , is defined as $R_0 = (m_{ox} - m_{red}) / m_{ox}$, where m_{ox} is the mass of the oxygen carrier after the oxidation period and m_{red} is that after the reduction period. Actually, the oxygen transport ratio is the mass fraction of the oxygen transported by the oxygen carrier from the air to the fuel, thereby representing the oxygen transport capacity of the oxygen carrier. The value of R_0 for CaSO₄/CaS is 0.4706 while the values are 0.2011, 0.2212 and 0.1001 for CuO/Cu, NiO/Ni and Fe₂O₃/FeO respectively. Moreover, anhydrite, of which the major composition is CaSO₄, is a stable ore distributed widely in nature. Phosphogypsum, of which the major composition is also CaSO₄, is the main byproduct of phosphoric acid plants. Therefore, the cost of CaSO₄ is

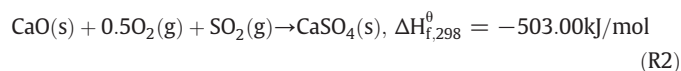
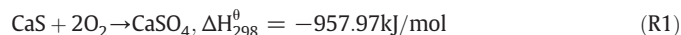
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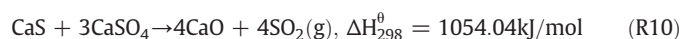
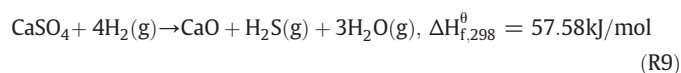
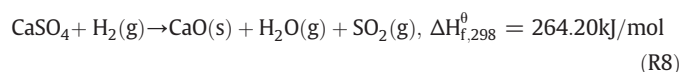
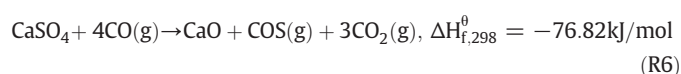
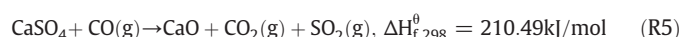
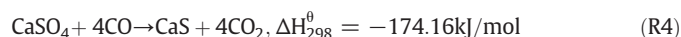
much lower than that of the metal oxides. In particular, CaSO_4 powders are friendly to the environment and seem more favorable for the CLC system.

Considering that the syngas derived from coal gasification is used as the gas fuel in most CLC cases [23–27], the compositions of a typical syngas are listed in Table 1. The possible reactions in the air reactor and the fuel reactor are shown as reactions (R1)–(R10):

Air reactor:



Fuel reactor:



CO and H_2 are two major compositions in the syngas. Consequently, it is significant to investigate the reactivity of CaSO_4 in the presence of CO and H_2 . Diaz-Bossio et al. [28] investigated the reductive decomposition of CaSO_4 by both CO and H_2 through the thermo-gravimetric analysis experiments. The treatment of experiment data was based on the assumption that the direct reductive products after the reduction of CaSO_4 were merely CaO , in the temperature range from 900 to 1180 °C. The reaction was simply first order with respect to the partial pressure of either CO or H_2 . By contrast, Shen et al. [29] found that in the same temperature range the reductive products of CaSO_4 by either CO or H_2 were actually the mixtures of CaO and CaS . The mole fraction of CaS is higher than CaO when the reacting temperature is below 1000 °C. In particular, CaSO_4 could only be converted into CaS when the reacting temperature is maintained at around 850 °C. In addition, the releases of SO_2 and COS are detected in the reduction of CaSO_4 by CO with the temperature changing from 950 °C to 1050 °C, which caused a dramatic decrease of the recyclability of CaSO_4 . Song et al. [30] investigated the effects of reacting temperature, gas flow rate and particle size on the reduction of CaSO_4 by CH_4 in a laboratory-scale fixed bed reactor. The results showed that CaSO_4 has a high reduction reactivity and stability in a long-time reduction/oxidation test. However, a significant SO_2

formation was observed at the temperature higher than 950 °C. Song et al. [31,32] also performed the recycle test of a natural anhydrite in alternating simulated syngas and air conditions in a fluidized bed reactor. Furthermore, they discovered the large formation of SO_2 and H_2S during the reduction section in the tests, which greatly weakened the recyclability of CaSO_4 .

Summarizing all the previous studies [28–32], sulfur evolution is unavoidable in the reduction of CaSO_4 by either CO or H_2 , defeating the environmental friendliness of CaSO_4 oxygen carrier. It can be controlled to some extent by lowering the reacting temperature. However, this is at the expense of harming the reaction rate between CaSO_4 and the reductive gases. The purpose of the research reported in this paper was to study the effects of reacting temperature, oxygen ratio number and the mole fraction of both carbon monoxide (CO) and hydrogen (H_2) in the syngas on the amounts of the sulfurous gases using thermodynamic simulation. A number of TGA experiments were also undertaken to shed light on the effects of the partial pressure of the reductive gases and the addition of CaCO_3 nanoparticles into CaSO_4 samples on the sulfur evolution, indicating the recyclability of the oxygen carrier to a certain extent, in the multi-cycle tests.

2. Thermodynamic analysis of sulfurous species in a fuel reactor

It is important to predict the amounts of various sulfurous species released from the fuel reactor by thermodynamic analysis. For the reactions between CaSO_4 and CO , shown as reactions (R4)–(R6), the equilibrium constant for every chemical reaction is calculated as Eq. (11). Thus the corresponding equilibrium gas ratio can be determined by Eqs. (12)–(14):

$$K_p = f(T) = \exp(-\Delta G^{\circ} / RT) \quad (11)$$

$$K_{p,R4} = (P_{\text{CO}_2} / P_{\text{CO}})^4 \quad (12)$$

$$K_{p,R5} = (P_{\text{CO}_2} / P_{\text{CO}}) \cdot P_{\text{SO}_2} \quad (13)$$

$$K_{p,R6} = (P_{\text{CO}_2} / P_{\text{CO}})^3 \cdot (P_{\text{COS}} / P_{\text{CO}}) \quad (14)$$

where K_p is the equilibrium constant of some reaction, $K_{p,R4}$, $K_{p,R5}$ and $K_{p,R6}$ are the equilibrium constant for reaction (R4), (R5) and (R6) respectively, ΔG° is the total changes of the standard Gibbs free energy of all components in a reaction, R is the gas constant, T is the reacting temperature, P_{CO_2} , P_{CO} , P_{SO_2} and P_{COS} are the equilibrium partial pressure of CO_2 , CO , SO_2 and COS respectively.

The equilibrium gas ratio for the reactions between CaSO_4 and H_2 , shown as reaction (R7)–(R9), can be calculated using the same method. Actually, the equilibrium constant is only affected by the equilibrium temperature according to Eq. (11). Therefore, the relationship between the equilibrium gas ratio and the temperature can be obtained. All the thermodynamic data for the components are provided from the NASA Glenn database [33].

Fig. 1 shows the relationship between the equilibrium partial pressure of the sulfurous gases and the reacting temperature for the reaction between CaSO_4 and CO while Fig. 2 for the reaction between CaSO_4 and H_2 . Both the equilibrium temperatures in Figs. 1 and 2 are ranging from 700 to 1300 °C. It can be seen that the higher reacting temperature causes the release of more sulfurous gases, which agrees well with the results reported by Shen et al. [29]. To reconcile the contradiction between enhancing the reacting rate and reducing the released amounts of the sulfurous gases, the reacting temperature in the fuel reactor is controlled within the range from 850 °C to 1050 °C. As shown in Figs. 1 and 2, when the reacting temperature is 850 °C, the equilibrium gas ratio of $P_{\text{CO}}/P_{\text{CO}_2}$ and $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ is 0.0069 and 0.0083 respectively. Then the corresponding mole fraction of SO_2 in the

Table 1
Mole fraction of H_2 , CO , CO_2 , $\text{H}_2\text{O}(\text{g})$, H_2S and N_2 in the simulated syngas (mol%).

H_2	CO	CO_2	$\text{H}_2\text{O}(\text{g})$	H_2S	N_2
23.7	36.3	12.5	17.5	2.3	Balance

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