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Thermodynamic investigation into carbon deposition and sulfur evolution in a Ca-based chemical-looping combustion system

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ABSTRACT

Chemical-looping combustion is a promising technology that concentrates CO_2 and separates it during combustion. In this study, both the carbon deposition and sulfur evolution in the reduction of a calcium sulfate ($CaSO_4$) oxygen carrier with a typical syngas were investigated using thermodynamic simulations. The effects of reaction temperature, operating pressure and the oxygen ratio number (defined in this paper) on the amount of deposited carbon and released sulfurous gases are discussed. A reaction temperature from 750 to 950 °C, an operating pressure from 1 to 15 bars and an oxygen ratio number between 0.4 and 0.8 were determined to be the most favorable operating conditions. In addition, the amounts of released sulfurous gases were found to be largely dependent on the partial pressures of H_2 and CO based on the thermo-gravimetric analyzer (TGA) tests. When the partial pressure of H_2 or CO was above 40 kPa, the release of sulfurous gases could be prevented in the reaction between $CaSO_4$ and syngas, even if the reaction temperature was as high as 1000 °C. The XRD profiles of the products also demonstrated that the mole fraction of CaS in the products increased gradually with an increasing partial pressure of H_2 or CO, until the products were almost pure CaS.

Keywords: Thermodynamic simulation; Carbon deposition; Sulfur evolution; Partial pressure

1. Introduction

It is generally accepted that CO_2 is an anthropogenic greenhouse gas that leads to global warming. However, in recent years, fossil fuel-related CO_2 emissions have continued to increase (IPCC, 2007). The current methods to reduce CO_2 emissions include increasing the use of alternative fuels, such as hydrogen, wind and solar energy; lowering global energy consumption; storing CO_2 underground in geological formations; and reducing the energy used during industrial production. However, fossil fuels will likely remain the primary source of heat and power in conventional combustion systems, in which the concentration of CO_2 in the flue gas can be as low as ~10–14%. With respect to the low concentration of CO_2, the available CO_2 capture technologies are energy intensive and costly. Chemical-looping combustion (CLC) is a novel combustion technology with an inherent separation of CO_2. The CLC concept realizes a transfer of oxygen from the combustion air to the fuel through the circulation of an oxygen carrier in two separate reactors. In a CLC system, CO_2 can be easily removed from the flue gas without any energy consuming gas separation processes.

In a CLC system, the separation of CO_2 is realized by performing the combustion in two interconnected reactors designated as the air and the fuel reactors, respectively. In the fuel reactor, the fuel is oxidized by the lattice oxygen of the oxygen carrier. At present, the oxygen carriers mainly include oxides of Ni, Fe, Cu and Co. Complete combustion in the fuel reactor attains a high concentration of CO_2 and water vapor in the flue gas. Therefore, almost pure CO_2 is obtained after condensation. Then, the oxygen carrier is reoxidized by oxygen (O_2) in the air reactor and is ready to begin a new cycle. In addition, NOx formation is prevented because the fuel burns in an air-free environment in the fuel reactor, and the reduced oxygen carrier is regenerated at a comparatively low temperature in the air reactor (Ishida and Jin, 2006).

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Selection of the oxygen carrying material is key in the development of CLC technology. Most of the past work on oxygen carriers was concentrated on preparing and testing metal oxide particles. The metal oxides of Ni (Gayán et al., 2009; Dueso et al., 2009; Jin and Ishida, 2001; Ishida et al., 1996, 1998; Ishida and Jin, 1997; Readman et al., 2006); Cu (De Diego et al., 2004; Corbella et al., 2005; Adanez et al., 2006); Co (Mattisson et al., 2003; Sturzenegger et al., 2006; Jin et al., 1998); Fe (Rubel et al., 2009; Chandel et al., 2009; Abad et al., 2007); and Mn (Zafar et al., 2007; Abad et al., 2006), and the bimetallic oxides (Mohammad and Hugo, 2010; Johansson et al., 2006; Hossain et al., 2007) have all been investigated on different scales. However, they all have the disadvantages of a weak capacity for oxygen and high cost. In addition, the relatively high endothermic enthalpy in the reduction of Fe-based oxygen carriers, the poor thermal stability of Cu-based oxygen carriers and the potential pollution to the environment from Co-based, Mn-based and Ni-based oxygen carriers prohibit their wide use in CLC systems.

Compared with the metal oxides, the advantages of calcium sulfate ($CaSO_4$) are obvious, and it is considered a promising oxygen carrier. First, the oxygen carrying ability of $CaSO_4$ is relatively high. One mole of $CaSO_4$/CaS oxygen carriers have 4 times the oxygen carrying ability of 1 mol of CuO/Cu or NiO/Ni and more than 10 times that of 1 mol of Fe_2O_3/Fe_3O_4. Additionally, $CaSO_4$ is a very inexpensive material. It is a stable and widespread natural sulfate. Additionally, $CaSO_4$ powder is eco-friendly.

At present, Alstom Power Inc. (Herbert et al., 2009) is developing a CLC process utilizing a $CaSO_4$ oxygen carrier. Limestone ($CaCO_3$) is used in the process to capture the sulfur in the coal, forming calcium sulfide (CaS) in the fuel reactor. CaS is then removed into the air reactor and burned with air through an exothermic reaction, producing hot $CaSO_4$. The hot $CaSO_4$ is cycled to the fuel reactor to supply the necessary oxygen and heat to burn the coal. The main product, CaS, is used for the new cycles, while the other products, including $CaSO_4$, coal ash and some unused CaO, are bled from the system. Fresh limestone is continuously added to replace the removed calcium. However, until now, no experimental data have been published concerning a Ca-based CLC system.

Diaz-Bossio et al. (1985) studied the reduction of $CaSO_4$ with both CO and H_2 through thermogravimetric analyzer (TGA) experiments. Analysis of the experimental data was based on the assumption that the direct reduction products of $CaSO_4$ were CaO at temperatures ranging from 900 to 1180 °C. In contrast, Shen et al. (2008) found that in the same temperature range, the reduction products of $CaSO_4$ with either CO or H_2 were actually mixtures of CaO and CaS. The mole fraction of CaS was higher than CaO when the reaction temperature was below 1000 °C. In particular, when the reaction temperature was maintained as low as 850 °C, the mole fraction of CaS in the solid products was close to 100%. During the reduction of $CaSO_4$ by CO, SO_2 and COS were detected in the gaseous products when the reaction temperature was changed from 950 to 1050 °C, which caused a drastic deterioration in the recyclability of the $CaSO_4$. Song et al. (2008a,b,c) investigated the effects of reaction 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 $CaSO_4$ had a high reductive reactivity in a long reduction/oxidation test. However, significant SO_2 evolution was observed when the temperature was higher than 950 °C. Song et al. (2008a,b,c) also performed a multi-cycle test on a type of $CaSO_4$ oxygen carrier (natural anhydrite) by repeatedly alternating simulated syngas and air in a fluidized bed reactor. They discovered the formation of a large amount of SO_2 and H_2S during the reduction, which greatly reduced the recyclability of the $CaSO_4$. Nevertheless, these studies only indicated that a low temperature is beneficial to reducing the amount of released sulfurous gases. Comprehensive research on carbon deposition and sulfur evolution in the fuel reactor with a $CaSO_4$ oxygen carrier is still lacking.

In this paper, the carbon deposition and sulfur evolution during the reduction of a $CaSO_4$ oxygen carrier with a typical coal gas is thermodynamically studied. The effects of reaction temperature, operating pressure and oxygen ratio number (defined in this paper) on the amounts of deposited elemental carbon and sulfurous gases, mainly sulfur dioxide (SO_2), hydrogen sulfide (H_2S) and carbonyl sulfide (COS), are discussed. In addition, TGA experiments reveal that the released sulfurous gases are highly dependent on the partial pressure of H_2 or CO. High partial pressures of H_2 or CO effectively inhibited the release of sulfurous gases.

2. Thermodynamic simulation method

Both carbon deposition and sulfur evolution are thought to be influenced by many factors, including reaction temperature, operating pressure, availability of lattice oxygen in the oxygen carrier and the concentration of CO_2 and water vapor in the syngas, among others.

Considering that syngas derived from coal gasification is a common fuel in most CLC cases, the representative composition of syngas is listed in Table 1. The formula of the syngas can be considered as $C_\alpha H_\beta O_\chi N_\delta S_\varepsilon (CO_2)_\gamma (H_2O)_\mu$ for convenience. For $CaSO_4$ oxygen carriers, the CLC process begins with reduction by CO and H_2, the two main components in the syngas, continues with oxidation by air, and then returns to the reduction to complete a repeating cycle. The main reactions in the fuel reactor and the air reactor are as follows:

Fuel reactor:

$$CaSO_4 + 4CO \rightarrow CaS + 4CO_2, \quad \Delta H^{\theta}_{298} = 174.16\,kJ/mol \tag{R1}$$

$$CaSO_4 + CO(g) \rightarrow CaO + CO_2(g) + SO_2(g), \quad \Delta H^{\theta}_{f,298} = 210.49\,kJ/mol \tag{R2}$$

$$CaSO_4 + 4CO(g) \rightarrow CaO + COS(g) + 3CO_2(g), \quad \Delta H^{\theta}_{f,298} = -76.82\,kJ/mol \tag{R3}$$

$$CaSO_4 + 4H_2 \rightarrow CaS + 4H_2O(g), \quad \Delta H^{\theta}_{298} = -24.51\,kJ/mol \tag{R4}$$

$$CaSO_4 + H_2(g) \rightarrow CaO(s) + H_2O(g) + SO_2(g), \quad \Delta H^{\theta}_{f,298} = 264.20\,kJ/mol \tag{R5}$$

$$CaSO_4 + 4H_2(g) \rightarrow CaO + H_2S(g) + 3H_2O(g), \quad \Delta H^{\theta}_{f,298} = 57.58\,kJ/mol \tag{R6}$$

Table 1 – Mole fraction of H_2, CO, CO_2, $H_2O(g)$, H_2S and N_2 in the simulated syngas (mol%).

H_2	CO	CO_2	H_2O (g)	H_2S	N_2
23.7	36.3	12.5	17.5	2.3	Balance