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Reaction Mechanism of Coal Chemical Looping Process for Syngas Production with CaSO$_4$ Oxygen Carrier in the CO$_2$ Atmosphere

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ABSTRACT: Chemical looping combustion process for gaseous and solid fuel has been investigated widely. Recently, particular attention is paid to syngas and hydrogen generation from natural gas or solid fuels. CaSO$_4$ has been proved to be a promising oxygen carrier for the chemical looping process with the merit of low price and environmental friendliness. The reaction mechanism of coal and pure CaSO$_4$ for syngas production in the CO$_2$ atmosphere was investigated using the simultaneous thermal analyzer in this paper. First, the thermodynamic analysis of reaction between coal and CaSO$_4$ with different mass ratios was carried out respectively in N$_2$ and CO$_2$ atmospheres. It predicted that the CO$_2$ can promote the reactions, while the coal-CaSO$_4$ mass ratios affected the fate of sulfurous gaseous species greatly. Subsequently, thermogravimetric experiments were conducted by the peak fitting technique. It concluded that the drying and pyrolysis of the coal were main reactions before 800 °C, while the complex reactions, including the reaction between CaSO$_4$ and coal char, gasification of coal char, and the decomposition of CaSO$_4$, occurred during 800−1100 °C. The reaction kinetics and types of the reaction between coal and CaSO$_4$ for syngas in the CO$_2$ atmosphere were explored by isoconversional method. It indicated that the complex processes were controlled by the diffusion of gas−solid or solid−solid first, followed by parallel competing reactions. Finally, the reaction residues between coal and pure CaSO$_4$ with different mole ratios were analyzed using scanning electron microscopy and energy dispersive spectrometer (SEM-EDS).

1. INTRODUCTION

It has been generally acknowledged that the emission of greenhouse gases (e.g., CO$_2$, CH$_4$, and NO$_x$) is the main contributor to global warming and sea level rise, with carbon dioxide being the most prevalent of these emissions. Among all the CO$_2$ sequestration technologies, chemical-looping combustion (CLC) was considered as the most promising one, which was originally proposed to improve thermal efficiency in power plants and afterward identified as having inherent advantages for CO$_2$ capture.[1]

With the development of recognition and investigation of chemical looping technology, more attention was paid to the CLC for solid fuel, such as coal,[2] biomass,[3] and oil coke,[4] than for gaseous fuel, such as natural gas and water coal gas. Two approaches are proposed for the chemical looping process with solid fuels.[5] One is to carry out first coal gasification and subsequently to introduce the syngas produced in the CLC system,[6] while the other is to feed the solid fuel directly to the fuel reactor in a CLC process. Two options of the latter are the solid fuel gasified in situ by H$_2$O or CO$_2$ supplied as fluidization agent (iG-CLC) and the so-called chemical-looping with oxygen uncoupled (CLOU) process, where the solid fuel is burned with gaseous oxygen released by the oxygen-carrier in the fuel-reactor.[7] Solid fuel direct chemical looping process is more potential in the view of energy utilization and economy, and many studies have been achieved. Leion[8] investigated the direct CLC using coal from different sources in a laboratory fluidized bed reactor. Meanwhile, Lyngfelt[9] designed a 10 kWth fluidized pilot using a South African coal as the fuel. Recently, Shen[10] investigated the effect of gasification intermediate and temperature on the solid fuel direct chemical looping combustion.

In recent years, the investigation into chemical looping process was expanded from combustion to hydrogen production and gasification for syngas. Fan et al.[11] proposed three chemical looping processes to convert carbonaceous fuels into products such as hydrogen, electricity, and synthetic fuels. Cleeton[12] identified a suitable operating regime through the simulation of a chemical looping combustion (CLC) system using hematite (Fe$_2$O$_3$) as an oxygen carrier in conjunction with a steam-coal gasification process. Andrus[13] proposed a calcium-based hybrid combustion-gasification chemical looping technology for electricity, syngas, or hydrogen from coal in three basic ways by controlling the air-to-coal ratio (i.e., oxygen carrier-to-coal ratio in the fuel reactor). When oxygen supported by oxygen carrier is enough for converting the coal into CO$_2$ and H$_2$O, a considerable amount of heat will produce for electricity generation. Otherwise, when inadequate oxygen carrier supports for coal, the syngas CO/H$_2$ will generate, while hydrogen can be produced coupling with water shift and CO$_2$-capture using CaO. However, the further result was not reported in the open literature.

The reaction mechanism of solid fuel-oxygen carrier in chemical looping process is very complicated. It is usually assumed that coal-oxygen carrier reactions proceeded through

Table 1. Proximate and Ultimate Analysis of Shenmu Coal (Air Dry Basis)

M%	V%	A%	FC%	C%	H%	N%	O%	Qnet (MJ/kg)
8.30	29.46	10.21	52.03	65.00	3.83	0.88	11.38	24.58

indirect reaction between oxygen carrier and gaseous products from coal gasification. Direct solid–solid reactions are very slow and have not been considered as a viable reaction mechanism for solid fuel CLC.[14] The dominant rate-determining step involved in the reaction of coal with oxygen carrier was actually the coal gasification, instead of the reduction of oxygen carrier with the gasification products generated from the coal inside.[4−6] In summary, the coal gasification and reduction of oxygen carrier were independent, and the solid–solid reactions of coal and oxygen carrier were hardly considered. Nevertheless, Siriwardane[15] evaluated the interactions of coal with metal oxide oxygen carriers and proposed a reaction mechanism called "fuel-induced oxygen release" that metal oxide can directly react with solid fuel if sufficient contacts are made between the metal oxide oxygen carrier and the solid fuel. Wang[16] investigated the reaction mechanism of chemical looping combustion of coal with Fe_2O_3 oxygen carrier in the N_2 atmosphere and concluded that the low rank coal with high volatile content should be preferred for the full conversion of coal into CO_2. However, further investigation into the complex reactions between the coal and oxygen carrier is needed.

On one hand, $CaSO_4$ has been proved to be a promising oxygen carrier candidate for the chemical looping process,[17,18] with a higher oxygen capacity compared with metal oxides. On the other hand, most of the research on the solid fuel direct chemical looping process used metal oxide and H_2O as the oxygen carrier and gasification agent respectively. CO_2 can also be used as the gasification agent, which is one approach for CO_2 utilization. With $CaSO_4$ and CO_2 selected as the oxygen carrier and gasification agent respectively, the following reactions may take place mainly

$$C_nH_{2m}O_x \rightarrow \text{tar} + \text{char} + \text{mixture gas (CO,} \quad H_2,$$
$$CO_2, \quad CH_4, \quad \text{and} \quad C_nH_m) \tag{R1}$$

$$C + CO_2(g) \rightarrow 2CO(g), \quad \Delta H_{298.15} = 172.423 \text{ kJ/mol} \tag{R2}$$

$$CaSO_4 + 4C \rightarrow CaS + 4CO(g),$$
$$\Delta H_{298.15} = 520.457 \text{ kJ/mol} \tag{R3}$$

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2(g),$$
$$\Delta H_{298.15} = 175.612 \text{ kJ/mol} \tag{R4}$$

$$CO(g) + 1/4CaSO_4 \rightarrow CO_2(g) + 1/4CaS,$$
$$\Delta H_{298.15} = -42.308 \text{ kJ/mol} \tag{R5}$$

$$CO(g) + CaSO_4 \rightarrow CaO + CO_2(g) + SO_2(g),$$
$$\Delta H_{298.15} = 222.926 \text{ kJ/mol} \tag{R6}$$

$$4CO(g) + CaSO_4 \rightarrow CaO + COS(g) + 3CO_2(g),$$
$$\Delta H_{298.15} = -77.348 \text{ kJ/mol} \tag{R7}$$

$$H_2(g) + 1/4CaSO_4 \rightarrow CaS + 1/4H_2O(g),$$
$$\Delta H_{298.15} = -24.51 \text{ kJ/mol} \tag{R8}$$

$$H_2(g) + CaSO_4 \rightarrow CaO + SO_2(g) + H_2O(g),$$
$$\Delta H_{298.15} = 264.20 \text{ kJ/mol} \tag{R9}$$

$$4H_2(g) + CaSO_4 \rightarrow CaO + H_2S(g) + 3H_2O(g),$$
$$\Delta H_{298.15} = 57.58 \text{ kJ/mol} \tag{R10}$$

$$CaS + 3CaSO_4 \rightarrow 4CaO + 4SO_2(g),$$
$$\Delta H_{298.15} = 1060.935 \text{ kJ/mol} \tag{R11}$$

$$CaSO_4 \rightarrow CaO + SO_2 + 1/2O_2,$$
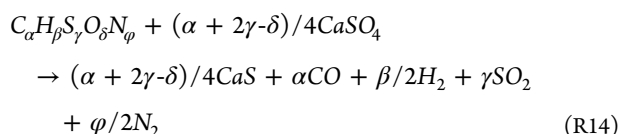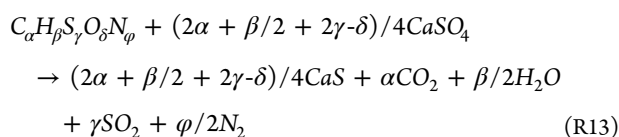$$\Delta H_{298.15} = 50.30 \text{ kJ/mol} \tag{R12}$$

R1 is the dried and pyrolysis of the coal. The gasification reaction R2 of char is an endothermic reaction. Reaction R3 and R4 are the solid–solid state reduction between coal char and oxygen carrier. The pyrolysis gas and gasification gas will react with $CaSO_4$ oxygen carrier to produce CO_2 simultaneously R5. Side reactions R6 and R7 and solid–solid reactions R11 takes place unavoidably using $CaSO_4$ as the oxygen carrier. Reductive reactions R8−R10 of $CaSO_4$ with H_2 in the pyrolysis gas may take place. The decomposition reaction R12 of $CaSO_4$ also occurs at high temperature.

In this paper, the mechanism of the solid fuel chemical looping process for syngas with $CaSO_4$ as the oxygen carrier in the CO_2 atmosphere was examined through thermodynamic analysis and thermogravimetric experiments. Furthermore, the reaction kinetics and types of coal and $CaSO_4$ in the CO_2 atmosphere were presented by the isoconversional method and peak fitting technique.

2. EXPERIMENT AND METHOD

2.1. Materials and Characterization. The oxygen carrier used in the experiment was the analytical pure $CaSO_4$ (Tianjin Basf Chemical Co., Ltd.), whose particle size distribution was evaluated using a Rise 2000 laser particle size analyzer, and the average diameter was 8.934 μm. Table 1 listed the proximate and ultimate analysis of the Shenmu coal used in this study (air-dry basis). The coal samples were ground under atmospheric condition, sieved into particles with a size range of 50−150 μm, and stored in a hermetic bag. Finally, the sample of coal and $CaSO_4$ was prepared by mechanical mixing according to the desired mass ratio.

2.2. Determination of the Related Parameters. The $CaSO_4$-to-coal mass ratio was determined by the ratio of available oxygen present in the oxygen carrier to the needed oxygen for coal conversion. A sufficient amount of the oxygen carrier is necessary for chemical looping combustion, while an inefficient supply can generate syngas. If coal was represented as $C_\alpha H_\beta S_\gamma O_\delta N_\varphi$, the following reactions may occur

$$C_\alpha H_\beta S_\gamma O_\delta N_\varphi + (2\alpha + \beta/2 + 2\gamma\text{-}\delta)/4CaSO_4$$

$$\rightarrow (2\alpha + \beta/2 + 2\gamma\text{-}\delta)/4CaS + \alpha CO_2 + \beta/2H_2O$$

$$+ \gamma SO_2 + \varphi/2N_2 \tag{R13}$$

$$C_\alpha H_\beta S_\gamma O_\delta N_\varphi + (\alpha + 2\gamma\text{-}\delta)/4CaSO_4$$

$$\rightarrow (\alpha + 2\gamma\text{-}\delta)/4CaS + \alpha CO + \beta/2H_2 + \gamma SO_2$$

$$+ \varphi/2N_2 \tag{R14}$$

According to the proximate and ultimate analysis results of Shenmu coal, the weight fractions of hydrogen and oxygen in the moisture were deducted, and the remaining free hydrogen and oxygen were determined. Taking 1 kg of Shenmu coal samples as a basis, the content of different atoms including C, H, O, N, and S in Shenmu coal was evaluated, and the relative chemical formula could be represented as $C_{54.2}H_{38.3}S_{0.52}O_{6.32}N_{0.63}\cdot(H_2O)_{4.6}$. From reactions R13 and R14, the theoretical needed oxygen for the full and partial conversion of coal is determined to $(2\alpha+\beta/2 + 2\gamma-\delta)/4$ and $(\alpha+\beta/2 + 2\gamma-\delta)/4$ respectively. Thus, the needed mass of $CaSO_4$ is 4.13 kg and 2.29 kg for 1 kg Shenmu coal respectively. In other words, the carbon and hydrogen in the coal leaves as CO_2 and H_2O when the oxygen carrier-to-coal mass ratio equals 4.13:1. The syngas CO/H_2 will generate when the oxygen carrier-to-coal mass ratio equals 2.29:1 approximately. Three oxygen carrier-to-coals mass ratios, 4.13:1, 3:1, and 2.29:1, were adopted in this study.

2.3. Experiment Procedure and Result Processing Method. The thermogravimetric experiments of coal and different oxygen-coal-ratio mixtures were carried out in the thermal gravimetric analyzer (TGA, Netzsch STA 409 PC, Germany). In the baseline experiment, about 12 mg coals or the desired mass ratio mixture were heated directly from ambient temperature to 1100 °C at the heating rate of 15 K/min in the N_2 or CO_2 atmosphere, respectively. In the kinetic analysis experiment with the oxygen carrier-to-coal mass ratio 2.29:1 in the CO_2 atmosphere, five heating rates, 5K, 10K, 15K, 20, 25 K/min, were selected to calculate the activation energy values at different degrees of conversion. The flow rate of N_2 or CO_2 was determined at 20 mL/min approximately, while the total mass of the mixture of coal and $CaSO_4$ oxygen carrier was determined at about 12 mg to eliminate the potential impact of mass transfer between gas and solid phases. The emission gases from TGA were analyzed directly by the gas chromatograph analyzer (PE Clarus 500), using TDX-01 packed column/thermal conductivity detector for syngas and Propark QS packed column/flame photometric detector for sulfurous gas.

Based on the nonisothermal kinetic analysis of solid state reactions, the basic model could be expressed as follows

$$d\alpha/dt = Ae^{-E/RT}f(\alpha) \tag{1}$$

where t is the reaction time, α is the degree of conversion, E is the activation energy, A is the exponential factor, R is the universal gas constant, and $f(\alpha)$ is the kinetic function related to the reaction mechanism.

Mechanisms of solid state processes are usually too complicated to be characterized by a simple kinetic model. Consequently, isoconversional methods are often used to describe their kinetics. The activation energy can be calculated from a multiheating rate at a fixed conversion degree by isoconversional methods. The Flynn-Wall-Ozawa (FWO)[19]

isoconversional method is used in this study, which is expressed as follows

$$\lg \beta = \lg\left(\frac{AE}{RG(\alpha)}\right) - 2.315 - 0.4567\frac{E}{RT} \tag{2}$$

where β is the rate of temperature increase, and $G(\alpha)$ is the integral form of the reaction mechanism function. The advantage of the FWO method is that the active energy E could be calculated directly without using the reaction mechanism function.

$CaSO_4$ will react with coal char or gasification products of coal under the CO_2 atmosphere. Thus, the degree of conversion of the reaction between coal and $CaSO_4$ as well as interaction of coal with the OC was defined as[20]

$$\alpha = \frac{W_{coal\text{-}OC}(t = 0) - W_{coal\text{-}OC}(t)}{x_1 \Delta W_{OC} + x_2 \Delta W_{coal}} \tag{3}$$

where $W_{coal\text{-}OC}$ $(t = 0)$ and $W_{coal\text{-}OC}$ (t) are the initial and instantaneous weight losses for the mixture of coal with the oxygen carrier (wt %), x_1 and x_2 the mass fractions of oxygen carrier and coal in their mixture (wt %), and ΔW_{OC} and ΔW_{coal} are the maximal weight losses of the oxygen carrier and coal respectively.

Vyazovkin[21] and Dowdy[22] presented that a complex process/reaction is identified by the changes in activation energy for different α while the activation energy of the single stage reaction keeps the constant with α changing, for the isoconversional method. The high sensitivity of the degree of conversion dependence of the activation energy provides a high efficiency of its application as a criterion of a complex process. Therefore, the analysis of a complex reaction is based on the dependence of α on the activation energy. It was further shown that simultaneous/parallel reactions occur with increasing in dependencies of activation energy on the degree of conversion, while decreasing dependencies are typical of complex reactions with a change in limiting stage. The limiting stage may be the particular processes containing a reversible intermediate stage or the proceeding with a change over from kinetic to the diffusion regime.

3. RESULTS AND DISCUSSION

3.1. Thermodynamic Analysis of the Reaction between Coal and CaSO4. Based on the Gibbs free energy minimization method, the thermodynamic analysis of reaction between coal and $CaSO_4$ varying with the temperature and oxygen carrier-to-coal mass ratios was performed. The coal was treated as five elements C, H, O, N, and S separately. The common gaseous species considered in the product after the reaction was H_2 (g), H_2O (g), N_2 (g), CO (g), CO_2 (g), and CH_4 (g). In particular, the considered sulfurous species were H_2S (g), SO_2 (g), S_2 (g), CS_2 (g), and COS (g), where the solid species were CaS, $CaSO_4$, CaO, and $CaCO_3$ mainly. 1 kg of Shenmu coal was taken into account for the thermodynamic analysis, and the corresponding mass of $CaSO_4$ was 4.13 kg and 2.29 kg to satisfy the total combustion of coal and to maximize the syngas respectively. It assumed that the amount of CO_2 in the CO_2 atmosphere was 60 mols, which is adequate for the total gasification of the coal in the investigated system.

Figure 1a and 1b demonstrated the effect of temperature on the gas species amount with a $CaSO_4$-to-coal mass ratio of 2.29:1 in N_2 and CO_2 atmospheres respectively. As shown in Figure 1a, the amount of CO increased rapidly from 10 mols to
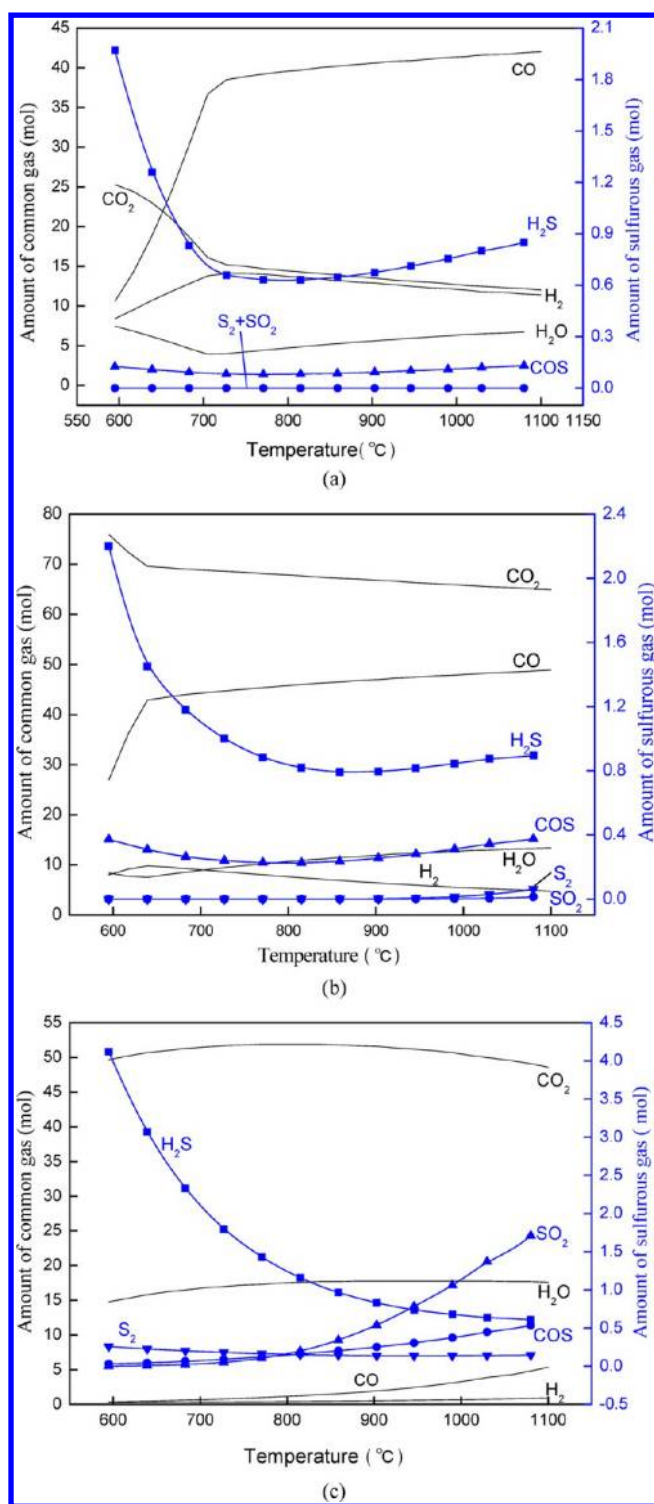
Figure 1. The effect of temperature on the gas species amount with different $CaSO_4$-to-coal ratios: (a) 2.29:1 in the N_2 atmosphere, (b) 2.29:1 in the CO_2 atmosphere, and (c) 4.13:1 in the N_2 atmosphere.

was shown in Figure 1a. The amount of H_2S decreased with the increasing temperature below than 750 °C and increased slightly greater than 750 °C. This is attributed to the side reaction R10 at high temperature exceeding 750 °C. It is observed that the amount of COS kept at a relatively low level and SO_2/S_2 can be ignored.

Comparing Figure 1a and Figure 1b, it presented that the equilibrium amount of CO is already stable at 640 °C in the CO_2 atmosphere while at 710 °C in the N_2 atmosphere. The excess CO_2 is in favor of the Ca-based chemical looping process for syngas generation thermodynamically. However, sulfurous species COS tended to increase in the excess CO_2 atmosphere. Reductive atmosphere benefits for COS generating from H_2S. Figure 1c indicated the $CaSO_4$-to-coal mass ratio of 4.13:1 in the N_2 atmosphere as a function of temperature. Adequate oxygen supported by $CaSO_4$ makes the main production CO_2 in this situation. The amount of sulfurous species SO_2 increased, while H_2S decreased with the temperature increasing. The amount of sulfurous species COS increased with the temperature increasing to 0.5 mols at 1090 °C, which was more than the amount of COS in Figure 1a. A comparison of Figure 1a and Figure 1c highlights the reaction that occurred in the system. When $CaSO_4$ is scarce, the reactions R7 and R10 generating H_2S and COS were the main side reactions. When $CaSO_4$ is sufficient; the reactions R6 and R9 were the main side reactions, and SO_2 was the main sulfurous gas. Accompanied with the generation of the sulfurous gas, the corresponding undesired solid CaO was produced. Actually, the high temperature tended to promote the occurrence of side reaction for sulfurous gas generation, while low temperature may reduce the reaction rate between coal char and $CaSO_4$ oxygen carrier. Thus, the temperature ranges from 850 to 950 °C might be optional for the chemical looping process.

The effect of the $CaSO_4$-to-coal mole ratio on the gas species amount at 900 °C was shown in Figure 2. The amount of CO
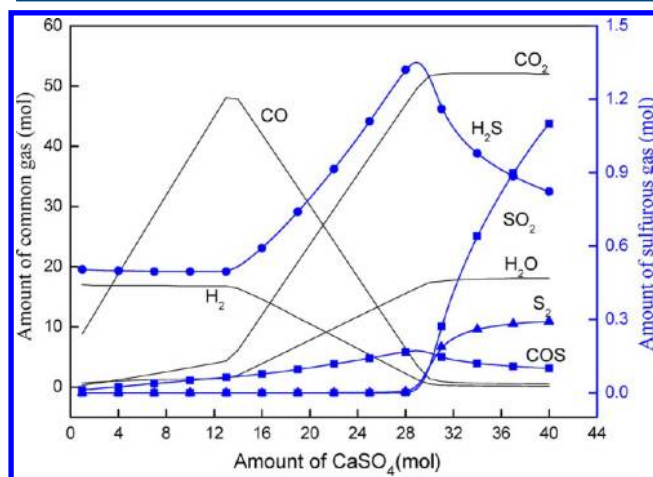

Figure 2. The effect of the amount of $CaSO_4$ on the gas species amount at 900 °C.

37 mols with the temperature increasing between 600 and 710 °C and then slightly after 710 °C, while the amount of CO_2 decreased rapidly before 710 °C and finally decreased slightly after 710 °C with the temperature increasing. It indicated that the high temperature is in favor of the reaction R2 to produce CO. Due to the low content of hydrogen in coal, the amount of H_2 and H_2O was at a relatively stable level compared with CO. Moreover, the equilibrium amount of various sulfurous gases

increased with the amount of $CaSO_4$ increasing until a peak value 47.1 mols, where the amount of $CaSO_4$ was 13.4 mols, subsequently decreased with the amount of $CaSO_4$ increasing until the amount of $CaSO_4$ equals 29.1 mols. Meanwhile, the amount of H_2, H_2O, and CO_2 changed slightly before the amount of $CaSO_4$ equals 13.4 mols. After that, the amounts of CO_2 changed in the opposite trend of CO. A maximum value of

CO corresponds with approximately the value of $CaSO_4$-to-coal mass ratio of 2.29:1, while 30.4 mols of $CaSO_4$ is the counterpart of 4.13:1 $CaSO_4$-to-coal mass ratio. Figure 2 also described the change of the sulfurous gas with the amount of $CaSO_4$ increasing. With the $CaSO_4$-to-coal mass ratio between 2.29 and 4.31, the amount of H_2S increased with an increasing $CaSO_4$-to-coal mass ratio, which was mainly due to side reaction R10. The decreasing H_2 can verify this phenomenon. When $CaSO_4$-to-coal mass ratio is higher than 4.13:1, the amount of H_2S decreased while the amount of SO_2 increased rapidly with the $CaSO_4$-to-coal mass ratio increasing. The possible reason is that the decomposition reactions R11 and R12 of the $CaSO_4$ are dominated with the increasing of $CaSO_4$.

3.2. Results of Thermogravimetric Experiments. To investigate the reaction mechanism of coal with $CaSO_4$ in the CO_2 atmosphere, the baseline experiments of coal pyrolysis in the inert atmosphere and coal gasification using CO_2 as gasification agent without oxygen carrier were carried out in the TGA. The mass loss and mass loss rate of the Shenmu coal as a function of temperature in N_2 and CO_2 atmospheres respectively were illustrated in Figure 3. There existed two
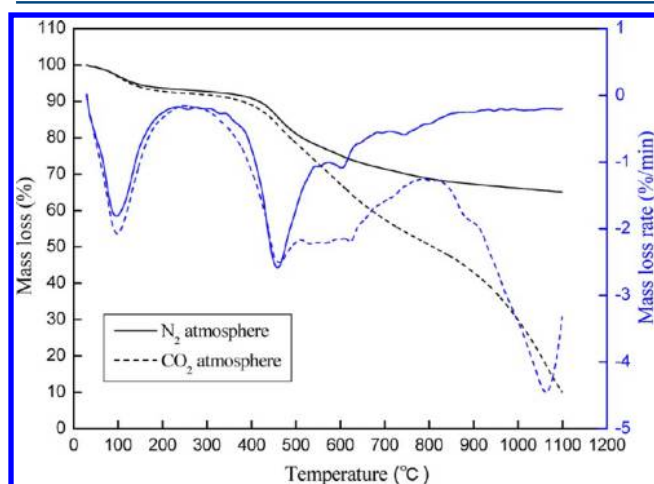

Figure 3. TG and DTG curves of coal in the N_2 and CO_2 atmospheres respectively.

mass loss peaks at the same temperature under both atmospheres when the temperature was lower than 600 °C. Generally, the mass loss peak at 100 °C mainly ascribes to the loss of moisture in the coal and at 450 °C was due to the coal pyrolysis. However, when the temperature was higher than 600 °C, the mass of coal in the N_2 atmosphere decreased slightly while decreased tremendously in the CO_2 atmosphere with the temperature increasing. A mass loss peak under the CO_2 atmosphere appears at 1050 °C, which ascribed to the gasification reaction R2 of coal char with CO_2 as gasification agent. The initial temperature of gasification reaction was higher than 850 °C. It was found that the mass loss is small when the temperature is higher than 800 °C both in N_2 and CO_2 atmospheres. Thus, the effect of volatiles on the reaction process was ignored.

The experiments of reaction between $CaSO_4$ and coal in the N_2 and CO_2 atmospheres were also conducted. Figure 4 illuminated the mass loss and mass loss rate of the mixture varied with the temperature. The mass loss curve of the mixture in both N_2 and CO_2 atmospheres shared the same rule when the temperature was lower than 850 °C. Similarly, the mass loss
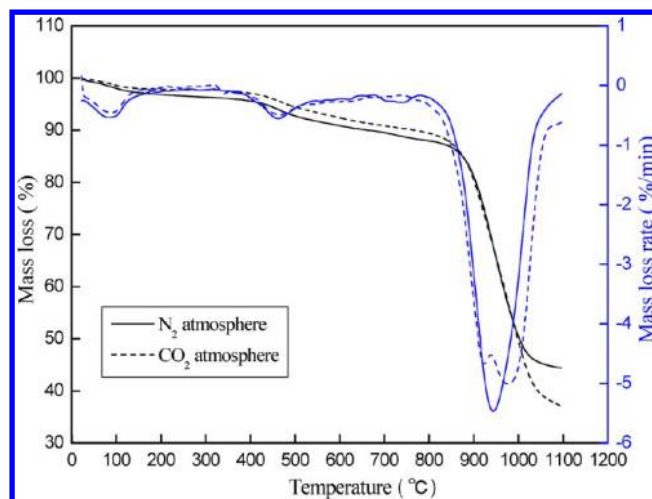

Figure 4. TG and DTG curves of reaction between $CaSO_4$ and coal with the mass ratio 2.29:1 in the N_2 and CO_2 atmospheres respectively.

peak at 100 and 450 °C was the peak of drying and pyrolysis of coal respectively. When the temperature was higher than 850 °C, the mass of the mixture decreased significantly with the temperature increasing, and the mass of mixture decreased slightly with the temperature higher than 1080 °C. Nevertheless, the mass loss rate curve under the CO_2 atmosphere was different from that under the N_2 atmosphere when the temperature exceeds higher than 850 °C. It is presented that the DTG curve under the CO_2 atmosphere contains two obvious down peaks, while the curve under the N_2 atmosphere contains a single down peak, which indicated that complex reactions occurred. The mass loss in the CO_2 atmosphere was also higher than that in the N_2 atmosphere. It ascribes the incomplete solid−solid reaction between $CaSO_4$ and coal in the N_2 atmosphere and the gas−solid reactions R5−R7 between the gasification product CO and $CaSO_4$ can promote solid−solid the reaction in the CO_2 atmosphere.

Emission gas from TGA was analyzed using a gas chromatograph analyzer (PE Clarus 500). The concentration based on the N_2-free normalization method is depicted in Figure 5a. The generation gases before 700 °C are due to mainly the pyrolysis of coal on the basis of a thermogravimetric curve in Figure 3. The concentration of CO increased with the temperature of 700−800 °C is mainly due to the reaction between $CaSO_4$ and coal char. After 880 °C, the concentration of CO decreased sharply was caused by mainly the reaction R5 between CO and $CaSO_4$ to produce CO_2. However, sulfurous gas was hardly detected in the emission gas in the N_2 atmosphere, while the concentration of sulfurous gas COS increased sharply when the temperature is higher than 950 °C in the CO_2 atmosphere (see Figure 5b). The main reason for no other sulfurous gas species may be that the concentration of those gases was diluted by the inert purge gas too small to be detected by the gas chromatograph analyzer. Nevertheless, detection of sulfurous gas COS indicates that the existence of CO_2 can promote the generation of sulfurous gas COS. The deep mechanism of sulfurous gas release should be investigated in the future.

3.3. Analysis of the Complex Reactions. To investigate the complex reaction between $CaSO_4$ and coal char in the CO_2 atmosphere mentioned above, the thermogravimetric experiments of the same mass of mixture with different $CaSO_4$-to-coal
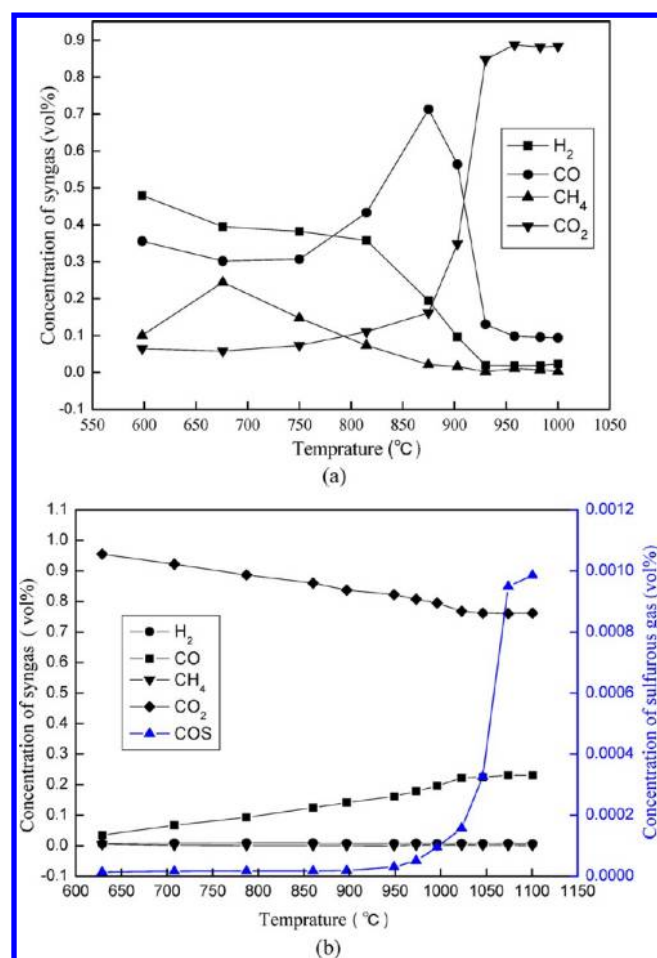
Figure 5. Concentration of production gas varied with temperature at the mass ratio 2.29:1: in the N_2 (a) and CO_2 (b) atmospheres respectively.

mass ratio at the heating rate of 15 K/min were carried out. Three $CaSO_4$-to-coal mass ratios, 4.13:1, 3:1, and 2.29:1, were selected according to the discussion in section 2.2. As Figure 6 illustrated, the mass loss and mass loss rate of the two ratios were different from each other when the temperature was higher than 800 °C. The initial temperature of dramatic
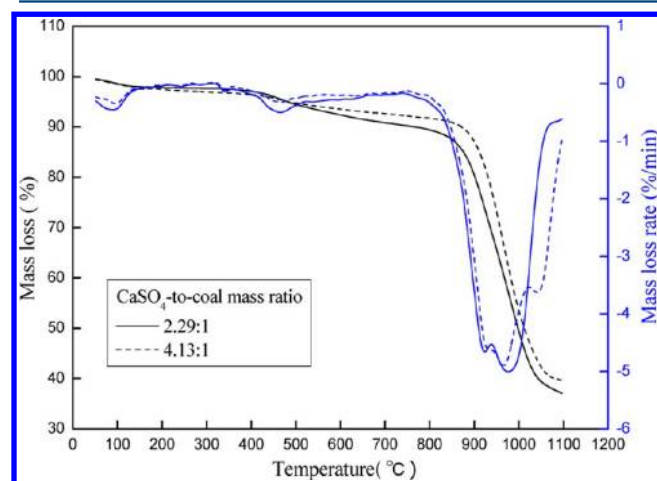

Figure 6. TG and DTG curves of reaction between $CaSO_4$ and coal with different mass ratio in the CO_2 atmosphere.

reaction of the sample with the mass ratio 4.13:1 was 860 °C, while the mass ratio of 2.29:1 changed to 820 °C. It is slightly lower with decreasing $CaSO_4$-to-coals mass ratio, indicating that the amount of $CaSO_4$ restrains the reaction between the coal and oxygen carrier to some extent. There were three DTG down peaks at 932, 966, and 1039 °C, while there were two DTG down peaks at 921 and 977 °C when $CaSO_4$-to-coal mass ratio was 2.29:1 and 4.13:1 respectively.

Considering the reactions between the $CaSO_4$ and coal, the DTG curve might be the superposition of the several mass loss peaks of the different reactions at different temperature. Hence, the peak fitting method was used to handle with the complex DTG curves with Gaussian function selected as the peak function type for the peak fitting method. As shown in Figure 7, the peak fitting of DTG curves with a different mass ratio in N_2 and CO_2 atmospheres was carried out for the determination of the reaction at the specified temperature. When the $CaSO_4$-to-coal mass ratio was 2.29:1, the lattice oxygen from $CaSO_4$ was insufficient for combustion of the coal. The fitting peak α at 950 °C might be the reaction between $CaSO_4$ and coal char (i.e., reaction R3 and/or R4 mainly), while the fitting peak β at 1000 °C might be the gasification of coal char using CO_2 (i.e., reaction R2 mainly). Figure 3 demonstrates that the existence of an oxygen carrier can promote the gasification reaction. From Figure 7A and B, it can be concluded that both the reaction between $CaSO_4$ and coal char and gasification reaction of coal char using CO_2 occurred in both N_2 and CO_2 atmospheres. The CO_2 for coal char gasification in the N_2 atmosphere came from the reaction R4. When the $CaSO_4$-to-coal mass ratio was 3.00:1, the gasification peak of coal char in the N_2 atmosphere disappeared, and even the rate of gasification reaction was small in the CO_2 atmosphere, which predicted that the solid−solid reaction R3 and/or R4 between $CaSO_4$ and coal char was the main reaction and the solid product restrained the further reaction. Another fitting peak γ at 1050 °C displays the reductive decomposition of $CaSO_4$. The temperature of reductive decomposition agreed with the literature.[23] When the $CaSO_4$-to-coal mass ratio was 4.13:1, the lattice oxygen from $CaSO_4$ was sufficient for combustion of the coal. However, reductive decomposition reaction of $CaSO_4$ took place obviously when the temperature is higher than 1000 °C. It can be concluded that the rate of reductive decomposition reaction increased with the $CaSO_4$-to-coal mass ratio increasing. Summarized from the six conditions in Figure 7, one can find that direct solid−solid reaction between $CaSO_4$ with coal occurred if sufficient contacts are made between the oxygen carrier and the solid fuel can be obtained. In summary, complex reactions between $CaSO_4$ and coal char were mainly divided into three dominant stages during 800− 1100 °C: the reactions between $CaSO_4$ and coal char, the gasification of coal char, and the decomposition of $CaSO_4$.

3.4. Kinetic Analysis. To investigate into the reaction mechanism of syngas production from the chemical looping process, the thermogravimetric experiments of the mixture of $CaSO_4$ oxygen carrier and coal with its mass ratio of 2.29:1 in the CO_2 atmosphere were carried out at five heating rates, 5 K, 10 K, 15 K, 20 K, and 25 K/min respectively. As Figure 8 illustrated, the initial temperature of mass loss of the mixture increased from 825 to 865 °C with the heating rate increasing from 5 K/min to 25 K/min. The lower heating rate can reduce the initial reaction temperature. According to the Flynn-Wall-Ozawa (FWO) multiheating rate methods, the logarithm of heat rate log β is in proportion to $1/T$ when the degree of
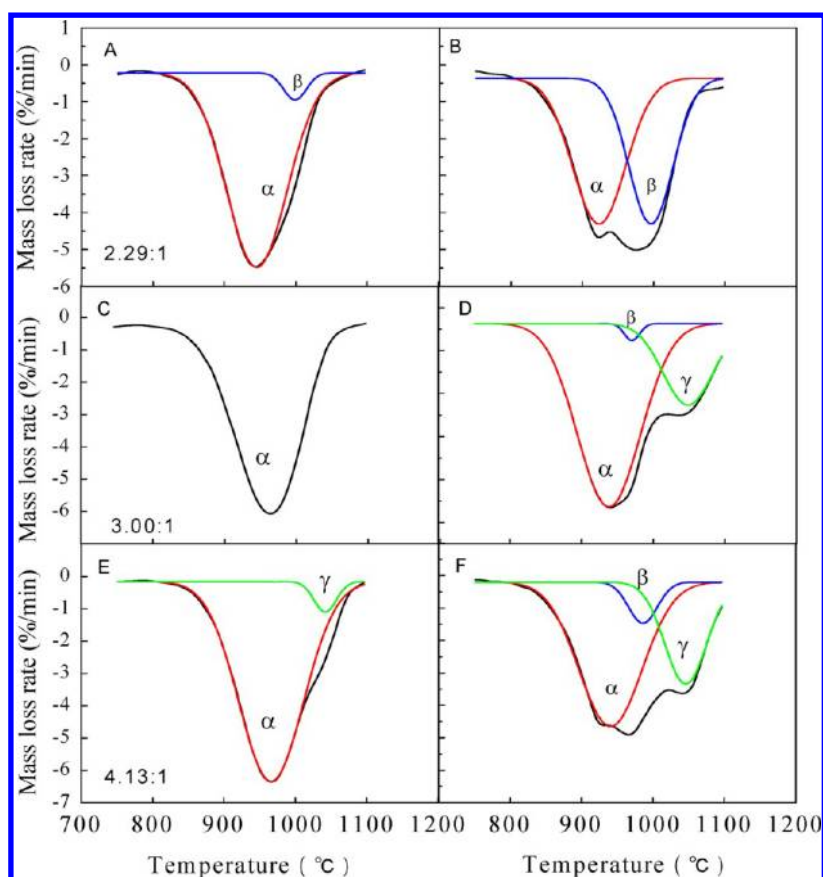
Figure 7. The peak fitting of DTG curves with different mass ratio in the N_2 or CO_2 atmosphere: A, C, and E − N_2 atmosphere; B, D, and F − CO_2 atmosphere; A, B − 2.29:1; C, D − 3.00:1; E, F − 4.13:1.
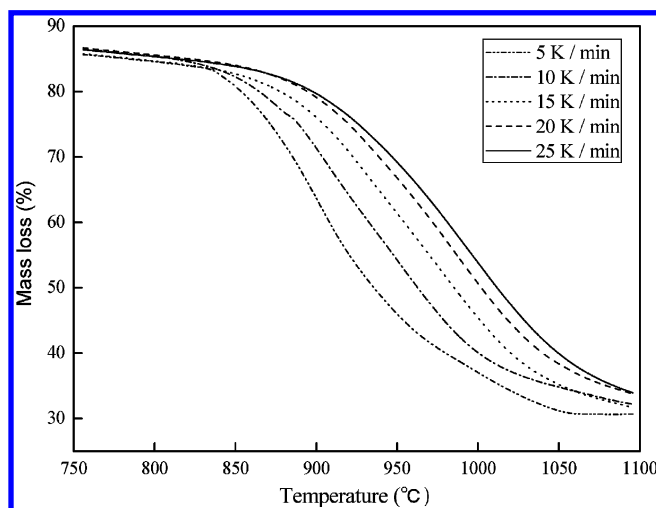

Figure 8. TG curves of $CaSO_4$ and coal with its mass ratio 2.29:1 in the CO_2 atmosphere at five heating rate.

Figure 9. The $\log\beta$ as the function of 1000/T at ten degrees of conversion α.

conversion α is confirmed. Figure 9 showed the $\log\beta$ versus 1000/T at ten degrees of conversion α. The activation energy at the ten degrees of conversion can be obtained by linear fitting.

The activation energy at the given conversion degree α and the corresponding temperature for the conversion degree at the heating rate 15 K/min was presented in Figure 10. It demonstrated that the activation energy decreased with the activation energy increasing before α = 0.65 while increasing in
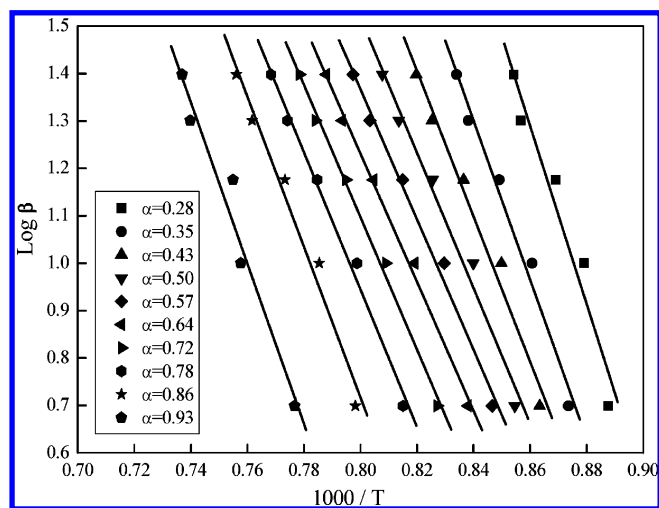
dependencies of activation energy after α = 0.65. Further, complex reactions with a change in limiting stage occurred before α = 0.65, while simultaneous/parallel reactions took place after α = 0.65 according to the mentioned literature above.[21,22] The corresponding temperature for the conversion degree α = 0.65 at the heating rate 15 K/min was higher than 950 °C, which can be inferred that the limiting stage of the reaction between $CaSO_4$ and coal char may be the change over from kinetic to the diffusion regime due to the solid−solid reaction feature that the solid product prevents the advanced
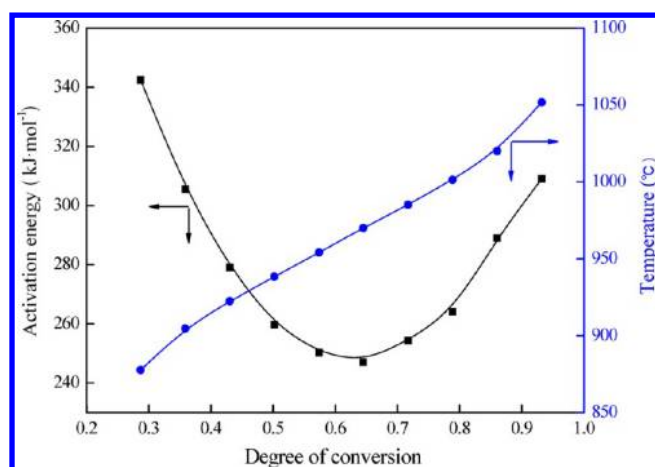
Figure 10. The activation energy as the function of conversion degree and the corresponding temperature for the conversion degree at the heating rate 15 K/min.

reaction. At the conversion degree above 0.65, the simultaneous/parallel reactions included the gasification of the coal char and the reductive decomposition of $CaSO_4$. The decomposition reaction included not only the main reaction R5 for the chemical looping process but also the side reaction for generation of sulfurous gas, especially COS with a $CaSO_4$-to-coal mass ratio of 2.29:1 in the CO_2 atmosphere.

3.5. SEM-EDS Analysis. SEM images of the reacted mixture of both $CaSO_4$-to-coal mass ratios in N_2/CO_2 atmospheres were illustrated in Figure 11. The magnification of the images was 50000×. When lattice oxygen supported by

$CaSO_4$ was insufficient for complete combustion, the mass amount of coal was relatively more. As illustrated in Figure 11A and B, surfaces of the residues clearly were glossy in both N_2 and CO_2 atmospheres. The cause may be the agglomeration of melted oxygen carrier on the ash and unreacted coal char, which would prevent further reaction between $CaSO_4$ and coal in the N_2 atmosphere. However, no porous structure and serious sintering was observed in the CO_2 atmosphere, because the ash would shrink after the gasification of coal char and the melted oxygen carrier agglomerated on the ash. This can be explained by the mass loss rate fitting peaks in Figure 7A and 7B. The gasification of coal char was observed obviously in the CO_2 atmosphere while not in the N_2 atmosphere. When the ratio of $CaSO_4$ in the mixture was 4.13:1, the surface of the residue was rough compared with the mass ratio 2.29:1. The mass amount of coal is relatively less and the coal particle distributed on the $CaSO_4$ particles. Different from the surface of the residue in Figure 11A, agglomeration occurred due to the block of the coal ash on the pore structure of $CaSO_4$ in the N_2 atmosphere. However, agglomerates are featured by more porous structure in the CO_2 atmosphere, where loose coal ash coated on the $CaSO_4$ particle would explain it.

The atomic percent-based composition of the main element after normalization was obtained from point scanning of EDS spectrum for the reacted particles. As Table 2 showed, the considered species were calcium, sulfur, oxygen, and carbon with the trace element in coal ash ignored. The carbon element came from unreacted coal char, while the other three elements came from three solid residues: unreacted $CaSO_4$, CaS, and CaO mainly. The qualitative analysis of every species in the mixture residue can be obtained. Analyzing the element carbon
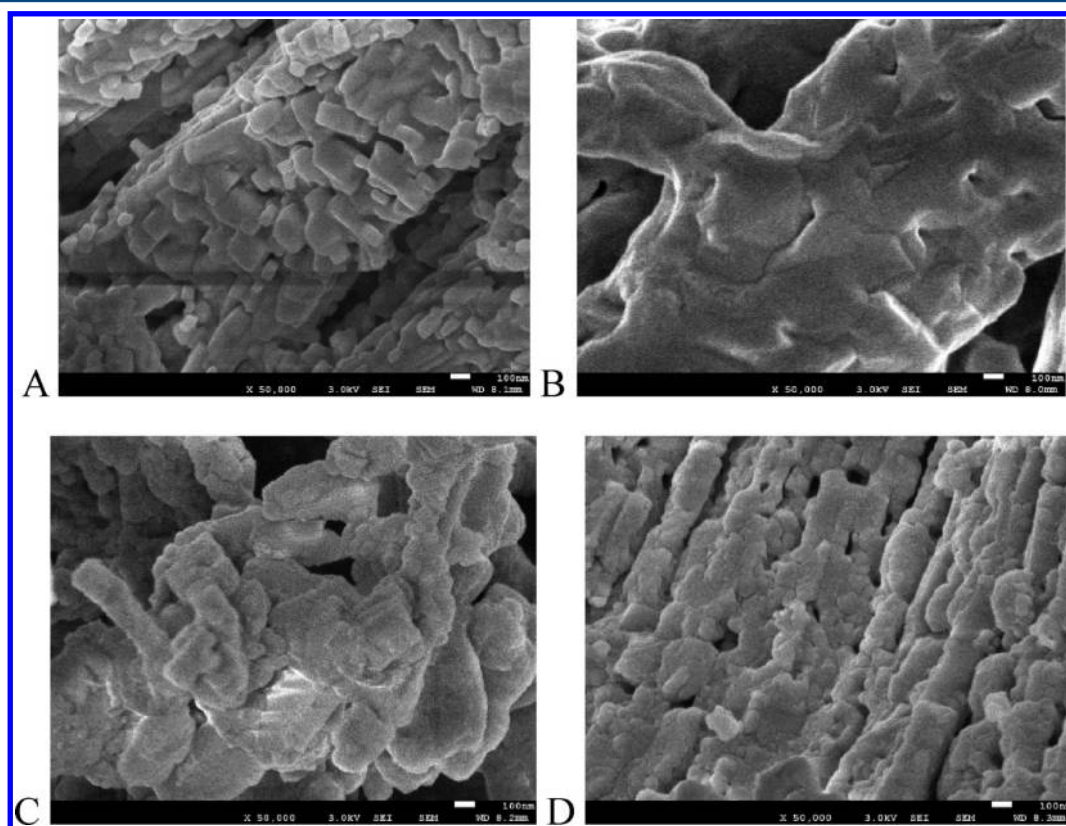

Figure 11. SEM images after reaction between $CaSO_4$ and coal at the heating rate of 15 K/min with different mass ratios in N_2/CO_2 atmospheres (A, B − 2.29:1; C, D − 4.13:1; A, C − N_2 atmosphere; B, D − CO_2 atmosphere).

Table 2. Element Composition of Residues Based Atomic Percent

sample	C %	O %	S %	Ca %
A	12.83	26.12	29.83	31.21
B	9.02	44.69	15.67	30.63
C	15.45	15.33	34.11	35.12
D	11.75	34.07	21.17	33.01

composition in all four samples, it can be verified that the gasification of coal in the CO_2 atmosphere was carried out with less carbon element left in residues in both $CaSO_4$-to-coal mass ratio. Calcium element was at the same concentration proximately, due to the calcium left in solid residues, $CaSO_4$, CaS, and CaO. The sulfur element existed in solid residues mainly in the form of desired CaS and unreacted $CaSO_4$. A decrease of sulfur element can predict the occurrence of undesired reaction generating sulfurous gas, moreover, the decrease amount of sulfur element in the CO_2 atmosphere was more than in the N_2 atmosphere, which denotes that more of the sulfurous gases generated in the CO_2 atmosphere, which is consistent with emission gas discussion in the preceding part of the text which also confirmed this result. Combined with the analysis of complex reactions in section 3.3, it also can be inferred that CO from coal gasification promoted obviously the side reactions generating sulfurous gas by the existence of CO_2 with the temperature higher than 950 °C.

4. CONCLUSIONS

Based on the thermodynamic analysis and experiments in TGA, the following conclusions of the chemical looping process for syngas generation in the CO_2 atmosphere can be obtained,

1) The existence of CO_2 can promote the reaction between $CaSO_4$ and coal, and the main sulfurous species were COS and H_2S. The higher temperature resulted in the generation of sulfurous species. The optimal temperature of chemical looping process for syngas generation might be from 850 to 950 °C.

2) Complex reactions of mixture in the CO_2 atmosphere were mainly divided into three dominant stages with the temperature increasing from 800 to 1100 °C, the reaction between $CaSO_4$ and coal char, the gasification of coal char, and the decomposition of $CaSO_4$. In the chemical looping process for syngas generation, it was a change in limiting stage from kinetic to the diffusion regime before $\alpha = 0.65$, due to the solid−solid reaction feature, while simultaneous/parallel reactions included the gasification of the coal char and the reductive decomposition of $CaSO_4$ took place with the conversion degree bigger than 0.65.

3) The reaction of $CaSO_4$ and coal was carried out through the solid−solid reaction between $CaSO_4$ and coal directly when the temperature was lower than 900 °C, while mainly through indirect reaction with gaseous from coal gasification with CO_2 at the higher temperature than 900 °C.

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Notes
The authors declare no competing financial interest.

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