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Kinetic model for calcium sulfate decomposition at high temperature

Zhi-giang YAN, Ze-an WANG, Xiao-feng WANG, Hao LIU, Jian-rong QIU

State Key laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China

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Abstract: A modified shrinking unreacted-core model, based on thermogravimetric analysis, was developed to investigate $CaSO_4$ decomposition in oxy-fuel combustion, especially under isothermal condition which is difficult to achieve in actual experiments due to high-temperature corrosion. A method was proposed to calculate the reaction rate constant for CaSO₄ decomposition. Meanwhile, the diffusion of SO₂ and O₂, and the sintering of CaO were fully considered during the development of model. The results indicate that the model can precisely predict the decomposition of $CaSO_4$ under high SO_2 concentration (>1100×10⁻⁶). Concentrations of SO_2 and O_2 on the unreacted-core surface were found to increase first and then decrease with increasing temperature, and the average specific surface area and porosity of each CaO sintering layer decreased with increasing time. The increase of SO₂ and/or O₂ concentration inhibited CaSO4 decomposition. Moreover, the kinetics of CaSO4 decomposition had obvious dependence on temperature and the decomposition rate can be dramatically accelerated with increasing temperature.

Key words: oxy-fuel combustion; shrinking unreacted-core model; CaSO₄; decomposition; CaO sintering

1 Introduction

Coal is the most significant energy source in China, and more than 70% of electricity is generated from coal-fired power plants. However, great amounts of air pollutants, including sulfur oxides (SO_x), nitrogen oxides (NO_x) , CO_2 , trace metals etc., are released along with the coal combustion. Since 2002, emissions from large industrial facilities have been strictly regulated by Chinese government. Simultaneously, a much more stringent regulation was issued by the National Environmental Protection Agency in 2013 [1].

Oxy-fuel combustion is one of the new promising technologies that mitigate the effect of CO₂ on climate change and meanwhile could reduce the emissions of NO and SO_2 [2–4]. This process uses oxygen mixed with recycled flue gas instead of air to support combustion, while only a small fraction of total flue gas is exhausted. In an oxy-fuel combustion system, SO_2 is enriched in furnace owing to the recirculation of flue gas, which provides a good sulfation condition [5]. Furthermore, in contrast with conventional air combustion, the sulfur retention efficiency by calcium-based sorbents is enhanced remarkably during oxy-fuel combustion because of the two types of sulfation mechanism: direct sulfation in Eq. (1) as well as indirect sulfation in Eq. (2) [3,5]. Hence, flue gas desulfurization can be substituted with more cost-effective in-furnace calciumbased sorbents injection technology in order to ensure the low SO₂ emission.

$$CaCO_3 + SO_2 + 1/2O_2 \longrightarrow CaSO_4 + CO_2$$
(1)

 $CaCO_3 \rightarrow CaO + CO_2$

$$CaO+SO_2+1/2O_2 \longrightarrow CaSO_4 \tag{2}$$

$$CaSO_4 \longrightarrow CaO + SO_2 + 1/2O_2 \tag{3}$$

Notably, the decomposition of desulfurization product, CaSO₄, may cause secondary release of SO₂ in furnace, as described in Eq. (3), and the corresponding decomposition mechanism under various conditions has been explored in recent years [3,6-15]. Thermal gravimetric analysis (TGA) has been widely used to investigate the decomposition behaviors of CaSO₄ in O_2/N_2 , O_2/CO_2 or other reducing atmospheres [7,9,11], meanwhile, some simplified kinetic models have been developed to study the mechanism of CaSO₄ decomposition in the presence of O_2 and SO_2 [15,16], as well as the mechanism of CaSO₄ reductive decomposition by methane, hydrogen and carbon monoxide [6,8,11].

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At high temperature with high SO_2 concentration, however, experimental methods suffer from many drawbacks due to stringent reaction conditions, i.e., serious instrument damage by highly corrosive SO_2 , while numerical simulation provides a viable method to explore the decomposition behavior of CaSO₄ [6,7, 17–19]. Nevertheless, the sintering of decomposition product CaO, which performs a significant role in the decomposition process [14], is always ignored when the model was developed [15,16].

In this work, a modified shrinking unreacted-core model was established to investigate the decomposition of $CaSO_4$ under temperature programmed and isothermal condition. In order to improve the accuracy of the model, temperature, diffusion behaviors of SO_2 and O_2 , as well as the sintering kinetics of CaO were fully considered. Based on the model, the conversion ratio of $CaSO_4$ was determined under various conditions, and the effects of temperature and concentrations of SO_2 and O_2 on the decomposition of $CaSO_4$ were discussed. Moreover, the average specific surface area and porosity were respectively determined to explore the sintering kinetics of CaO.

2 Model development

2.1 Decomposition model of CaSO₄

Figure 1 gives the schematic model of $CaSO_4$ decomposition at high temperature. The model is based on the unreacted shrinking core [20], which assumes that the thermal decomposition of $CaSO_4$ occurs at an explicit chemical interface, i.e., the unreacted core surface. At the reaction interface, no decomposition of $CaSO_4$ happens, while outside the interface, a product layer of CaO is generated from the decomposition of $CaSO_4$. The gasous products, SO_2 and O_2 , diffuse through the pores of the CaO layer. At the same time, the newly-formed CaO layer sinters gradually with the increasing temperature.



Fig. 1 Schematic model of CaSO₄ decomposition at high temperature

The following assumptions are made when the model of $CaSO_4$ decomposition is developed.

1) Sintering decreases the specific surface area and the average pore size of decomposition product CaO at high temperature.

2) The decomposition of $CaSO_4$ only occurs at the interface of unreacted core.

3) The spherical particles of $CaSO_4$ keep the same during the reaction process.

4) The particle temperature is the same as the ambient temperature.

5) The concentration of CO_2 in atmosphere is fixed and its effect on $CaSO_4$ decomposition is ignored.

6) The decomposition of $CaSO_4$ is based on the quasi-steady-state assumption, which means that the partial derivative of time in differential equations is zero.

7) During $CaSO_4$ decomposition, the product layers of CaO are generated one by one, and each specified layer has constant physical properties.

The conversion ratio is defined to describe the decomposition progress, which can be calculated according to the following equation:

$$X = \frac{m - m_0}{m_0} \left/ \left(\frac{M_{\text{CaO}} - M_{\text{CaSO}_4}}{M_{\text{CaSO}_4}} \right)$$
(4)

where *m* and m_0 indicate the instant sample mass during experiment and the initial sample mass, respectively; and M_{CaO} and M_{CaSO_4} represent the relative molecular mass of CaO and CaSO₄, respectively.

2.1.1 Reaction kinetics

The decomposition reaction kinetics can be described as the following equation:

$$\frac{dr_{\rm c}}{dt} = -k_{\rm c} V_{\rm CaSO4} f(p_{\rm SO_2}, p_{\rm O_2})$$
(5)

where r_c is the unreacted core radius of CaSO₄; *t* stands for the reaction time; k_c represents the decomposition reaction rate constant; V_{CaSO_4} is the molar volume of CaSO₄; and $f(p_{SO_2}, p_{O_2})$ is the function of SO₂ and O₂ partial pressure, and can be calculated according to Eq. (6).

$$f(p_{SO_2}, p_{O_2}) = (1 - p_{c,SO_2} p_{c,O_2}^{0.5} / p_e) \exp(-ap_{b,SO_2}) \exp(-bp_{b,O_2})$$
(6)

where p_{c,SO_2} , and p_{c,O_2} are the partial pressures of SO₂ and O₂ at the CaO–CaSO₄ interface, respectively; p_e is the equilibrium partial pressure of SO₂ and O₂, which can be calculated by $p_e=(exp29.297)exp(-54865/T)$; p_{b,SO_2} and p_{b,O_2} are the partial pressures of SO₂ and O₂ in the reaction atmosphere, respectively; *a* and *b* are constants to be determined.

The decomposition reaction rate is shown in Eq. (7), which can be transformed to Eq. (8) by dividing

 $4/3\pi r_{\rm c}^{3}\rho$:

$$W = k_{\rm c} A f(p_{\rm SO_2}, p_{\rm O_2})$$
(7)

$$\frac{W}{\frac{4}{3}\pi r_{\rm c}^{3}\rho} = \frac{k_{\rm c}}{\frac{1}{3}r_{\rm c}\rho}f(p_{\rm SO_{2}}, p_{\rm O_{2}}) \tag{8}$$

where W is the reaction rate; A represents the surface area of unreacted core; ρ is the density of CaSO₄. Thus, the conversion ratio can be expressed as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{k_{\rm c}}{\frac{1}{3}r_{\rm c}\rho}f(p_{\rm SO_2}, p_{\rm O_2}) \tag{9}$$

where α stands for the transformation rate of CaSO₄ to CaO. At the initial stage of decomposition, the CaO layer is pretty thin, so the diffusion of SO₂ and O₂ can be ignored. Consequently, the gases own the same partial pressure on the unreacted-core surface and in the environment. According to the shrinking unreacted-core model, the kinetic mechanism function for CaSO₄ decomposition is $2(1-\alpha)^{2/3}$, and then

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = 3k_{\mathrm{c}}'(1-\alpha)^{\frac{2}{3}} \tag{10}$$

where $k'_{\rm c}$ is the constant reaction rate. If the decomposition is carried out in an inert atmosphere, $f(p_{\rm SO_2}, p_{\rm O_2})$ is approximately 1 at the initial stage. Then, the following equation can be deduced from Eqs. (9) and (10):

$$k_{\rm c} = k_{\rm c}' r_{\rm c} \rho \tag{11}$$

If k'_{c} follows the Arrhenius law, then

$$k_{\rm c}' = a_{\rm c} \exp(-\frac{E_{\rm c}}{RT}) \tag{12}$$

where a_c is the pre-exponential factor; E_c is the activation energy; R is the mole gas constant and T is the reaction temperature.

Figure 2 shows the fitting line for $CaSO_4$ decomposition according to experimental data in argon atmosphere [21], therefore, k'_c can be expressed as the function of temperature:

$$k'_{\rm c} = \frac{1}{3} \exp(36.188) \exp(-70012/T)$$
 (13)

Thus, k_c can be calculated based on Eq. (11).

2.1.2 Mass transfer

For spherical particles, the mass transfer equation is

$$\frac{\partial^2 p}{\partial r^2} + \left(\frac{2}{r} + \frac{1}{D_e}\frac{\partial D_e}{\partial r}\right)\frac{\partial p}{\partial r} = \frac{1}{D_e}\frac{\partial p}{\partial t}$$
(14)

where r is the radius, p is the system pressure. The boundary conditions are



Fig. 2 Linear fitting for $CaSO_4$ decomposition in argon atmosphere

$$p=p_{\rm b}, \ r=r_0 \tag{15}$$

$$-\frac{nD_{\rm e}}{RT}\frac{\partial p}{\partial r} = k_{\rm c}f(p_{\rm SO_2}, p_{\rm O_2}), r = r_{\rm c}$$
(16)

where n=1 for SO₂, and n=2 for O₂. The mass transfer outside the particle surface is ignored. For small particles, the gas concentration on the particle surface can be approximately equal to that in the atmosphere [22].

The effective gas diffusion coefficient (D_e) inside the particle can be calculated as follows [23]:

$$D_{\rm g} = D_{\rm g} \, \varepsilon^2$$
 (17)

where ε is the porosity of decomposition product CaO; and $D_{\rm g}$ is the gas diffusion coefficient in the following equation:

$$D_{\rm g} = (D_{\rm mol}^{-1} + D_{\rm kn}^{-1})^{-1}$$
(18)

 $D_{\rm mol}$ and $D_{\rm kn}$ can be respectively determined by [24]

$$D_{\rm mol} = \frac{1 \times 10^{-7} T^{1.75} (M_{\rm A}^{-1} + M_{\rm B}^{-1})^{0.5}}{p (V_{\rm A}^{1/3} + V_{\rm B}^{1/3})^2}$$
(19)

$$D_{\rm kn} = 97r_{\rm av} \left(\frac{T}{M}\right)^{0.5} \tag{20}$$

where M_A and M_B stand for relative molecular mass of gases A and B, respectively; V_A and V_B are respectively liquid molecular volumes of A and B under normal boiling point; M denotes the relative molecular mass of gas O₂ or SO₂. The liquid molar volumes of air, CO₂, SO₂ and O₂ are 29.9, 34.0, 44.8 and 25.6 m³/kmol, respectively.

2.1.3 Sintering of CaO

So far, rare research has been carried out on the properties of sintered CaO from $CaSO_4$ decomposition at high temperature. In this work, the decomposition of $CaSO_4$ is considered to be similar to that of limestone, and hence, the sintering behavior of $CaSO_4$

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decomposition product was investigated based on the chracteristics of sintered CaO from limestone calcination.

During limestone calcination, the decomposition product layer would garadually occupy the volume of limestone particles, and the decomposition product layer would possess the largest specific surface area and the highest porosity without the sintering of CaO [25]. However, the specific surface area of CaO is influenced by the sintering process. The sintering rate follows the second-order reaction dynamics [26], and the relationship bwtween sintering rate and time can be expressed as

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -k_{\mathrm{sin}} \left(S - S_{\mathrm{a}}\right)^2 \tag{21}$$

where *S* is the specific surface area of CaO at time *t*; S_a , also known as asymptotic surface area, denotes the specific surface area of CaO at infinite time; k_{sin} , the sintering rate constant, can be calculated from Eq. (22) [27]:

$$k_{\rm sin} = 0.286 \exp(14500/T) \tag{22}$$

It can be found that the change of porosity is proportional to the change of specific surface area [22,26]. The porosity is colse to zero when the specific surface area reaches critical value S_a ($S_a=5 \text{ m}^2/\text{g}$ when temperature is over 1200 K). The relationship between porosity and specific surface area can be obtained:

$$\varepsilon = \varepsilon_0 \left(\frac{S - S_a}{S_0 - S_a} \right) \tag{23}$$

where ε_0 is the initial porosity of decomposition product CaO (ε_0 =0.54 for the initial porosity of CaO from CaCO₃ decomposition) [25]; S_0 represents the initial specific surface area of CaO, 104 m²/g [25].

It is supposed that CaO from $CaSO_4$ decomposition occupies the volume of $CaSO_4$ particles in the non-sintering situation, and the initial porosity of CaO from $CaSO_4$ decomposition can be calculated according to the molar volumes of $CaSO_4$ and CaO. At high temperature, the molar volume ratio of $CaSO_4$ to CaO is 2.72 [25]. Hence, the initial porosity of CaO from $CaSO_4$ decomposition is

$$\varepsilon_0 = (2.72 - 1)/2.72 = 0.63$$
 (24)

The average pore diameter of CaO from $CaSO_4$ decomposition can be considered to be similar with that from limestone calcination. Then, the initial specific surface area of CaO from $CaSO_4$ decomposition should be:

$$S_0 = 104 \times 0.63 / 0.54 = 121.33 \text{ m}^2/\text{g}$$
 (25)

2.2 Model solution

In our calculation, the time interval Δt was set as

10 s. The physical properties were assumed to be constant, while the thickness of CaO layer varied in different time intervals, as shown in Fig. 3.



Fig. 3 Solution procedure of model

During temperautre programmed process, CaSO₄ starts to decompose when $p_{c,SO_2} p_{c,O_2}^{0.5} < p_e$ (p_e is the equilibrium partial pressure). In each calculation, the outermost CaSO₄ layer, namely the surface of unreacted core, decomposes into CaO. Every specific CaO layer has different sintering time and thicknesses, while posseses the same physical properties such as the average porosity, pore diameter and specific surface area. Before next iteration, the average porosity ($\bar{\varepsilon}$), pore diameter (r_{av}) and specific surface area of CaO (\bar{S}) must be updated according to the following equations:

$$\overline{S} = \sum_{i=1}^{N} S_i f_{\mathrm{V},i} \tag{26}$$

$$S_i^m = S_i^{m-1} - k_{\sin} (S_i^{m-1} - S_a)^2 \Delta t$$
(27)

$$\overline{\varepsilon} = \sum_{i=1}^{N} \varepsilon_i f_{\mathrm{V},i} \tag{28}$$

$$r_{\rm av} = \frac{2\overline{\varepsilon}}{\overline{S}\rho_{\rm CaO}(1-\overline{\varepsilon})}$$
(29)

where $\overline{\varepsilon}$, S_i and $f_{V,i}$ are the average porosity, specific surface area and volume proportion at the *i*th product layer; ρ_{CaO} is the density of product layer; m-1 denotes the (m-1)th calculation. The conversion ratio of CaO from CaSO₄ decomposition is

$$\alpha = 1 - (r_c/r_0)^3 \tag{30}$$

According to the quasi-steady-state assumption, the effective diffusion coefficient of CaO layers, D_{e} , is a constant, and thus Eq. (14) can be simplified as follows:

$$\frac{\mathrm{d}^2 p}{\mathrm{d}r^2} + \frac{2\mathrm{d}p}{r\mathrm{d}r} = 0 \tag{31}$$

The solution of Eq. (31) is

$$p_{\rm SO_2} = -\frac{A_1}{r} + B_1 \tag{32}$$

$$p_{O_2} = -\frac{A_2}{r} + B_2 \tag{33}$$

where A_1 , A_2 , B_1 and B_2 are constants to be determined. For each calculation, the differential equations can be written as

$$\frac{-D_{e,O_{2}}}{RT} \left(\frac{A_{1}}{r_{c}^{2}}\right) = \\
0.5k_{c} \left(1 - \frac{p_{c,SO_{2}}p_{e,O_{2}}^{0.5}}{p_{e}}\right) \exp(-ap_{b,SO_{2}}) \exp(-bp_{b,O_{2}}) \\
\frac{-D_{e,SO_{2}}}{RT} \left(\frac{A_{1}}{r_{c}^{2}}\right) = \\
k_{c} \left(1 - \frac{p_{c,SO_{2}}p_{e,O_{2}}^{0.5}}{p_{e}}\right) \exp(-ap_{b,SO_{2}}) \exp(-bp_{b,O_{2}})$$
(34)

Combining with the boundary conditions, the equations can be solved as

$$\begin{cases} p_{b,SO_2} = -\frac{A_1}{r_0} + B_1, p_{c,SO_2} = -\frac{A_1}{r_c} + B_1 \\ p_{b,O_2} = -\frac{A_2}{r_0} + B_2, p_{c,O_2} = -\frac{A_2}{r_c} + B_2 \end{cases}$$
(35)

From Eq. (35), A_1 , B_1 , A_2 and B_2 can also be expressed as the function of p_{c,SO_2} , p_{b,SO_2} , $p_{,O_2}$ and p_{b,SO_2} :

$$\begin{cases} A_{1} = \frac{p_{b,SO_{2}} - p_{c,SO_{2}}}{1/r_{c} - 1/r_{0}}, B_{1} = \frac{p_{b,SO_{2}}r_{0} - p_{c,SO_{2}}r_{c}}{r_{0} - r_{c}} \\ A_{2} = \frac{p_{b,O_{2}} - p_{c,O_{2}}}{1/r_{c} - 1/r_{0}}, B_{2} = \frac{p_{b,O_{2}}r_{0} - p_{c,O_{2}}r_{c}}{r_{0} - r_{c}} \end{cases}$$
(36)

Comparing the expressions of A_1 and A_2 in Eqs. (34) and (36), the nonlinear equations of p_{c,SO_2} and p_{c,O_2} can be obtained as

$$\begin{cases} \frac{-D_{e,O_2}}{RT} \left(\frac{p_{b,SO_2} - p_{e,SO_2}}{r_e^2 (1/r_e - 1/r_0)} \right) = \\ 0.5k_e \left(1 - \frac{p_{e,SO_2} p_{e,O_2}^{0.5}}{p_e} \right) \exp(-ap_{b,SO_2}) \exp(-bp_{b,O_2}) \\ \frac{-D_{e,SO_2}}{RT} \left(\frac{p_{b,O_2} - p_{e,O_2}}{r_e^2 (1/r_e - 1/r_0)} \right) = \\ k_e \left(1 - \frac{p_{e,SO_2} p_{e,O_2}^{0.5}}{p_e} \right) \exp(-ap_{b,SO_2}) \exp(-bp_{b,O_2}) \end{cases}$$

$$(37)$$

Thus, the numerical solutions are obtained.

3 Results and discussion

3.1 Model validation

The proposed model for decomposition of CaSO₄ is

verified based on the experimental data from TGA experiments under various conditions [21], and constants a and b in Eq. (6) are respectively determined as 250 and 3 after iterative calculations. Figures 4 and 5 show the comparison of experimental data and modeling results at high temperature. It can be easily found that the CaSO₄ conversion ratios exhibit an "S" type curve under temperature programmed condition. To be specific, in the initial stage of decomposition (<1600 K), the gas diffusion rate and chemical reaction rate are slow, while with the rise of temperature, the gas diffusion rate and the chemical reaction rate are boosted, leading to a sharp increase of the conversion ratio. In the final stage (>1750 K), the decomposition rate is kept low due to the shrinking of unreacted core and the sintering of CaO though the chemical reaction rate is the highest. Overall, the model can precisely describe the decomposition behavior of CaSO₄ when the temperature is lower than



Fig. 4 Experimental and simulated conversion curves with various SO_2 initial concentrations (Heating rate: 13 K/min, initial atmosphere: 10% O_2 + 79% CO_2 + balanced Ar, volume fraction)



Fig. 5 Experimental and simulated conversion curves with various O_2 initial concentrations (Heating rate: 13 K/min, initial atmosphere: 1160×10^{-6} SO₂ + 79% CO₂ + balanced Ar, volume fraction)

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1700 K. Simultaneously, with increasing temperature, the modeling results were close to actual data when the concentration of SO_2 or O_2 was high. In particular, the kinetics derived in this work is appropriate for studying the decomposition of CaSO₄ during oxy-fuel combustion because of the enriched SO₂ in flue gas.

3.2 Decomposition of CaSO₄ under temperature programmed condition

Based on the proposed model, the changes of O_2 and SO_2 concentrations on the unreacted core surface are presented in Fig. 6. On the other hand, the variation of the average porosity as well as specific surface area of product layer is shown in Fig. 7. In the initial stage (<1650 K), CaSO₄ starts to decompose and the partial pressures of SO₂ and O₂ increase slowly while steadily. Meanwhile, the sintering of product layer occurs on the unreacted core surface. With the proceeding of decomposition, the concentrations of SO₂ and O₂ experience a sharp increase followed by a rapid drop at



Fig. 6 Partial pressures of SO_2 and O_2 on unreacted core surface (Initial atmosphere: $1160 \times 10^{-6} SO_2 + 20\% O_2 + 79\% CO_2 + balanced Ar)$



Fig. 7 Average pore diameter and average porosity of product layer (Initial atmosphere: $1160 \times 10^{-6} \text{ SO}_2 + 20\% \text{ O}_2 + 79\% \text{ CO}_2$ + balanced Ar)

1785 K. During this process, the average porosity and specific surface area decrease all the time.

3.3 Decomposition of CaSO₄ under isothermal condition

As a matter of fact, it is much more important to investigate the kinetics of $CaSO_4$ decomposition under isothermal condition because $CaSO_4$ particles suffer from the cruel actual conditions, i.e., high temperature and short residence time. Fortunately, the effects of temperature, SO_2 and O_2 concentrations on the $CaSO_4$ decomposition properties can be discussed under isothermal condition according to the proposed model, simultaneously, the average pore size and the average porosity were also studied.

There is no doubt that temperature performs an important role in the $CaSO_4$ decomposition, and thus a short and a long temperature interval such as 5 and 25 K were selected to study the sensitivity of temperature. As can be seen from Fig. 8, the $CaSO_4$ conversion experiences a notable increase with the rise of temperature. Figure 9 illustrates the impact of SO_2 over



Fig. 8 Simulated conversion curves at various temperatures (Initial atmosphere: 1160×10^{-6} SO₂ + 20% O₂ + 79% CO₂ + balanced Ar)



Fig. 9 Simulated conversion curves for various O_2 initial concentrations (Temperature: 1725 K, initial atmosphere: $1160 \times 10^{-6} \text{ SO}_2 + 79\% \text{ CO}_2 + \text{ balanced Ar}$)

the conversion ratio of $CaSO_4$, and the effect of O_2 is shown in Fig. 10. Conclusion can be drawn that the partial pressure increase of either O_2 or SO_2 can effectively inhibit the decomposition of $CaSO_4$.



Fig. 10 Simulated conversion curves for various SO_2 initial concentrations (Temperature: 1750 K, initial atmosphere: 20% O_2 +79% CO_2 + balanced Ar)

For better understanding the decomposition of CaSO₄ under isothermal condition, surface properties of the unreacted core including partial pressures of SO₂ and O_2 , the average porosity and specific surface area, were also examined. Figure 11 displays the variation of O₂ and SO₂ concentrations on the unreacted core surface at 1750 K, and the average porosity and specific surface area of product layer are given in Fig. 12. As can be seen from Fig. 11, over the unreacted core surface, the concentrations of O₂ and SO₂ are found to increase first and then decrease, indicating very similar profiles with those under temperature programmed condition (Fig. 6). However, curves in Fig. 11 are much smoother than those under temperature programmed condition (Fig. 6) perhaps due to much higher reaction rate and shorter residence time under isothermal condition. In addition,



Fig. 11 SO₂ and O₂ concentrations on unreacted core surface (Temperature: 1750 K, Initial atmosphere: 2000×10^{-6} SO₂ + 20% O₂ + 79% CO₂ + balanced Ar)



Fig. 12 Average specific surface area and average porosity of product layers (Temperature: 1750 K, initial atmosphere: 2000×10^{-6} SO₂+20% O₂+79% CO₂+ balanced Ar)

the average porosity and specific surface area decrease with increasing time; however, the decreasing rate is much lower than that under temperature programmed condition, suggesting that the sintering of CaO is much mitigated under isothermal condition.

4 Conclusions

1) The decomposition of $CaSO_4$ has a significant dependence on the temperature, and the decomposition rate is accelerated with the increase of temperature.

2) The increase of SO_2 or O_2 concentration obviously inhibits the decomposition of $CaSO_4$.

3) The concentrations of SO_2 and O_2 over the unreacted-core surface are found to increase first and then decrease with the proceeding of reaction, while the average porosity and pore size for each CaO sintering layer decrease with increasing time.

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硫酸钙高温分解的动力学模型

闫志强,王泽安,王小锋,刘豪,邱建荣

华中科技大学 煤燃烧国家重点实验室, 武汉 430074

摘 要: 基于硫酸钙程序升温实验计算并得到其煅烧反应速率常数,综合考虑 SO₂ 与 O₂ 的表面扩散以及煅烧分 解产物氧化钙的烧结过程,建立修正的硫酸钙分解未反应缩核模型。结果表明,硫酸钙的高温分解对温度非常 敏感,提高 SO₂和 O₂的分压/抑制硫酸钙的高温分解。随着分解反应的进行,氧化钙烧结产物层的平均比表面积 和平均孔隙率逐渐降低,同时未反应核表面 SO₂和 O₂浓度先增大后减小,在高 SO₂浓度(>1100×10⁻⁶)条件下模拟 计算结果与实验值吻合良好。

关键词: 氧燃烧; 未反应缩核模型; 硫酸钙; 分解; 氧化钙烧结