Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 25(2015) 3490−3497
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Kinetic model for calcium sulfate decomposition at high temperature

Zhi-qiang 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

Received 21 November 2014; accepted 25 May 2015

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 $CaSO_4$ decomposition. Meanwhile, the diffusion of SO_2 and O_2, 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 ($>1100\times10^{-6}$). 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 SO_2 and/or O_2 concentration inhibited $CaSO_4$ decomposition. Moreover, the kinetics of $CaSO_4$ 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; $CaSO_4$; 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 CO_2 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 calcium-based sorbents injection technology in order to ensure the low SO_2 emission.

$$CaCO_3+SO_2+1/2O_2\longrightarrow CaSO_4+CO_2 \tag{1}$$

$$CaCO_3\longrightarrow CaO+CO_2$$

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

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

Notably, the decomposition of desulfurization product, $CaSO_4$, may cause secondary release of SO_2 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 $CaSO_4$ 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 $CaSO_4$ decomposition in the presence of O_2 and SO_2 [15,16], as well as the mechanism of $CaSO_4$ reductive decomposition by methane, hydrogen and carbon monoxide [6,8,11].

Foundation item: Project (51276074) supported by the National Natural Science Foundation of China; Project (2014NY008) supported by Innovation Research Foundation of Huazhong University of Science and Technology, China

Corresponding author: Hao LIU; Tel: +86-27-87545526; E-mail: liuhao@ hust.edu.cn

DOI: 10.1016/S1003-6326(15)63986-3

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 $CaSO_4$ [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 $CaSO_4$

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 decompostion 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.

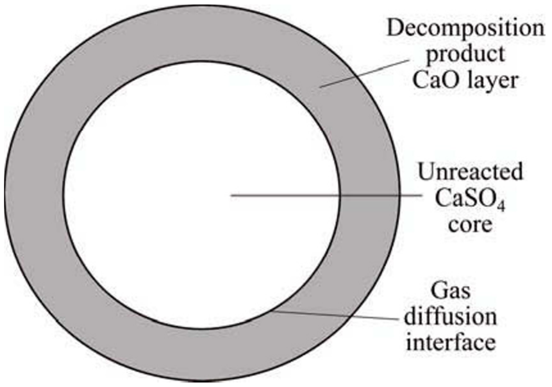

Fig. 1 Schematic model of $CaSO_4$ decomposition at high temperature

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:

$$X=\frac{m-m_0}{m_0}\Bigg/\left(\frac{M_{CaO}-M_{CaSO_4}}{M_{CaSO_4}}\right) \tag{4}$$

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 $CaSO_4$, respectively.

2.1.1 Reaction kinetics

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

$$\frac{dr_c}{dt}=-k_c V_{CaSO4} f(p_{SO_2},p_{O_2}) \tag{5}$$

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

$$f(p_{SO_2},p_{O_2})=$$

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

where p_{c,SO_2}, and p_{c,O_2} are the partial pressures of SO_2 and O_2 at the CaO−$CaSO_4$ interface, respectively; p_e is the equilibrium partial pressure of SO_2 and O_2, 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 SO_2 and O_2 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