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THE MODULATION OF DESULPHURIZATION PROPERTIES OF CALCIUM OXIDE BY ALKALI CARBONATES

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Abstract

Kinetics of CaO desulphurization reaction and the effects of alkali carbonates on it have been investigated by thermogravimetric analysis. A grain model was applied successfully to describe the kinetic behavior of the reactions. The activation energy of surface reaction and that of the product layer diffusion were determined by using the model. It was found that the overall desulphurization rate was controlled initially by surface chemical reaction and, in a later stage, by product layer diffusion. Addition of alkali carbonates can decrease the activation energy of the surface chemical reaction, with increasing effectiveness in the order of potassium, sodium and lithium. Such a property of alkali carbonates has also been demonstrated on a raw coal. The process is discussed in terms of a working mechanism of solid-state ionic diffusion.

Keywords: alkali carbonate, calcium oxide, cation effect, desulfurization, grain model, thermal analysis

Introduction

One of the environmental problems associated with coal combustion is the emission of sulphur-containing gases, including SO_2 [1–2]. An inexpensive way to control the emission of SO_2 is to use calcium-based agents, such as CaO or limestone, as sorbent [3–7]. The main reaction concerned is a solid-gas reaction, which can be represented as:

$$2CaO+2SO_2+O_2 \rightarrow 2CaSO_4$$

The main drawback of this method, however, is the low absorbing efficiency of CaO, particularly at high temperatures. A great deal of effort has been devoted to understand the mechanism of the heterogeneous reaction process so as to find ways to improve the utilization of absorbent CaO. Many investigations demonstrated that limestones from different places showed many different activities, indicating possi-

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ble modulation effect of some minor species in the limestone on CaO. It has been proposed that solid-state ionic diffusion plays a key role in the chemical reaction [3, 4, 8]. Thus investigation of the role of different ionic guest compounds in the desulphurization process will supply crucial evidence in the evaluation of the above hypothesis. The objective of this work is just to examine the effects of some alkali carbonates on the kinetic behavior of the desulphurization reaction by using thermogravimetric analysis technique. A grain model [9] has been employed to describe the chemical kinetics.

Experimental

AR grade reagents including calcium oxide, potassium iodide, and all alkalis carbonates, i.e. Li_2CO_3, Na_2CO_3, and K_2CO_3, were purchased from Beijing Chemical Ind. Sulphur dioxide, better than 99% in purity, was also from Beijing Chemical Ind. Beisu coal, a kind of natural coal, was from Shandong Province, China. Its carbon content is 40.44%, volatile matter 39.83%, moisture 1.7%, ash level 13.92% and sulphur 4.11%.

The absorbents were prepared by adding CaO to a solution containing the selected alkali carbonate to achieve a final alkali salt concentration of 10 mass%. After sufficient time to absorb the carbonate, the mixture was dried in air at 100°C. The particle size of the absorbents was made in the range of a few micrometers.

A WCT-1 thermobalance (Beijing Optical Instrument Inc.) was used to determine the kinetic behavior of the desulphurization process of different absorbents. The furnace was first heated with a scanning rate of 30°C min^{-1} to a temperature between 800 and 1300°C. Then about 4 mg of absorbent was put inside the furnace. A gas mixture containing 0.43 mol m^{-3} of SO_2 and 8.1 mol m^{-3} of oxygen, or otherwise as specified individually, was allowed to pass through the absorbents with a flow rate of 330 mL min^{-1}. Mass change of samples was recorded automatically by the computer of the TG system. The conversion ratio of the absorbents is calculated by the following equation

$$X=\frac{\Delta m M(\mathrm{CaO})}{m_0 W(\mathrm{CaO})[M(\mathrm{CaSO_4})-M(\mathrm{CaO})]} \tag{1}$$

where m_0 and Δm are the starting mass and its increase of the absorbent, $M(\mathrm{CaSO_4})$ and $M(\mathrm{CaO})$ the molar mass of the corresponding molecules, and $W(\mathrm{CaO})$ the mass percentage of CaO in the absorbent. An example of the conversion ratio at a few temperatures is depicted in Fig. 1.

Sulphur content of the raw coal and exhaust gas from the combustion chamber was determined by a Coulomb titration method described in Chinese National Standard GB/T 214-1996. Briefly, sulphur in any compound is oxidized firstly to sulphur dioxide, which is absorbed immediately by aqueous potassium iodide. The sulphur content is then determined by using a method of Coulomb titration of the potassium iodide solution.

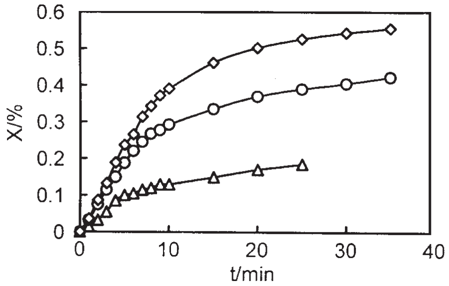

Fig. 1 The conversion ratio of calcium oxide at 920°C (◇), 800°C (o) and 710°C (Δ) with a SO_2 concentration of $3.30\cdot10^{-4}$ mol L^{-1} in the gas mixture

A grain model was used to describe the kinetics of the desulphurization process [10–12]. The absorbent is thought to be consisting of numerous solid particles, which are considered to be small but dense grains. In early stages, the reaction initiates on the grain surface. This is called the chemical-reaction-controlled stage. As the reaction goes on, a layer of products is formed around each grain that separates the reaction surface of the solid from gas reactant. The gas molecules have to diffuse through the product layer to the reaction surface. The reaction then shifts to the product-layer-diffusion-controlled stage. The relationship between the conversion fraction X and time t are given as

$$G_{FP}(X)=A(T)t \tag{2}$$

for chemical-reaction-controlled process and

$$P_{FP}(X)=B(T)t \tag{3}$$

for product-layer-diffusion-controlled process.

$G_{FP}(X)$ and $P_{FP}(X)$ are two functions related to the conversion ratio in the forms of:

$$G_{FP}(X)=1-(1-X)^{1/3} \tag{4}$$

$$P_{FP}(X)=1-3(1-X)^{2/3}+2(1-X) \tag{5}$$

$A(T)$ and $B(T)$ are two temperature-dependent parameters which can be derived from the linear relationship between G and P functions at different temperatures. The activation energy in two stages, E_a and E_p, can then be calculated with the following Arrhenius equations

$$\ln(A(T))=A_1-\frac{E_a}{RT} \tag{6}$$

$$\ln(B(T))=B_1-\frac{E_p}{RT} \tag{7}$$

where A_1 and B_1 are constants associated with the particle size of the absorbents and concentration of SO_2.

Results and discussion

Effect of alkali carbonates on kinetic parameters of desulphurization

The kinetic behaviour of the desulphurization reactions at surface reaction and product-layer-diffusion stages, respectively, are shown in Figs 2 and 3.

Conversion ratio was calculated with Eq. (1) and the dependence of the functions $G_{FP}(X)$ and $P_{FP}(X)$ on it was calculated from Eqs (2) and (3). Three mixed absorbents, CaO+Li_2CO_3, CaO+Na_2CO_3, CaO+K_2CO_3, were used for the investigation in addition to the control measurement without any additives. The time to separate the two stages was determined in such a way that both *G* and *P* functions could show linear relationships with time. Thus the time lasted for the surface reaction stage is about 400, 300 and 200 s for the lithium-, sodium- and potassium-containing absorbents, respectively. This indicates that the size of the alkali cations affect the time required to allow surface reactions.

Values of $A(T)$ and $B(T)$ can be calculated with Eqs (1) and (2) using the linear relationships shown in Figs 2 and 3. The activation energies of the two reaction stages can be calculated from the least-square depression method using plots of $\ln A(T)$ and $\ln B(T)$ *vs.* reciprocal temperature. They are listed in Table 1. The conclusion might be drawn from the table is that the addition of alkali carbonates to calcium oxide reduced

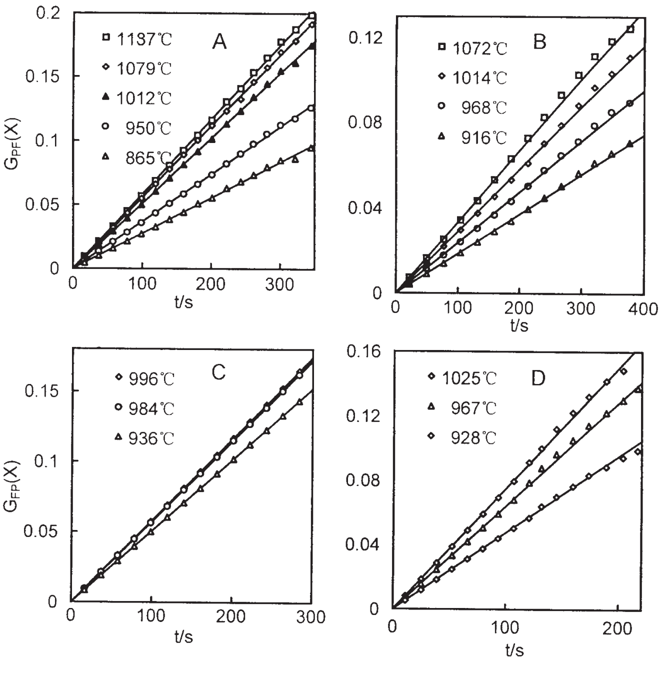

Fig. 2 Temperature-dependence of the desulphurization kinetics of CaO in the absence of additives (A) and presence of Li_2CO_3 (B), Na_2CO_3 (C), and K_2CO_3 (D) at early stages. For the explanation of the *P* and *G* functions see texts for details

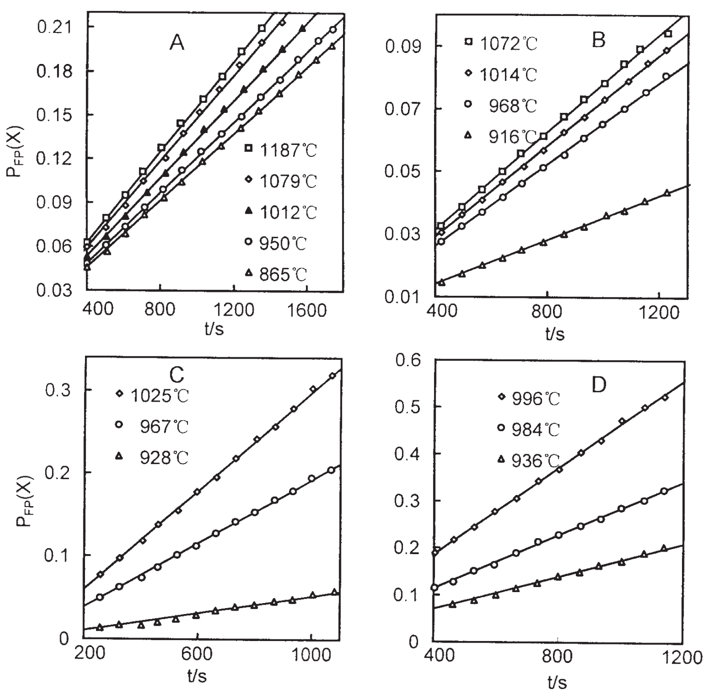

Fig. 3 Temperature-dependence of the desulphurization kinetics of CaO in the absence of additives (A) and presence of Li_2CO_3 (B), K_2CO_3 (C), and Na_2CO_3 (D) at late stages

the activation energy of the surface reaction process, in an extent of about 20% in the case of potassium salt. However, the activation energy of the second stage, i.e. the product-layer-diffusion process, is increased by 12 to 22%.

Table 1 Sulphidation kinetic parameters of CaO doped with carbonates

Additive	E_a/kJ mol^{-1}	E_p/kJ mol^{-1}
None	20.94	92.36
Li_2CO_3	20.79	103.37
Na_2CO_3	18.19	110.09
K_2CO_3	16.97	112.92

In a previous study on the gas-solid reaction of SO_2 with CaO, Hsia and co-workers concluded that the diffusion of calcium cation played an important role in the desulphurization efficiency [4]. Factors including lattice defects and guest ions would influence the cation diffusion. The effect of alkali carbonates on the activation energies could be a result of their influence on the diffusion of calcium cations.

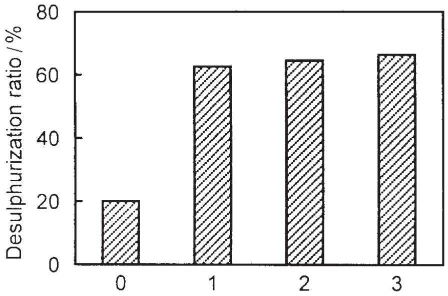

Fig. 4 Desulphurization ratio of CaO to raw coal in the absence (0) and presence of carbonates of lithium (1), sodium (2) and potassium (3) at 1200°C

Effect of alkali carbonates on the desulphurization of raw coal

Beisu coal, a kind of raw coal from Shandong Province of China, has been used in the present study to examine the influence of alkali carbonates on the desulphurization of calcium oxide. The mixed absorbents, containing CaO and alkali carbonates, were mixed with raw coal thoroughly with a Ca/S ratio of 2. The prepared molding coal was then burnt at 1200°C at a gas flow of 300 mL min^{-1} for 20 min. Desulphurization results of different samples obtained are depicted in Fig. 4. It can thus be concluded that the efficiency of desulphurization of CaO can significantly be raised with the addition of 10 mass% of alkali carbonates, from about 20% to a level between 60 and 70%. This could be explained by the effect of the alkali cations on the diffusion of calcium ions. This is consistent with the result of Borgwardt and co-workers [3].

In summary, the kinetic behaviour of desulphurization can be described by a grain model. The overall rate of desulphurization reaction is controlled initially by the surface chemical reaction, and then by the product layer diffusion reaction. Addition of alkali carbonates to the CaO-based sorbents can improve the conversion ratio (efficiency) of CaO. It can also reduce the activation energy of the surface chemical reaction and thus raise the reaction rate.

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