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# KINETIC STUDY OF THE ACCELERATING EFFECT OF COAL-BURNING ADDITIVES ON THE COMBUSTION OF GRAPHITE

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## Abstract

The catalytic and accelerating effects of three coal-burning additives (CBA) on the burning of graphite were studied with the help of thermogravimetric (TG) analysis. The kinetic study on the catalytic oxidation of the graphite doped with CBA was carried out and the results were presented. The results show that the CBA can change the carbon oxidation / combustion course by catalytic action and change the activation energy, thus improving the combustion efficiency.

**Keywords:** coal-burning additive, combustion, graphite, kinetics

## Introduction

In China, production and consumption of coal are very great and most of the raw coal mined every year is directly used as fuels [1]. It is very important and necessary to improve the burning effectiveness of the coals so as to save energy and to limit environmental pollution [2]. Generally, high efficiency and low pollution are required for the coal burning. In order to achieve the above purposes, using coal-burning additives in the process of coal burning is an effective method. In recent years, the application of coal-burning additives has been quickly developed, the coals doped with the coal-burning additive have been used as fuels in power stations, cement industry and some other civil utilization in China. So, the fundamental research work on the burning characteristics of coals doped with the coal-burning additives should be carried out so as to give theoretical guides to the application of the coal-burning additives. In this paper, as a part of the studies of the CBAs, the accelerating effects of the CBAs on the burning of graphite are investigated with thermogravimetry. At the same time a kinetic study is performed on the catalytic oxidation of graphite by the CBA.

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## Experimental

### *Sample*

Three coal-burning additives were produced by Xian environment protection equipment factory, Shandong University of Technology and Dalian coal-burning additive factory respectively (be abbreviated to XA, SD, DL, the same blow). These additives are mainly composed of metal and semi-metal oxides such as sodium, potassium, magnesium, calcium, iron, boron, aluminium and silicon oxides. The main compositions are listed in Table 1. Highly pure graphite was employed, whose purity was determined to be 99.99% by spectrographic analysis. The coal-burning additives and graphite were ground and a particle size small than 180 μm was used. In the experiment, every coal-burning additive was thoroughly mixed with graphite. The additive added in the graphite was 5 per cent (m).

**Table 1** Main compositions of three coal-burning additives (mass%)

| Additives | $Na_2O$ | $K_2O$ | MgO | CaO | $Fe_2O_3$ | $B_2O_3$ | $Al_2O_3$ | $SiO_2$ |
|---|---|---|---|---|---|---|---|---|
| XA | 1.3 | 1.9 | 32.1 | 7.2 | 12.2 | 1.9 | 2.9 | 29.9 |
| SD | 0.9 | 2.1 | 26.8 | 3.7 | 13.6 | 2.0 | 3.5 | 32.4 |
| DL | 2.1 | 1.5 | 22.5 | 7.8 | 16.5 | 3.1 | 4.3 | 35.1 |

### *Thermogravimetry*

A DuPont TA 2000 thermal analysis system was used, which was equipped with a TG951 thermobalance, a platinum wire furnace and platinum-rhodium thermocouples to measure mass loss and heat and to control temperature, respectively. The sample was placed in an isothermal area in the tube of the furnace where the temperature was controlled from room temperature to 1473 K. For comparison of the different samples, factors such as sample mass, heating rate and air flow rate should be well established in order to have experimental runs with good repeatability. In all the experiments carried out in this work, a sample of 50 mg, an air flow rate of 100 ml $min^{-1}$ and a linear heating rate of 10 K $min^{-1}$ were employed.

## Results and discussion

### *The accelerating effect of coal-burning additives on burning graphite*

The TG and DTG curves of undoped and of 5%-CBA-doped graphite are shown in Figs 1 and 2, respectively. In the DTG curves, it can be observed that for samples doped with CBAs the initial temperature, the maximum burning rate temperature and the final temperature of the burning of the graphite were all obviously reduced. The comparison of the main parameters is listed in Table 1. For example, the temperature of the maximum burning rate reduces from 1093 to 943, 903 and 913K for XA, SD, DL, respectively, with respect to graphite. At the same time, the combustion rate of

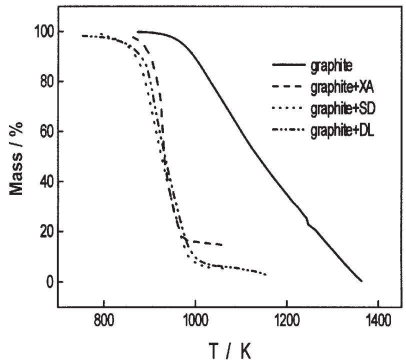


**Fig. 1** Comparison of TG curves of undoped and of 5%-CBA-doped graphite

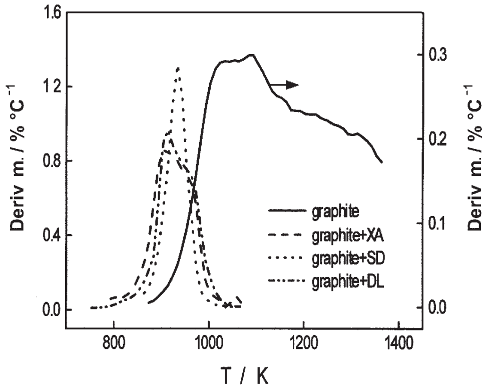


**Fig. 2** Comparison of DTG curves of undoped and of 5%-CBA-doped graphite

the CBA-doped graphite is quicker than that of the undoped graphite. In other words, the combustion amount of the CBA-doped graphite is much more than that of the undoped graphite during the same period. It means that the coal-burning additive can decrease clearly the initial temperature, the maximum burning rate temperature and the final temperature, and accelerate the burning of carbon obviously.

*The kinetics of the catalytic oxidation of graphite*

Graphite is totally composed of pure carbons, and the kinetic study of CBA on the catalytic oxidation of graphite will help us understand the action mechanism of CBA on the burning of coals. In the process of the kinetic study, the oxidation of the graphite is approximately regarded as a simple reaction, and no diffuse obstacle exists under the conditions of this experiment. The Arrhenius equation is used to describe the apparent reaction rate (Eq. (1)).

$$k=A\mathrm{e}^{-E/RT} \tag{1}$$

The differential method of Freeman and Carroll is used to obtain the kinetic parameters with the thermogravimetric data [3–5]:

$$\frac{\mathrm{d}C}{\mathrm{d}T}=\frac{A}{\beta}\mathrm{e}^{-E/RT}C^{n} \tag{2}$$

and

$$\frac{\Delta\ln(-\mathrm{d}C/\mathrm{d}T)}{\Delta\ln C}=-\frac{E}{R}\frac{\Delta(1/T)}{\Delta\ln C}+n \tag{3}$$

where *k* is the apparent reaction rate, *A* the pre-exponential factor, *E* the activation energy, *R* the gas constant, *T* the temperature, *C* the remainder percentage, β the linear heating rate and *n* the reaction order.

**Table 2** Comparison of main parameters of oxidation of the undoped and the doped graphite

| Parameter | Graphite | Graphite +XA | Graphite +SD | Graphite +DL |
|---|---|---|---|---|
| Initial temperature/K | 873 | 833 | 763 | 753 |
| Temperature at DTG curve peak/K | 1093 | 943 | 903 | 913 |
| Mass-loss at DTG curve peak/% | 38.0 | 53.1 | 30.8 | 32.1 |
| Final temperature/K | 1363 | 1093 | 1073 | 1163 |
| Activation energy/kJ $mol^{-1}$ | 274.91 | 334.61 | 247.80 | 141.86 |
| Reaction order | 7.93 | 1.16 | 1.41 | –2.46 |
| Frequency factor/$s^{-1}$ | 2.38E11 | 2.25E16 | 5.25E11 | 8.17E4 |

By using Eq. (3) to deal with the thermogravimetric data of graphite, a straight-line chart of Δln(–d*C*/d*T*)/Δln*C* *vs.* Δ(1/*T*)/Δln*C* can be obtained (shown in Fig. 3), in which –*E*/*R* is the slope of the line and *n* is the intercept. The pre-exponential factor *A* can be calculated from *E* and *n* according to Eq. (2). The obtained kinetic parameters

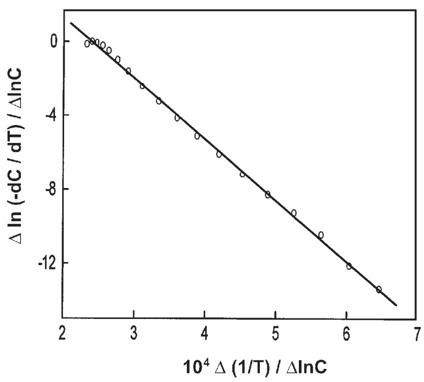


**Fig. 3** Chart of Δln(–d*C*/d*T*)/Δln*C* *vs.* Δ(1/*T*)/Δln*C*

of the undoped and 5%-CBA-doped graphite are also listed in Table 2. It can be seen that both SD and DL reduce the apparent activation energy of combustion of graphite (according to the applied Freeman and Carroll method), only XA makes it increase. The results show that the CBA can change the carbon oxidation (or combustion) course by the catalytic action, resulting in an increase of the overall combustion rate. The above results indicate that the CBAs can improve coal combustion effectiveness.

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