ELSEVIER

Thermochimica Acta 299 (1997) 13–17

thermochimica
acta

Combustion calorimetric and thermogravimetric studies of graphite and coals doped with a coal-burning additive

Li-Ming Zhang, Zhi-Cheng Tan*, Shu-Dong Wang, Di-Yong Wu

Dalian Institute of Chemical Physics, Academia Sinica, Dalian 116023, P.R. China

Abstract

The effect of a coal-burning additive (CBA) on the calorific values of a high-rank coal and a low-rank coal was determined by using combustion calorimetry. The results showed that CBA has no significant effect on the calorific values of the two coals. The catalytic and accelerating effects of CBA on the burning of the two coals were studied with the help of thermogravimetric (TG) analysis. CBA speeds up the burning/oxidation of the coals. The effect of CBA due to its catalysis focuses on the burning of the carbons of the coals. The more the combustible carbons in a coal, the more is the effective accelerating effects of CBA on the burning of the coal. In addition, the catalysis of CBA on the oxidation of a graphite was observed. The kinetic study on the catalytic oxidation of the graphite by CBA was also carried out and the results were presented.

Keywords: Coal; Coal-burning additive; Combustion calorimetry; Graphite; TG

1. Introduction

In China, production and consumption of coal are very great and most of the raw coals mined every year are directly used as fuels. It is very important and necessary to improve the burning of the coals so as to save energy and limit environmental pollution. Generally, high efficiency and low pollution are required for the coal burning. In addition, how to fully utilize low-rank coals, which occupy many lands and pollute environment, is a problem that have to be solved. Of all the kinds of the methods achieving the above purposes, the use of coal-burning additives in the process of coal burning is an effectual one [1]. In recent years, the application of coal-burning additives is developed quickly, the coals doped with the coal-burning additive have been used as fuels in electricity generation, cement industry and civil utilization in China. But fundamental research works on the burning characteristics of coals doped with the coal-burning additives should be carried out in order to give scientific guides to the application of the coal-burning additives. In this paper, as a part of the studies of the coal-burning additives, the effects of the coal-burning additive on the calorific values of a high-rank coal and a low-rank coal are determined and the catalytic and the accelerating effects of the coal-burning additive on the burning of the two coals are studied with combustion calorimetry and thermogravimetry. The kinetic study on the catalytic oxidation of graphite by the coal-burning additive is also carried out.

2. Experimental

2.1. Sample

2.1.1. Raw coals and graphite for experiments

Two raw coals from the northeastern region of China were selected. One is a high-rank Nanpiao coal

---

*Corresponding author. Fax: 86 411 4691570.

PII S0040-6031(97)00130-5

Table 1
Characteristics of the coals used

Coal	Proximate analysis (wt%, ad)			Ultimate analysis (wt%, daf)				
	M	A	V	C	H	N	S	O
Nanpiao	3.99	25.42	7.38	80.13	5.36	1.80	1.72	11.02
Fuxin	3.17	62.82	29.78	85.59	4.67	0.96	1.05	7.71

(22.6 MJ/kg) and the other is a low-rank Fuxin coal (8.96 MJ/kg). The most important analytical characteristics of the two coals are shown in Table 1. Highly pure graphite was employed, whose purity is determined to be 99.99% by spectrographic analysis. The coal and the graphite samples were ground and a particle size inferior to 180 μm was used.

2.1.2. Coal-burning additive (CBA)

The CBA is produced by Beijing Hairun Huangshi Purification Powder Co., Ltd., P.R. China and mainly composed of metal and semi-metal oxides such as magnesium, iron, manganese, aluminium, silicon and boron oxides. In the experiment, the CBA was thoroughly mixed with the coals or the graphite.

2.2. Combustion calorimetry

The oxygen bomb calorimeter used in our laboratory is briefly described below. The schematic of temperature measuring is shown in Fig. 1. The temperature in calorimetric experiments was measured by a precise Pt resistance thermometer with a digital multimeter based on IPTS-90. A computer was employed to collect and handle experimental data.

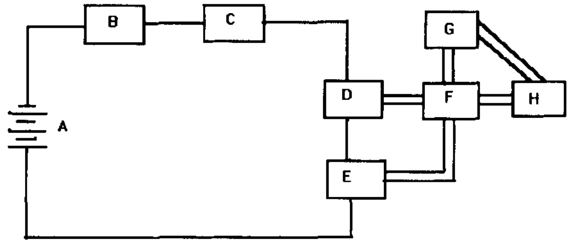

Fig. 1. Schematic of temperature measuring the oxygen bomb combustion calorimeter. A: Battery, B: mA meter, C: Adjustable resistance box, D: Pt resistance thermometer, E: Standard resistance, F: Alternate switch, G: Digital multimeter, H: Computer.

The energy equivalent of the empty calorimeter was determined by burning a thermochemical standard benzoic acid (purity 99.992%, 26437 J g^{-1}) under certificate conditions. The average and standard deviation of the observed energy equivalent was 13567.6 ± 56.6 J K^{-1} from eleven calibration runs. The measuring inaccuracy of the calorimeter was 0.42%.

2.3. Thermogravimetry

A Dupout TA 2000 thermal analysis system, which is equipped with a TG951 thermobalance, a platinum wire furnace and platinum–rhodium thermocouples to measure mass loss and heat and to control temperature, respectively, and is furnished with a gas alternate switch to change measuring atmosphere, was employed. The sample was placed to an isothermal area in the tube of the furnace where the temperature was controlled from room temperature to 1473 K. In order to make the comparison of different samples possible, the factors such as the sample weight, the heating rate and the air flow rate should be well established to have good repeatability among experimental runs. 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 20 K min^{-1} were employed.

3. Results and discussion

3.1. The effects of CBA on calorific values of coals

The effects of CBA on the calorific values of the high-rank Nanpiao coal and the low-rank Fuxin coal were measured. The calorific value of CBA-doped benzoic acid was also measured as a blank test. In order to compare easily, the doping amount of CBA in

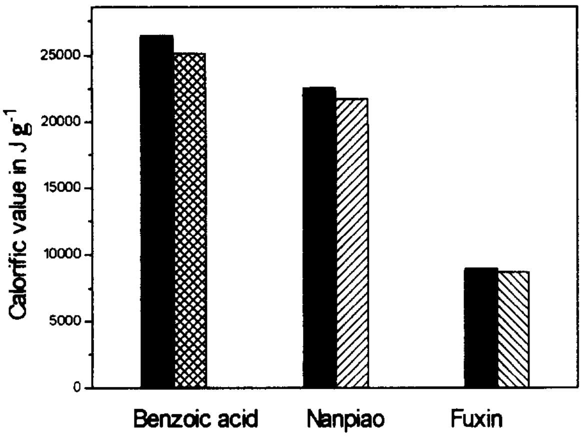

Fig. 2. Comparison of calorific values of the undoped with those of the 5 wt%-CBA-doped.

each measurement was controlled to 5 wt%. The results are shown in Fig. 2. It can be seen from the figure that: (a) for blank test, the calorific value of 5 wt%-CBA-doped benzoic acid decreases by 4.87%, it means that there is no combustible content in CBA; (b) comparing the calorific values of the undoped with those of the 5 wt%-CBA-doped coals, CBA has no significant effect on the calorific values of the high-rank and the low-rank coals.

3.2. The catalytic and accelerating effect of CBA on burning high-rank Nanpiao coal

The comparison of the TG and DTG curves of the undoped with those of 5 wt%-CBA-doped Nanpiao coal is given in Fig. 3. In the DTG curves, three stages are observed. The first one is 353–453 K where the broad peak results from the loss of the moisture of the two samples, the second is of 573–683 K which indicates the burning of the volatile contents of the two samples and the third is of 683–813 K which means the burning/oxidation of the carbons of the two samples. Comparing the DTG curve of the doped with that of the undoped, the effect of CBA due to its catalysis focuses on the burning of the carbons in the coal. It makes the initial temperature of the burning of the carbons decrease from 683 to 663 K, the rate of the mass loss of the carbons increase, for example, by 14.4% at 713 K, in addition, the temperature of maximum burning rate reduces from 803 to 723 K. It means that the dope of CBA speeds up the burning/oxidation of the carbons of the coal.

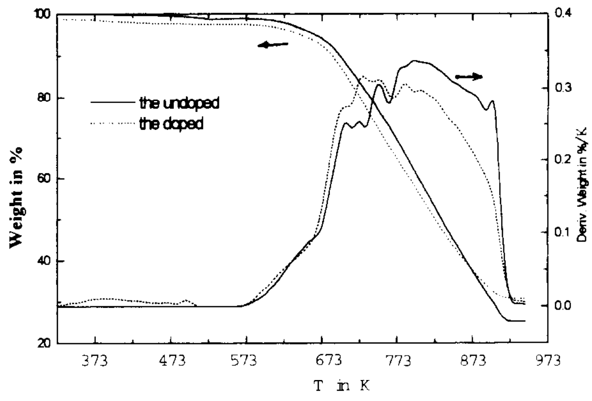

Fig. 3. Comparison of TG and DTG curves of the undoped and 5 wt%-CBA-doped Nanpiao coal.

3.3. The catalytic and accelerating effect of CBA on the burning of low-rank Fuxin coal

The low-rank Fuxin coal is gangue mineral. The TG and DTG curves of the undoped and 5 wt%-CBA-doped Fuxin coal are shown in Fig. 4. Though the similar catalytic and accelerating effect of CBA on the burning of the low-rank Fuxin coal was observed, the effect was obviously less than that on the high-rank Nanpiao coal. That there are less combustible carbons in the low-rank Fuxin coal than in the high-rank Nanpiao coal is a proposed reason.

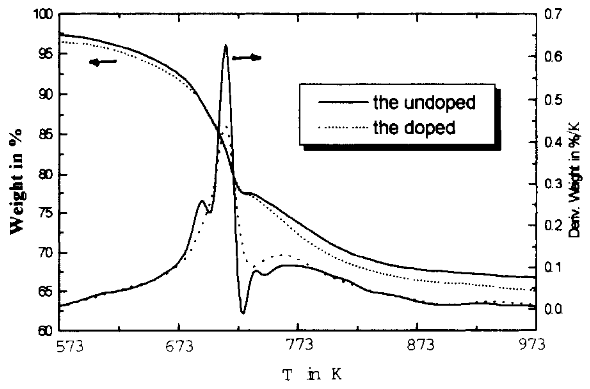

Fig. 4. Comparison of TG and DTG curves of the undoped and 5 wt%-CBA-doped Fuxin coal.

3.4. The kinetics of the catalytic oxidation of graphite by CBA

The graphite is totally composed of carbons, and the kinetic study of CBA on the catalytic oxidation of the graphite will help us understand the action mechanism of CBA on the burning of the coals. In the process of the kinetic study, the oxidation of the graphite was approximately regarded as a simple reaction, and no diffuse obstacle existed under the conditions of this experiment. Arrhenius equation was used to deal with the apparent reaction rate [2].

For the process of linear heating temperature (non-isothermal process), there is [3]:

$$-\frac{dC}{dT} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)C^n \qquad (1)$$

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

From Eq. (1), the following form can be derived:

$$\frac{\Delta\ln(-\frac{dC}{dT})}{\Delta\ln C} = -\frac{E}{R}\times\frac{\Delta(\frac{1}{T})}{\Delta\ln C}+n \qquad (2)$$

By using Eq. (2) to deal with the DTG result, a straight line chart of $\Delta\ln(-dC/dT)/\Delta\ln C$ versus $\Delta(1/T)/\Delta\ln C$ can be obtained, in which $-E/R$ is the slope of the line and n the intercept. Pre-exponential factor A can be calculated from E and n according to Eq. (1).

The TG and DTG curves of the undoped and the 5 wt%-CBA-doped graphite are shown in Fig. 5, the results derived from Eq. (2) are shown in Fig. 6. The obtained kinetic parameters and the other main results from the TG and DTG curves of the two samples are listed in Table 2. It can be seen that the CBA can change the carbon oxidation course by the catalytic action, reduce the apparent activation energy and finally speed the burning/oxidation of the graphite.

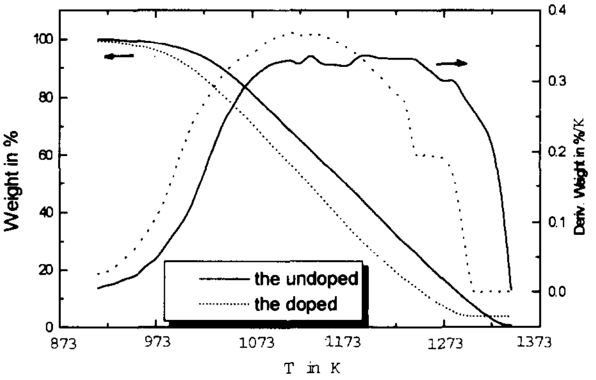

Fig. 5. Comparison of TG and DTG curves of the undoped and 5 wt%-CBA-doped graphite.

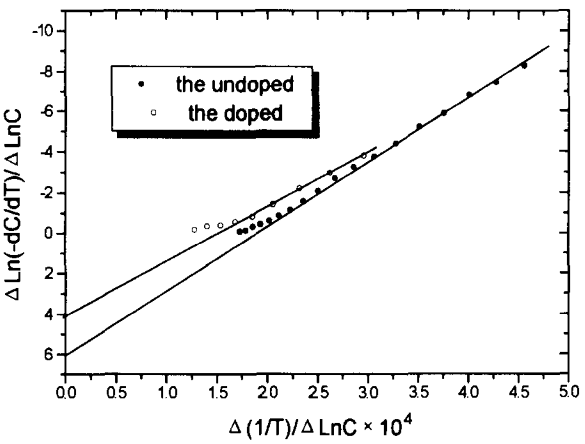

Fig. 6. Chart of $\Delta\ln(-dC/dT)/\Delta\ln C$ vs. $\Delta(1/T)/\Delta\ln C$, temperature range: 933–1113 K.

Generally, a burning reaction of a coal is a normal gas–solid thermochemical reaction. In the presence of CBA, which serves as a catalytic active center, the gas (oxygen)–solid (catalyst)–solid (carbon) catalytic

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

Sample	Graphite	5 wt%-CBA-doped graphite
Initial temperature in K	903	873
Final temperature in K	1343	1303
Temperature at DTG curve peak in K	1193	1113
Deriv. weight at DTG curve peak in %/K	0.336	0.368
Weight at DTG curve peak in %	42.4	56.7
Apparent activation energy in kJ/mol	237.6	250.6
Reaction order	6	4
Pre-exponential factor in s^{-1}	3.51×10^{14}	5.63×10^{13}

burning reaction takes place. In the burning of the coal, many holes and grooves on the surface of the coal particles are formed because the carbons around the catalytic active center burn faster than those away from the catalytic active center. The controlling course of the reaction changes from outer oxygen diffusion to inner oxygen diffusion [4]. The oxygen transfer speeds up. Finally, the accelerating effects of CBA on the burning of the coal are observed. The more the combustible carbons in a coal, the more is the effective accelerating effects of CBA on the burning of the coal.

Acknowledgements

This work was supported by the National Nature Science Foundation of China under grant No. 29573133 and the State Science and Technology Commission of P.R. China under the contract No. 85-925-23-02. The authors express their gratitude to Mr. Shao-Hui Li and Ms. Yun-Wei Kong for their kindly assistance in the experiments, and to Beijing Hairun Huangshi Purification Powder Co., Ltd., P.R. China for providing the coal-burning additive sample.

References

[1] Xu Wqnren and Du Hegui, Chinese J. Fuel Chemistry and Technology, 3 (1995) 272.
[2] M.A. Elliot (Ed.), Chemistry of Coal Utilization, Second Supplementary Volume, John Wiley & Sons, New York, 1981, p. 394.
[3] J.H. Flynn and L.A. Wall, J. Res. NBS., 70A (1996) 487.
[4] P.L. Walker Jr.F. Rusinko and L.G. Austin, Adv. Catal., 11 (1959) 33.