

## Evaluation of the susceptibility of coal to spontaneous combustion by a TG profile subtraction method

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**Abstract**—It is imperative to have an in-depth understanding of the intrinsic reaction between coal and oxygen during low-temperature oxidation, as the reaction is the main source responsible for the self-heating and spontaneous combustion of coal. As low-temperature oxidation of coal involves a series of physical and chemical process and many parallel reactions, it is difficult to directly investigate the intrinsic reaction between coal and oxygen by conventional analytical method. Thermogravimetric analysis (TGA) was used to investigate the intrinsic reaction between coal and oxygen based on the mass change. By means of the subtraction analysis method of TGA, the TG-subtraction curves were obtained by subtracting the TG-N<sub>2</sub> curves from the TG-air curves. The results indicate that a TG-subtraction curve can better reflect the intrinsic reaction of coal oxidation than a TG-air curve by eliminating the influence of evaporation of water and thermal decomposition of inherent oxygen-containing groups. In terms of the rate of mass increase, the intrinsic reactions can be divided into three stages: slow oxidation stage, advanced oxidation stage and rapid oxidation stage. The activation energy at each of the stages, obtained by Coats and Redfern's model, can be used to as a technical parameter to evaluate the proneness of coal spontaneous combustion. The optimum experiment conditions were also developed to study low-temperature coal oxidation with the subtraction method of TGA.

Keywords: TGA, Coal, Low-temperature Oxidation, Subtraction Method, Kinetics

### INTRODUCTION

The low-temperature oxidation of coal is the major heat source responsible for self-heating and spontaneous combustion of coal. The spontaneous combustion of coal caused by low-temperature oxidation is a key safety issue in the mining, storage and transportation of coal, which continues to severely restrict the development of the coal industry [1,2]. The oxidation between coal and atmosphere oxygen can take place as soon as the coal is extracted from a seam and exposed into the air. When the rate of heat accumulated is greater than the rate of heat dissipated, it will lead to the self-heating and eventual spontaneous combustion of coal. In addition to the safety problems, the oxidation of coal also can have significant impact on the molecular structure and cause significantly environmental problems such as pollutant emission [3-5].

Many studies, including macroscopic and microscopic studies, have been carried out to explore the mechanism of low-temperature oxidation of coal. Most of them have focused on gaining a fundamental understanding of oxygen consumption, nature of gaseous products, heat evolution, concentration of bound oxygen and oxygenated complexes at coal surfaces, and major pathways of the

oxidation [6-8]. Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) have been used to observe the changes in coal active groups, indicating that the aliphatic groups on coal are primarily oxidized into oxygen-containing functional groups such as peroxides, carbonyls, carboxyls, and esters [9,10]. Some thermal analysis technology such as crossing-point temperature (CPT), crossing-point slope (CPS), differential scanning calorimetry (DSC), and calorimeter have been used to test the heat release and self-heating temperature, with the aim of identifying and evaluating the proneness of coal spontaneous combustion [11-13].

However, very few studies have focused on the mass evolution during the low-temperature oxidation of coal. While, some studies using TGA have shown an increase of the sample mass when coals were exposed to a heating ramp, suggesting a link between the mass change and the oxidation characteristics of coal associated with the spontaneous combustion phenomenon [14-16]. Other similar studies did not identify these characteristic. As such, the TGA method has not been established as a trusted methodology for spontaneous combustion prediction [17,18].

Characterizing the intrinsic reactivity properties of coals is a potential key to improving these prediction tests. As mentioned, low-temperature oxidation of coal is a complex process that involves a series of physical and chemical processes and many parallel reactions such as evaporation of water, oxidation reaction between oxygen and coal, and thermal decomposition of inherent oxygen-con-

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taining functional groups. The co-existence of these processes makes the study of the intrinsic reaction between oxygen and coal difficult, but the oxidation reaction between oxygen and coal is the main source responsible for the self-heating and spontaneous combustion of coal. Many investigators have taken these processes only as a whole to study the mass change characteristics, few studies have been carried out to explore the intrinsic reactivity of low-temperature oxidation of coal. It is well known that the low-temperature oxidation of coal in air atmosphere involves the evaporation of water, oxidation reaction and thermal decomposition of inner oxygen containing functional groups. The heating of coal in nitrogen atmosphere involves only the evaporation of water and thermal decomposition of inherent oxygen containing functional groups. By subtracting the TG-N<sub>2</sub> curve from the TG-air curve, the common processes occurred in both atmospheres, i.e. water evaporation and thermal decomposition, are eliminated and the intrinsic oxidation reaction between oxygen and coal can be obtained. We propose a new approach to deriving kinetic parameters based on the mass change using the subtraction method of thermal analysis technology. An optimum experimental parameter for this techniques was investigated. The relationship between the kinetic parameter and self-oxidative potential of coal was also explored.

## EXPERIMENTAL

### 1. Coal Samples

Three ranks of coal, lignite, sub-bituminous, and bituminous, were used in this study. The lignite (denoted as XM) was from the

Chinese Ximeng coal mine in the north of Inner Mongolia; the sub-bituminous coal (denoted as SD) was collected from the Chinese Shendong coal mine in the southwest of Inner Mongolia; and the bituminous (denoted as ZZ) was obtained from the Chinese Zaozhuang coal mine in the south of Shandong. These coal samples were obtained fresh from the recently-worked faces of the mine, using a chain saw, after first removing a layer of coal about 25 cm thick to avoid the possibility of peroxidation. The coal core selected for testing came from the one borehole, thus representing an isorank suite of samples. All coal samples were first wrapped in sealed plastic cling wrap filled with nitrogen. The samples were then transported to the laboratory in an insulated container full of ice. On arrival, the coals were transferred to a freezer for storage until required for testing. The coals were crushed and sieved to a particle size range of 0.120–0.250 mm before testing. Table 1 shows the proximate and ultimate analyses of the coals used in this study.

### 2. Chromatographic Analysis of Gaseous Products

A schematic diagram of the experimental apparatus is shown in Fig. 1. Each sample was loaded into a cylindrical reactor of 5 cm in diameter and 10 cm in height, and the actual weight of coal sample in the reactor was 50.0 g. The reactor was then placed in an oven. Experiments were performed in both nitrogen and air atmospheres. In the nitrogen atmosphere experiments, high-purity nitrogen was introduced into the reactor at a flow rate of 150 mL min<sup>-1</sup> to replace the air in the reactor. After 30 min, the sample was heated from 25 °C to 230 °C at the rate of 1 K min<sup>-1</sup> while high-purity nitrogen flow was maintained at 100 mL min<sup>-1</sup>. At the same time, the gaseous atmosphere was analyzed with a GC-950 gas chro-

Table 1. Proximate and ultimate analyses of coal samples used in experiments

Coal sample	Proximate analysis, wt%				Ultimate analysis, wt%, daf				
	M <sub>ar</sub>	M <sub>ad</sub>	A <sub>d</sub>	V <sub>daf</sub>	C	H	O*	S	N
XM coal	34.40	24.48	18.05	42.70	69.79	2.99	24.73	1.36	1.13
SD coal	11.25	9.43	7.15	28.24	76.29	4.07	17.34	0.91	1.39
ZZ coal	1.36	0.39	6.4	37.88	82.22	5.21	10.71	1.47	0.39

Note: ar, as received basis; ad, air-dried basis; d, dry basis; daf, dry and ash-free basis; \* by difference

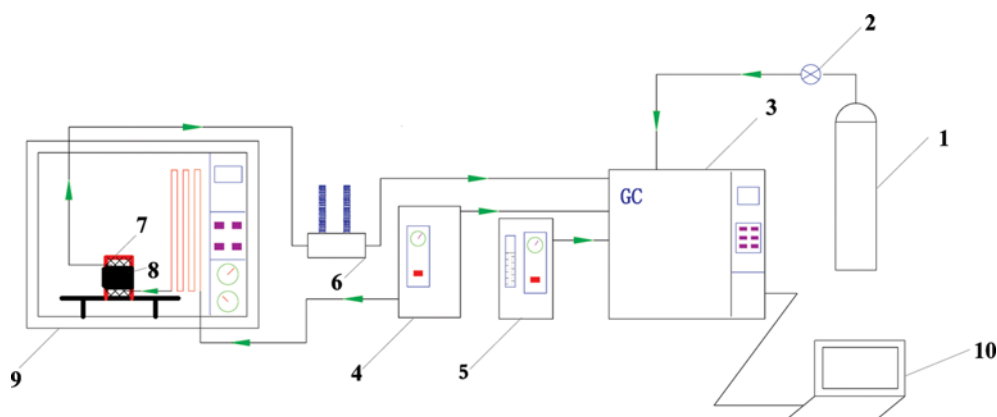


Fig. 1. A schematic diagram of the experimental apparatus.

- |                      |                                   |                        |              |
|----------------------|-----------------------------------|------------------------|--------------|
| 1. Gas cylinder      | 4. Air pump                       | 7. Reactor             | 10. Computer |
| 2. Reducing valve    | 5. High-purity hydrogen generator | 8. Coal sample         |              |
| 3. Gas chromatograph | 6. Gas purifying apparatus        | 9. Program temperature |              |

matography spectrometer. In the air atmosphere experiments, the reactor was again first purged with high-purity nitrogen at 150 mL min<sup>-1</sup> for 30 min, the sample was heated from 25 °C to 230 °C at the rate of 1 K min<sup>-1</sup>, dry air was introduced into the reactor at 100 mL min<sup>-1</sup>, and the gaseous atmosphere was then analyzed.

### 3. Thermogravimetric Analysis of Mass Change

A sensitive thermogravimetric analyzer (TGA) (NETZSCH STA 409 C from Boston, USA) equipped with an Al<sub>2</sub>O<sub>3</sub> ceramic crucible (flat tray) was used to measure the mass change. A certain quality of coal sample (5 mg, 10 mg and 20 mg) was quickly and loosely placed on the sample pan. Experiments were then performed in both nitrogen and air atmospheres. In the nitrogen atmosphere experiments, high-purity nitrogen was introduced into the chamber at a flow rate of 100 mL min<sup>-1</sup> to replace the air in the chamber. After 30 min, the sample was heated from 25 °C to 200 °C at a set of different ramp rates (0.5, 1, 3 and 5 K min<sup>-1</sup>) while high-purity nitrogen flow was maintained at 60 mL min<sup>-1</sup>. The mass change was then recorded. In the air atmosphere experiments, the chamber was again first purged with high-purity nitrogen at 100 mL min<sup>-1</sup> for 30 min, the sample was heated from 25 °C to 200 °C at a set of different ramp rates (0.5, 1, 3 and 5 K min<sup>-1</sup>), dry air was introduced into the chamber at 60 mL min<sup>-1</sup>, and the mass change was then measured. The mass change in the nitrogen atmosphere experiments was due to liberation of water and thermal decomposition of unstable ingredient, and the mass change in the air was attributed to liberation of water, thermal decomposition of unstable ingredient, and oxidation reaction between coal and oxygen. The mass change solely due to the oxidation reaction between coal and oxygen was obtained by subtracting the TG-N<sub>2</sub> curve from the TG-air curve. Several blank experiments without a coal sample were also carried out to calibrate the effects of the buoyancy and the mass of crucible with samples. Experimental results showed that the TG curve of 0.5 K min<sup>-1</sup> fluctuates substantially over time due to instrumental sensitivity. Therefore, we mainly focused on the data of 1, 3 and 5 K min<sup>-1</sup> to investigate the effect of heating rate. Each experiment was repeated to eliminate risks of test error and the reproducibility turned out to be quite good.

## THEORETICAL ANALYSIS

For a reaction of mass increase due to chemisorption, kinetic parameter calculations from the thermogravimetric data usually proceed from the basic kinetic equation [19]:

$$-\frac{dm}{dt} = k(T)g(m) \quad (1)$$

where,  $t$  is the reaction time;  $m$  is the sample mass at time  $t$ ; and  $T$  is the absolute temperature.

The mass function  $g(m)$  is dependent on the assumed reaction mechanism. The form of  $g(m)$  has been generally described as:

$$g(m) = m^n \quad (2)$$

where,  $n$  is the reaction order.

The Arrhenius equation relates the rate constant  $K$  to the pre-exponential factor  $A$  and the activation energy  $E_a$ :

$$K = A \exp(-E_a/RT) \quad (3)$$

where,  $R$  is the molar gas constant, 8.314 J·K<sup>-1</sup>·mol<sup>-1</sup>.

Although reactions of many substances are complex, the air oxidation of coal has been described as pseudo-first-order reaction kinetics as long as the reactant oxygen is present in large excesses so that its concentration is effectively constant for the duration of the reaction [16,20]. Thus, following pseudo-first-order kinetics, the rate of the change in coal mass will be proportional to its concentration. The kinetic parameters of the low-temperature oxidation of coal can be determined by observing the change of mass as the reaction proceeds and can be evaluated by the following expression:

$$-\frac{dm}{dt} = A e^{-\frac{E_a}{RT}} m \quad (4)$$

In this study, temperature changed at a constant positive rate  $\beta = dT/dt$ . Hence, Eq. (4) becomes,

$$-\frac{dm}{dT} = \frac{A}{\beta} e^{-\frac{E_a}{RT}} m \quad (5)$$

Solving Eq. (5) via integration, subject to the initial condition  $m = m_0$ ,  $T = T_0$  yields:

$$\int_{m_0}^m -\frac{dm}{m} = \frac{A}{\beta} \int_{T_0}^T e^{-\frac{E_a}{RT}} dT \quad (6)$$

Since there is no oxidation ( $m = m_0$ ) up to  $T_0$ , the limit of the integral is conventionally changed to  $\int_0^T e^{-\frac{E_a}{RT}} dT$ , hence the function  $\theta(x)$  could be introduced as follows:

$$\theta(x) = \int_x^\infty \frac{e^{-x}}{x^2} dx \quad (7)$$

where,  $x = E/RT$ . Therefore, Eq. (6) becomes,

$$\int_{m_0}^m -\frac{dm}{m} = \frac{AE}{\beta R} \theta(x) \quad (8)$$

The function  $\theta(x)$  can be expressed by some approximate equations. Among them, the Coats-Redfern approximation is commonly used for its simplicity. In this approximation, the first term of an asymptotic expansion of  $\theta(x)$  is retained:

$$\theta(x) = \frac{e^{-x}}{x^2} [1 - (2!/x) + 3!/(x^2) - (4!/x^3) + \dots + (-1)^n (n+1)!/x^n + \dots] \quad (9)$$

Eq. (9) may be incorporated into Eq. (8) to yield a linear equation:

$$\ln \left[ \frac{\ln(m/m_0)}{T^2} \right] = \ln \left( \frac{AR}{\beta E} \right) - \frac{E}{RT} \quad (10)$$

Hence for a given heating rate,  $A$  and  $E$  can be calculated from the intercept and slope of a plot of  $\ln[\ln(m/m_0)/T^2]$  versus  $1/T$ , respectively.

## RESULTS AND DISCUSSION

### 1. General Trends for the Emission of Gaseous Products

It is well known that the gaseous products released in the coal

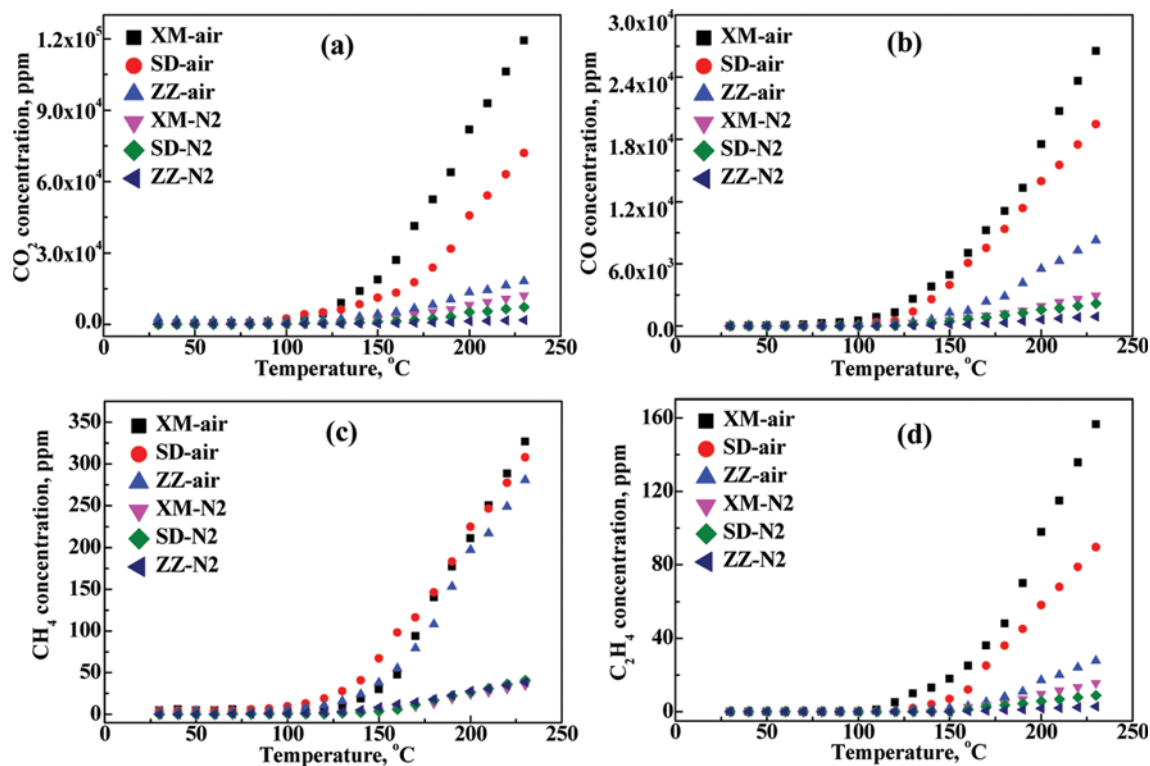


Fig. 2. Concentration of gaseous products released in the coal reaction under air and nitrogen atmospheres. (a)  $\text{CO}_2$ ; (b)  $\text{CO}$ ; (c)  $\text{CH}_4$ ; (d)  $\text{C}_2\text{H}_4$ .

oxidation at low temperature include  $\text{CO}_2$ ,  $\text{CO}$ , and minor amounts of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , etc [21]. Fig. 2 presents the concentrations of  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{C}_2\text{H}_4$  released from the coal reaction under nitrogen and air atmospheres. These data show that  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$  can be generated from coal reaction under nitrogen and air atmospheres.  $\text{CO}_2$  and  $\text{CO}$  can be observed even at  $30^\circ\text{C}$  under both atmospheres.  $\text{CH}_4$  can be detected at  $30^\circ\text{C}$  and  $50^\circ\text{C}$  for air atmosphere and nitrogen atmosphere, respectively. And  $\text{C}_2\text{H}_4$  can be detected at  $100^\circ\text{C}$  and  $150^\circ\text{C}$  for air atmosphere and nitrogen atmosphere, respectively. Furthermore, the release rates of these gaseous products are increased with the increase of the temperature. Also, the characteristic of coal type has a great effect on the release of gaseous products. At both atmospheres, the release rate of these gaseous products is related to the metamorphic degree of coal with the order of  $\text{XM} > \text{SD} > \text{ZZ}$ . This result indicates that the lower the metamorphic degree of coal is, the higher is the coal reactivity for the release of gaseous products.

Fig. 2 also shows that the release rates of gaseous products under air atmosphere are obviously larger than these under nitrogen atmosphere. This difference can be attributed to the mechanism of coal reaction under different atmosphere.  $\text{CO}_2$  and  $\text{CO}$  were formed under inert atmosphere only from the decomposition of inherent oxygen-containing groups in the coal matrix, while carbon oxides were formed under air atmosphere not only from the decomposition of the decomposition of inherent oxygen-containing groups, but also from surface oxides produced by the reaction between coal and oxygen [8].  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$  were formed under inert atmosphere from the cleavage of the bridged linkage in coal matrix, while under air atmosphere the oxygen molecules can accelerate this cle-

avage rate and more  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$  can be produced. These results indicate that the coal reaction under air atmosphere can accelerate the release rate of these gaseous products. Furthermore, the release of the gaseous products is closely related to the change of the coal mass under different atmospheres.

## 2. General Trends of Mass Change During Low-temperature Oxidation of Coal

Fig. 3 shows the thermogravimetric profiles measured at a heating rate of  $1\text{ K min}^{-1}$  during the heating of 10 mg SD coal under air atmosphere (TG-air) and  $\text{N}_2$  atmosphere (TG- $\text{N}_2$ ), which are taken as examples to elucidate the characteristics of mass change during

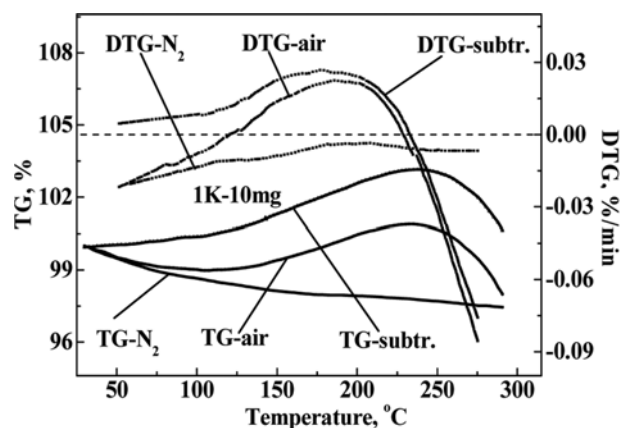


Fig. 3. Typical curves for mass change during the oxidation of SD coal at heating rate of  $1\text{ K min}^{-1}$  under different atmosphere conditions.

low-temperature oxidation of coal. The TG subtraction curve (TG-subtr.) obtained by subtracting the TG-N<sub>2</sub> curve from the TG-air curve is also shown in Fig. 3.

The thermogravimetric profile of the low-temperature coal oxidation process in air atmosphere reveals that the thermogram can be divided into three stages. At the first stage the obvious decrease in coal mass was observed when the oxidation temperature ranged from the ambient temperature to around 110 °C. It can be seen from Fig. 3 that the DTG-air curve at this stage was below the x axis. The mass loss could be attributed to the loss of water from coal pores. This stage is denoted the “dehydration stage.” At the second stage a gradual increase of coal mass was observed as the oxidation temperature increased from 110 to 230 °C. The DTG-air curve at this stage was above the x axis and the maximum DTG value was at around 180 °C. These results showed that the increase rate of coal mass was initially high, peaked at around 180 °C, and then dropped. The mass gain at this stage could be attributed to the chemisorption of oxygen in coal matrix and the formation of unstable intermediates. This stage is defined as “oxidation stage.” At the third stage the temperature was higher than 230 °C and the coal mass loss was drastic and the most part of the DTG-air curve was well below the x axis. This stage is denoted as “spontaneous ignition” zone.

From the TG-N<sub>2</sub> curve in Fig. 3, the coal mass decreased gradually with the increase of temperature under the N<sub>2</sub> atmosphere. The curve of DTG-N<sub>2</sub> was below the x axis and it showed two peak values. The first peak value occurred at around 115 °C, which

is attributed to loss of water from coal pores. The second peak value was at around 180 °C, which is due to the thermal decomposition of inherent oxygen-containing groups in the coal matrix. Accordingly, the first stage is defined as “dehydration stage” and the second stage is denoted “thermal decomposition stage.” It can be seen by comparison that the TG-air profile was obviously higher than the TG-N<sub>2</sub> profile when the temperature was above 60 °C. This difference can be clearly observed in the TG-subtraction profile and was attributed to the interaction between coal and oxygen.

It can be seen from the TG-subtraction curve in Fig. 3 that the coal mass showed a trend of increase with temperature. The mass increased slowly as the temperature rose to 80 °C and this stage is defined as “slow oxidation stage.” As the temperature rose from 80 to 150 °C, the coal mass increased gradually and this stage is denoted as “advanced oxidation stage.” As the temperature rose further from 150 °C to 230 °C, the coal mass increased significantly, and this stage is defined as “rapid oxidation stage.” The increase of the coal mass over the three stages suggests that the TG-subtraction profile eliminates the effect of the mass change caused by release of water and thermal decomposition of inherent oxygen containing groups in coal, and reveals the mass change due only to the reaction between coal and oxygen. These results indicate that TG-subtraction curve can better reflect the mass change due to the intrinsic reaction of coal oxidation at low temperature, and this characteristic is related to the tendency of coal spontaneous combustion by chemisorption.

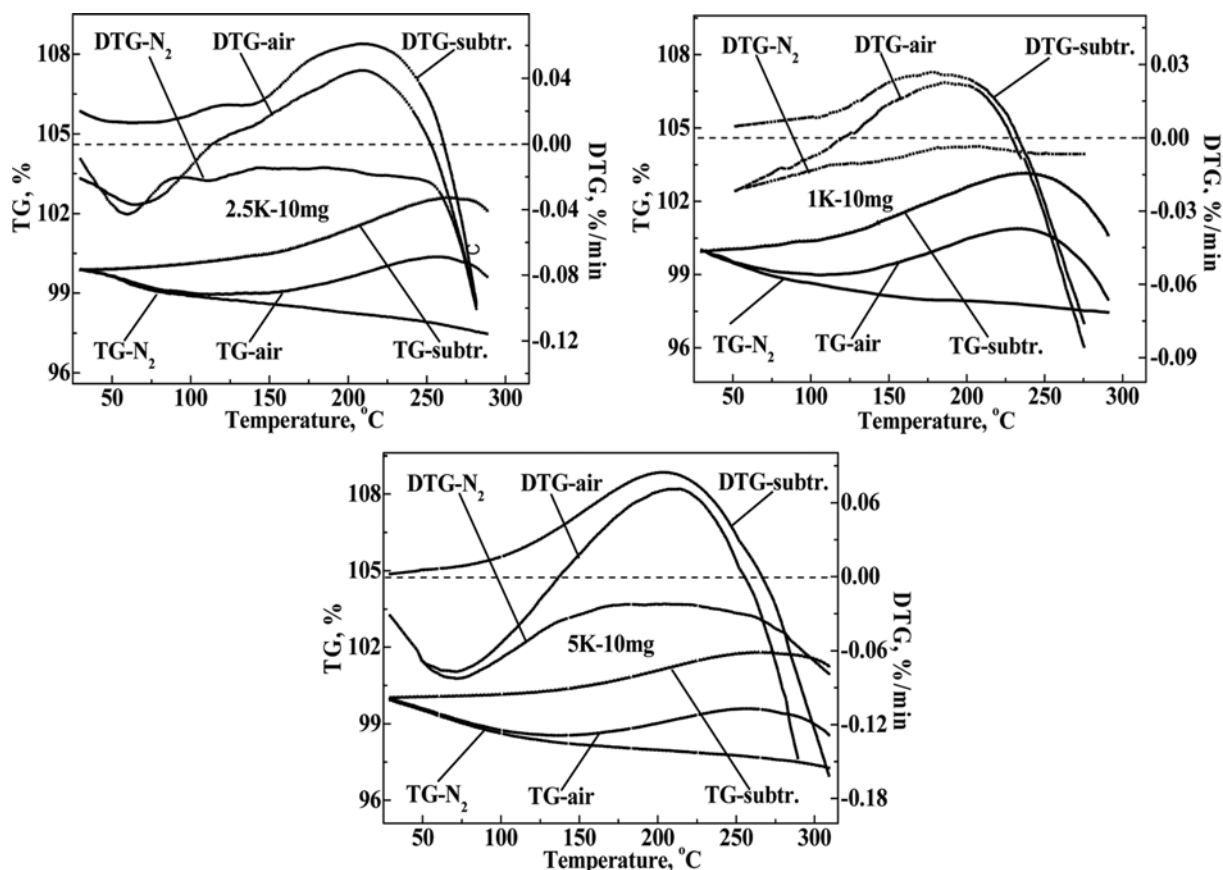


Fig. 4. Effect of heating rate on the mass changes during low-temperature oxidation of coal.

### 3. Analyses of Factors Affecting the Oxidation

In spite of the long-term benefit of using TGA for the characterization of oxidation reaction between coal and oxygen, the reliability and reproducibility of the experimental parameters of this method have not been established because of their dependence on a larger number of variables such as sample mass, heating rate, oxygen concentration. The determination of the optimum experimental parameters of this method will help classify coals with respect to their proneness to spontaneous combustion.

#### 3-1. Effect of Heating Rate

Coal oxidation at low temperature is a slow process, and hence the heating rate will affect the experimental results. A high heating rate will lead to an increase in the internal temperature gradient of coal samples, which would result in uneven heating and incomplete reaction. Conversely, if the heating rate is too slow, a higher sensitivity of TGA equipment is required and it will also take a long time to conduct experiments. Therefore, an optimum heating rate is necessary. TGA experiments were done with SD coal throughout a temperature range of 30–230 °C with an initial sample mass of 10 mg under different heating rates. The curves of TG-air, TG-N<sub>2</sub> and TG-subtraction under heating rates of 1.0 °C min<sup>-1</sup>, 2.5 °C min<sup>-1</sup>, and 5.0 °C min<sup>-1</sup> are shown as Fig. 4.

To better illustrate the effect of experimental conditions on the process of coal oxidation at low temperature, two characteristic temperature  $T_1$  and  $T_2$  were defined. Note that  $T_1$  and  $T_2$  refer to different meanings for different TG curves. For a TG-air curve,  $T_{1A}$  and  $T_{2A}$  refer to the temperatures at which the coal mass presents the minimal value and maximal value, respectively; and these parameters can be directly evaluated from TG-air experimental curves. For a TG-N<sub>2</sub> curve,  $T_{1N}$  corresponds to the temperature at which the rate of water release presents its maximal value, and  $T_{2N}$  corresponds to the temperature at which the thermal decomposition rate of inherent oxygen-containing groups presents its maximal value; these two parameters can be obtained from its DTG-N<sub>2</sub> curve. For a TG-subtraction curve,  $T_{1S}$  is the temperature at which

the increase rate of coal mass presents the maximal value which can be obtained from the corresponding DTG-subtraction curve;  $T_{2S}$  is the temperature at which the coal mass begins to decrease, which is the intersection point between the DTG-subtraction curve and the x axis. The characteristic temperature parameters under different heating rates are shown in Table 2.

From Table 2, both  $T_1$  and  $T_2$  for different TG curves increased with the increase of heating rate. For instance, in the TG-air curve  $T_{1A}$  increased from 109.3 °C to 143.4 °C and  $T_{2A}$  from 227.9 °C to 254.9 °C as the heating rate increased from 1 K min<sup>-1</sup> to 5 K min<sup>-1</sup>, respectively. These results show that with a high heating rate, the characteristic temperature parameters increased or so-called “hysteresis” occurred. This increase did not mean an increase in the actual temperature of coal sample, because a high heating rate led to an increased internal temperature gradient between coal sample and atmosphere temperature and uneven heating.

In terms of the change rate of coal mass, the process of coal oxidation at low temperature can be divided into several stages as follows. In nitrogen atmosphere, it involves desorption of water and thermal decomposition of inherent oxygen-containing groups in coal. In air atmosphere, it has three stages: desorption of water, advanced oxidation stage and rapid oxidation stage. The activation energy at each of these stages was calculated by Eq. (10) and the effect of heating rate on the activation energy was presented in Table 3.

With the increase of heating rate in air atmosphere, the activation energies at all stages showed an obvious increase. The activation energy at the advanced oxidation stage could not be calculated with the heating rate of 5 K min<sup>-1</sup> due to the hysteresis of  $T_{2A}$  at around 150 °C. However, the activation energies for these three stages obtained from the TG-subtraction curve showed a slight increase with the increase of heating rate. These results indicate that the activation energies obtained by the subtraction curve can not only reflect the activation energies at slow oxidation stage, advanced oxidation stage and rapid oxidation stage, but can also eliminate the experiment error caused by heating rate to some extent. On

**Table 2. Effect of heating rate on characteristic temperature of  $T_1$  and  $T_2$  during coal oxidation at low temperature**

Heating rate (K min <sup>-1</sup> )	TG-air		TG-N <sub>2</sub>		Subtraction	
	$T_{1A}$ (°C)	$T_{2A}$ (°C)	$T_{1N}$ (°C)	$T_{2N}$ (°C)	$T_{1S}$ (°C)	$T_{2S}$ (°C)
1.0	109.3	227.9	97.1	176.7	184.3	232.5
2.5	114.8	252.2	110.7	215.3	208.7	261.1
5.0	143.4	254.9	NA <sup>a</sup>	NA <sup>a</sup>	210.3	269.9

<sup>a</sup>Not available

**Table 3. Effect of heating rate on the activation energy**

Heating rate (K min <sup>-1</sup> )	$E_{Air}$ (kJ mol <sup>-1</sup> )			$E_{N_2}$ (kJ mol <sup>-1</sup> )		$E_{subtr.}$ (kJ mol <sup>-1</sup> )		
	Dehydration stage	Advanced oxidation stage	Rapid oxidation stage	Dehydration stage	Thermal decomposition stage	Slow oxidation stage	Advance oxidation stage	Rapid oxidation stage
1.0	40.55	77.83	96.82	26.88	36.08	32.16	48.68	78.75
2.5	41.77	83.15	103.48	39.6	48.79	27.34	49.07	75.16
5.0	42.32	NA <sup>a</sup>	110.11	41.51	45.15	32.06	49.69	80.88

<sup>a</sup>Not available

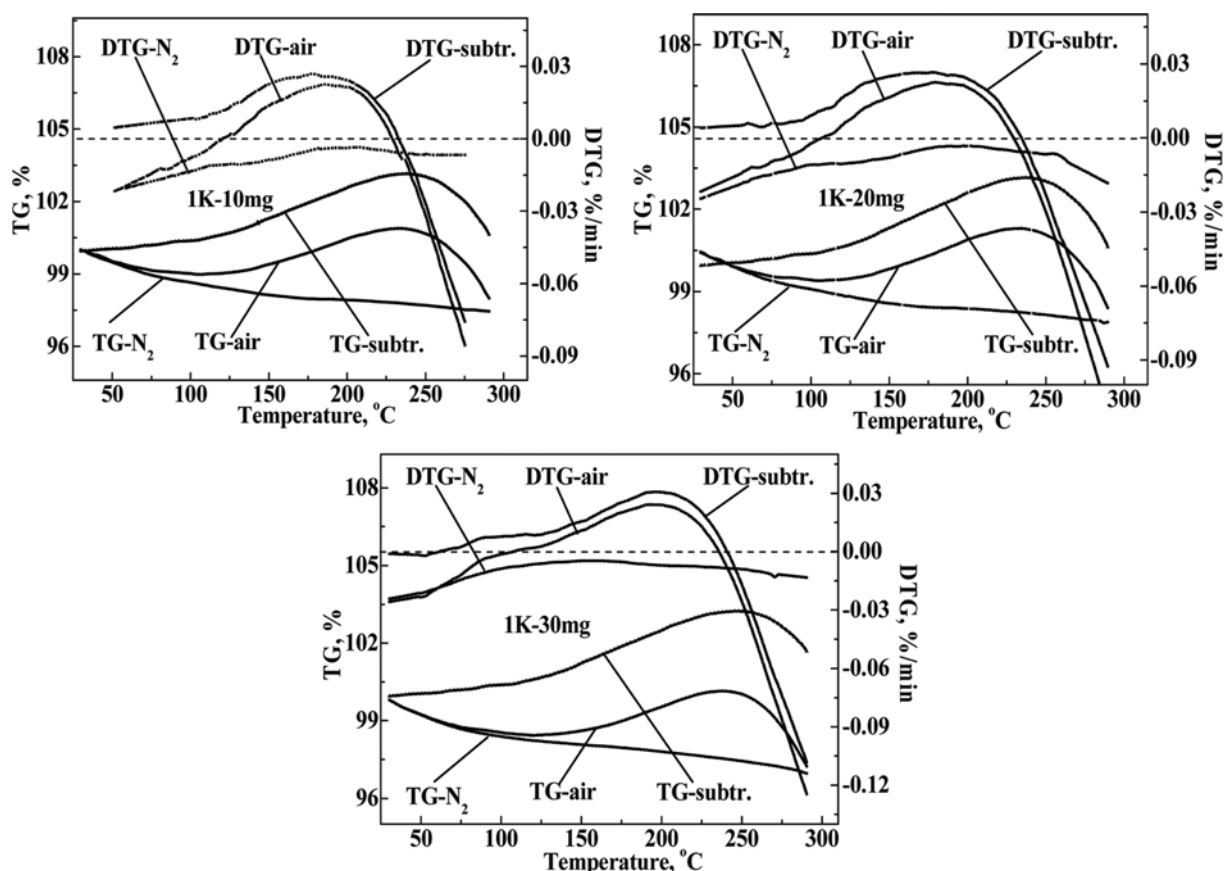


Fig. 5. Effect of sample mass during low-temperature oxidation of coal.

the basis of these findings, it is expected that a lower heating rate such as  $1 \text{ K min}^{-1}$  should be used for the study of coal spontaneous combustion. The use of a lower heating rate was also determined by the slow process of coal self-heating.

### 3-2. Effect of Sample Mass

Based on the above discussions, the heating rate of  $1 \text{ K min}^{-1}$  was used for the study of the effect of sample mass on the TGA results. Fig. 5 shows the effect of coal mass on the TG curves in temperature range of  $30\text{--}230^\circ\text{C}$ . The effect of sample mass on the characteristic temperatures is listed in Table 4.

The data in Table 4 show that the sample mass had significant influence on the curves of TG- $\text{N}_2$  and showed no effect on the curves of TG-air. These results indicate that the effect of sample mass was at the dehydration and thermal decomposition stages. At these two stages the peak temperatures increased with the increase of coal sample mass. For instance, the characteristic temperature point  $T_{1N}$  of the TG- $\text{N}_2$  curve rose from  $96.1^\circ\text{C}$  to  $103.6^\circ\text{C}$ , and

$T_{2N}$  from  $176.7^\circ\text{C}$  to  $186.3^\circ\text{C}$  with the increase of coal mass from 10 mg to 30 mg, respectively. Similarly, the characteristic temperature  $T_{1A}$  of the TG-air curve increased from  $105.3^\circ\text{C}$  to  $110.7^\circ\text{C}$ , and  $T_{2A}$  from  $227.9^\circ\text{C}$  to  $235.6^\circ\text{C}$  with the increase of coal mass from 10 mg to 30 mg, respectively. However, in the subtractive spectra, the characteristic temperature point  $T_{1S}$  did not change significantly with sample mass, but  $T_{2S}$  was lower for a sample mass of 5 mg than that for sample masses of 10 mg and 20 mg. The effect of sample mass on the low temperature oxidation process was similar to the effect of heating rate, but the effect of coal mass on the characteristic temperature points was less than that of heating rate. From Table 4, also, the characteristic temperature points obtained from the TG-subtraction curves were not affected by the increase of coal mass, with the average values of  $184.6^\circ\text{C}$  and  $233.8^\circ\text{C}$  for  $T_{1S}$  and  $T_{2S}$ , respectively.

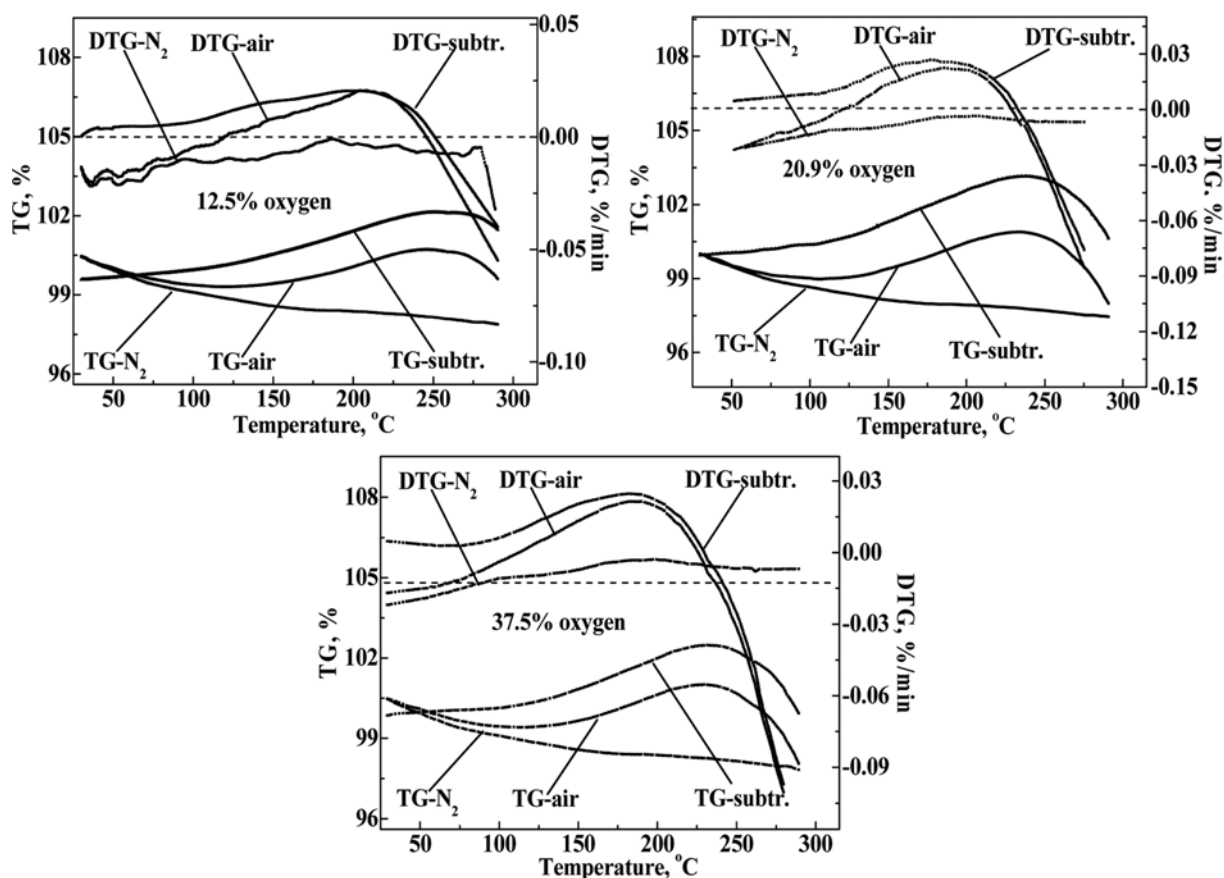
The effect of coal mass on the activation energy at each stage obtained from different TG curves is shown in Table 5. The coal

Table 4. Effects of coal mass on the characteristic temperatures of  $T_1$  and  $T_2$  during coal oxidation at low-temperature

Coal mass (mg)	Air atmosphere		Nitrogen atmosphere		Subtraction	
	$T_{1A}$ ( $^\circ\text{C}$ )	$T_{2A}$ ( $^\circ\text{C}$ )	$T_{1N}$ ( $^\circ\text{C}$ )	$T_{2N}$ ( $^\circ\text{C}$ )	$T_{1S}$ ( $^\circ\text{C}$ )	$T_{2S}$ ( $^\circ\text{C}$ )
10	105.3	227.9	96.1	176.7	183.3	232.5
20	108.1	229.4	99.2	183.5	184.9	233.6
30	110.7	235.6	103.6	186.3	185.7	235.3

**Table 5. Effect of coal mass on the activation energy**

Coal mass (mg)	$E_{Air}$ (kJ mol <sup>-1</sup> )			$E_{N_2}$ (kJ mol <sup>-1</sup> )		$E_{subtr.}$ (kJ mol <sup>-1</sup> )		
	Dehydration stage	Advanced oxidation stage	Rapid oxidation stage	Dehydration stage	Thermal decomposition stage	Slow oxidation stage	Advance oxidation stage	Rapid oxidation stage
10	40.55	78.83	96.82	26.88	36.08	32.16	48.68	78.75
20	41.06	80.33	98.59	26.87	42.97	32.79	49.12	77.08
30	41.11	80.96	98.59	27.95	46.31	32.65	47.04	77.98

**Fig. 6. Effect of oxygen concentration on the mass changes during low-temperature oxidation of coal.**

mass shows only slight influence on the activation energies at the thermal decomposition stage obtained from the TG-air curves, while it shows no effect at other stages such as dehydration stage and oxidation stage. As Table 5 shows, the activation energies at these three stages obtained from the TG-subtraction curves were basically unchanged with the increase of coal mass, with the average values of 32.53 kJ mol<sup>-1</sup>, 48.29 kJ mol<sup>-1</sup> and 77.93 kJ mol<sup>-1</sup> at slow oxidation stage, advanced oxidation stage and rapid oxidation stage, respectively. These results indicate that the activation energies obtained from the TG-subtraction curves can be used to describe the intrinsic reaction between coal and oxygen in low-temperature oxidation of coal.

### 3-3. Effect of Oxygen Concentration

Oxygen concentration is also an important factor affecting the process of coal oxidation at low temperature. Fig. 6 shows the

effect of oxygen concentration on the changes of coal mass in the oxidation. It can be seen from Fig. 6 that while oxygen concentration showed no effect on the characteristic temperature  $T_1$ , it had obvious influence on the characteristic temperature parameter  $T_2$ .  $T_2$  was around 246.0 °C, 228.5 °C and 226.3 °C for the oxygen concentration of 12.5%, 20.9% and 37.5%, respectively. This result indicates that the temperature at which coal mass achieved its maximum value due to the chemisorption of oxygen rose with the increase of oxygen concentration. Also, the rise in  $T_2$  was only about approximately 2 °C with the increase of oxygen concentration from 20.9% to 37.5%. This observation suggests that the internal diffusion control of oxygen in coal pore structure might be neglected when oxygen concentration is up to 20.9%.

Based on the data in Fig. 6, the calculated activation energies at these three stages are presented in Table 6. As can be seen the oxy-



**Table 6.** Effect of oxygen concentration on the activation energy

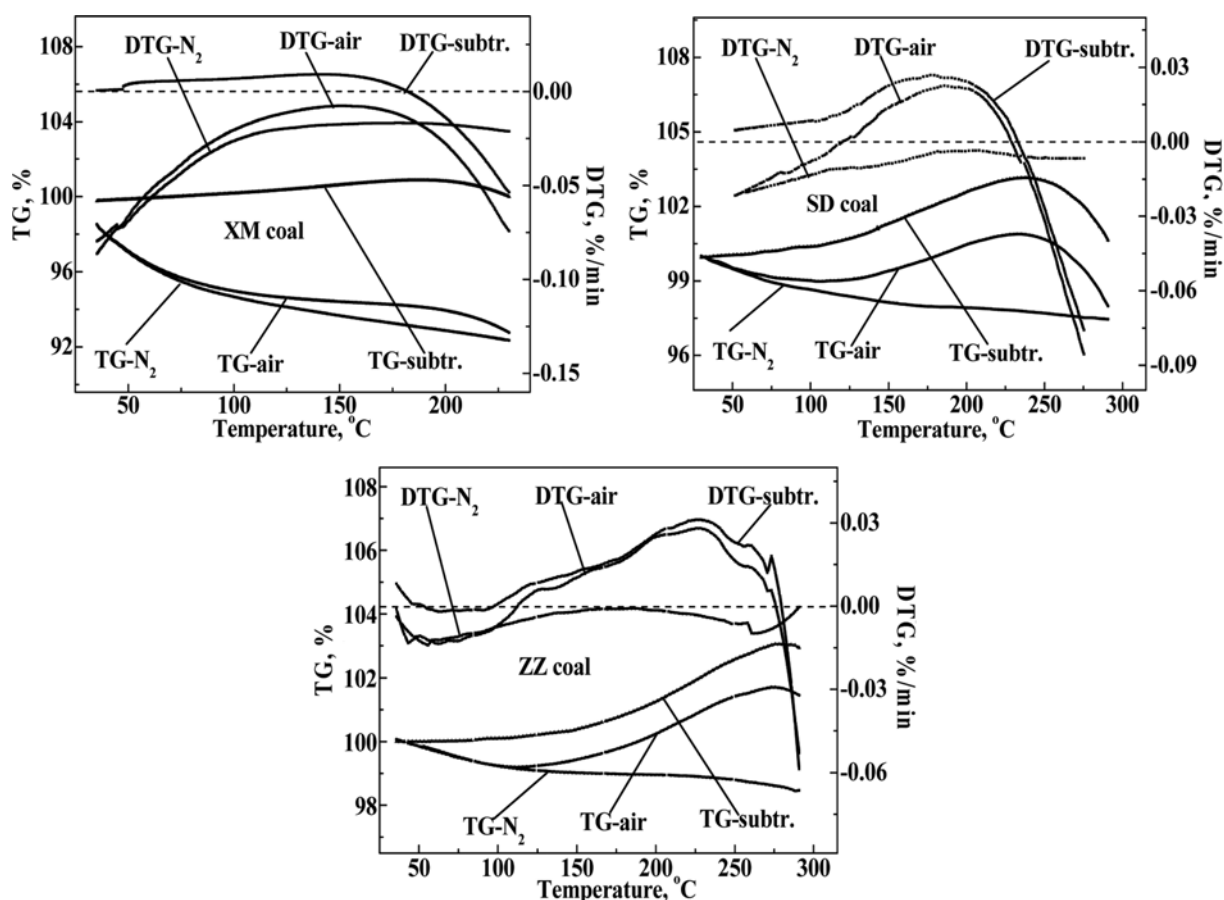
Oxygen concentration (%)	$E_{Air}$ (kJ mol <sup>-1</sup> )			$E_{N_2}$ (kJ mol <sup>-1</sup> )		$E_{subtr.}$ (kJ mol <sup>-1</sup> )		
	Dehydration stage	Advanced oxidation stage	Rapid oxidation stage	Dehydration stage	Thermal decomposition stage	Slow oxidation stage	Advance oxidation stage	Rapid oxidation stage
12.5	41.25	83.15	120.56	25.26	30.75	31.21	53.95	91.23
20.9	40.55	77.83	95.82	26.88	36.08	32.16	48.68	78.75
37.5	42.11	75.56	96.25	27.95	46.31	30.56	47.37	77.21

gen concentration showed no effect on the activation energies at the dehydration stage, while its effect at the oxidation stage was obvious. The activation energies at these three oxidation stages decreased with the increase of oxygen concentration. For instance, the activation energy at the advanced oxidation stage, obtained from the TG-air, increased from 77.83 to 83.15 kJ mol<sup>-1</sup>, and the activation energy at the rapid oxidation stage increased from 95.82 to 120.56 kJ mol<sup>-1</sup> with the decrease of oxygen concentration from 20.9% to 12.5%. Also, oxygen concentration had negligible effect on the activation energies at the slow oxidation stage obtained from the TG-subtraction curves. However, oxygen concentration had an obvious effect on the activation energies at the advanced oxidation and rapid oxidation stages obtained from the TG-subtraction curves. These results indicate that the effect of oxygen concentra-

tion on the process of coal oxidation at low temperature is mainly reflected at the stage of the oxidation reaction between coal and atmospheric oxygen. Because of small oxygen consumption, the oxygen concentration had nearly no effect on the activation energies at the slow oxidation stage. When the coal self-heating developed into an advanced stage, the demand for oxygen consumption increased and the effect of oxygen concentration appeared. Table 6 also shows that when oxygen concentration was above 20.9%, there should have been enough oxygen in the atmosphere for the oxidation reaction. This might be the reason why the oxygen concentration showed no effect on the oxidation process, as the oxygen concentration was above 20.9%.

#### 4. Relevance between Mass Change and Coal Rank

As stated above, the low-temperature oxidation of coal involves

**Fig. 7.** Effect of coal characteristics on the changes of coal mass during low-temperature oxidation of coal.

the processes of water evaporation, thermal decomposition of inherent oxygen-containing groups, and the oxidation reaction between atmospheric oxygen and active groups within coal matrix. Due to the difference in the content of inherent water, oxygen-containing groups and active groups of different coals, the low-temperature oxidation of coal is closely related to the rank of coal. The difference in the tendency of the spontaneous combustion of different coal ranks is mainly reflected by the content and occurrence of active groups and inherent oxygen-containing species. To investigate the relevance between mass change and coal rank during oxidation at low temperature, the three 0.5 g coal samples were respectively heated at a heating rate of  $1 \text{ k min}^{-1}$  under different atmospheres, and their TG curves are shown in Fig. 7.

The TG- $\text{N}_2$  curves in Fig. 7 depict the mass loss due to the moisture evaporation and thermal decomposition of inherent oxygen-containing groups. Because the inherent moisture and oxygen-containing groups in XM lignite is more than these in SD and ZZ coal samples, the highest value for mass loss was found in XM coal and the lowest value in ZZ coal. As the results show, the mass of these three coal samples used in this study has the same trend of increase even below  $100^\circ\text{C}$ , though their increments were different with the order of  $\text{XM} > \text{SD} > \text{ZZ}$ . The TG-subtraction curves illustrate the mass increase due to the oxidation reaction between coal and oxygen, and this mass increase can be attributed to the formation of intermediate oxides. From these results it can be inferred that the stability of intermediate oxides due to chemisorption was increased with the rise of the coal rank. It can then be concluded that coal is more prone to spontaneous combustion if it is more prone to decompose its intermediate oxides formed during low-temperature oxidation.

The activation energy is one of the important indices for evaluating the spontaneous combustion of coal. The activation energies of these three coal samples oxidized under different atmospheres are shown in Table 7. Because every stage of coal oxidation at low temperature is determined by the coal characteristics, the activation energy at each stage is related to the coal rank. From Table 7, the activation energies for moisture evaporation and thermal decomposition increased with the rise of coal rank. And the activation energies at the advanced oxidation and rapid oxidation stages, obtained from TG-air curves, also increased with the increase of coal rank.

From Table 7, it can be seen that the activation energies at the slow oxidation and advanced oxidation stages, obtained from the TG-subtraction Curves, increased with coal rank, while the activation energies at the rapid oxidation stage remained almost the

same. These results indicate that the activation energies at the first two stages can be considered to be index parameters for identifying the tendency of spontaneous combustion of coal. Table 7 also shows that the activation energies at the three stages, obtained from the TG-subtraction curves, were lower than these obtained from the TG-air curves. This is because coal oxidation under air atmosphere contains at least three parallel processes and the activation energies obtained from the TG-air curves reflect combinations of activation energy due to overlapping mechanisms. However, the activation energies obtained from the TG-subtraction curves only represented the activation energies of oxidation reaction between coal and oxygen, and these values elucidate the intrinsic reaction of coal oxidation at low temperature. Furthermore, the activation energies at the slow oxidation stage can be obtained from the TG-subtraction curves and cannot be calculated from the TG-air curves. The subtraction method applied in this study is a quite promising method in deriving the kinetics of low-temperature coal oxidation to determine the susceptibility of coal to self-heating and spontaneous combustion.

## CONCLUSION

The subtraction method of TGA was used in this study to investigate the intrinsic reaction between coal and atmospheric oxygen, which is the main heating source in coal self-heating and spontaneous combustion. By means of the subtraction analysis method of TGA, the TG-subtraction curves were obtained by subtracting the TG- $\text{N}_2$  curves from the TG-air curves. These results indicate that the TG-subtraction curves can represent the intrinsic reaction of coal oxidation by eliminating the influence of evaporation of water and thermal decomposition of inherent oxygen-containing groups. Compared with the TG-air curves, not only can the TG-subtraction curves minimize the experiment error resulting from experimental conditions, but also reflect the intrinsic reaction of coal spontaneous combustion. The stability of intermediate oxides due to chemisorption can also be improved with the rise of coal rank. In terms of the rate of mass change, the intrinsic reactions can be divided into three stages: slow oxidation stage, advanced oxidation stage and rapid oxidation stage. The activation energies at the slow oxidation and advanced oxidation stages, obtained from the TG-subtraction curves, increased with coal rank, while the activation energies at the rapid oxidation stage remained almost unchanged. These results indicate that the activation energies at the first two stages can be considered to be index parameters for identifying the tendency of spontaneous combustion of

**Table 7. Effect of coal characteristics on the activation energy**

Coal rank	$E_{\text{Air}} (\text{kJ mol}^{-1})$			$E_{\text{N}_2} (\text{kJ mol}^{-1})$		$E_{\text{subtr.}} (\text{kJ mol}^{-1})$		
	Dehydration stage	Advanced oxidation stage	Rapid oxidation stage	Dehydration stage	Thermal decomposition stage	Slow oxidation stage	Advance oxidation stage	Rapid oxidation stage
XM coal	35.5	65.12	86.26	23.26	30.75	30.21	42.56	76.23
SD coal	40.55	77.83	95.82	26.88	36.08	32.16	48.68	78.75
ZZ coal	42.11	82.96	105.59	27.95	46.31	40.56	56.23	80.98

coal. The subtraction method applied in this study is a quite promising method in deriving the kinetics of low-temperature coal oxidation to determine the susceptibility of coal to self-heating and spontaneous combustion.

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