

Research Article

Inhibition Effect of Phosphorus Flame Retardants on the Fire Disasters Induced by Spontaneous Combustion of Coal

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Coal spontaneous combustion (CSC) generally induces fire disasters in underground mines, thus causing serious casualties, environmental pollution, and property loss around the world. By using six P-containing additives to process three typical coal samples, this study investigated the variations of the self-ignition characteristics of the coal samples before and after treatment. The analysis was performed by combining thermogravimetric analysis/differential scanning calorimetry (TG/DSC) Fourier transform infrared spectrometer (FTIR) and low temperature oxidation. Experimental results showed that P-containing inhibitors could effectively restrain the heat emitted in the combustion of coal samples and therefore the ignition temperature of the coal samples was delayed at varying degrees. The combustion rate of the coal samples was reduced as well. At the temperatures ranging from 50°C to 150°C, the activation energy of the coal samples after the treatment was found to increase, which indicated that the coal samples were more difficult to be oxidized. After being treated with phosphorus flame retardants (PFRs), the content of several active groups represented by the C-O structure in the three coal samples was proved to be obviously changed. This suggested that PFRs could significantly inhibit the content of CO generated by the low temperature oxidation of coal, and the flame-retardant efficiency grew with the increasing temperature. At 200°C, the maximal inhibition efficiency reached approximately 85%.

1. Introduction

Coal-mine fire hazards caused by CSC have always been one of the main disasters found in underground mines [1, 2]. During 2001–2013, hundreds of serious fire accidents have occurred in China, resulting in over 800 casualties [3]. It is well known that the CSC is one of main reasons responsible for underground mine fire [4]. According to reports, fire disasters aroused by CSC in goafs have occurred in a vast area reaching 56.59 km² in Shanxi, China, at present. Accordingly, 240 million tons of coal resource is lost, leading to a direct economic loss over 15 billion dollars [5, 6]. CSC can not only consume valuable coal resource but also generate a large amount of fumes including CO, CO₂, SO₂, and NO_x [7–9]. As a consequence, it significantly damages and influences the atmospheric environment, vegetation, water, and land resources and also induces various geologic hazards [9, 10]. To prevent such disasters, people have developed various fire preventing and extinguishing methods [11]. Initially,

yellow mud or sand was used to mix with water to prepare grouting [12]. However, this kind of material showed poor performance in some harsh environment. Subsequently, people adopted gel [13], foams [14], and so on to control the low temperature oxidation of coal and prevent fire disasters in goafs. But these materials are expensive and the fire extinguishment efficiency mainly depends on the isolation of coal from air. In terms of chemical flame retardants, the commonly used ones are inorganic salt including MgCl₂ and CaCl₂ [15]. So far, there are few studies on the effects of P-containing inhibitors. Characterized by halogen-free, low smoke, and low toxicity, PFRs show a high efficiency in few amounts and can be used in various fields. As a result, they have been rapidly developed in recent years. With excellent thermostability, PFRs can generate glassy substances with rich phosphor after dehydration by continuous heating. These glassy substances cover the surface of base materials, thus isolating the air to hinder the continuous combustion of material. Compounds including ammonium polyphosphate

TABLE 1: Technical parameters of experimental coal samples.

Name	Proximate analysis				Elemental analysis					Calorific value MJ·kg ⁻¹	Coal rank
	Moisture%	Ash%	Volatile%	Fixed carbon%	C	H	O	N	S		
Zhaotong coal	8.01	20.16	48.93	30.91	52.29	3.92	30.66	1.71	0.16	18.25	Lignite
Bulianta coal	4.98	6.44	32.31	63.33	81.05	4.13	13.46	0.96	0.40	32.10	Subbituminous
Xiqu coal	0.46	10.64	21.18	70.48	91.12	4.76	2.30	1.48	0.43	27.32	Bituminous

TABLE 2: Additives used in the experiment.

Name	Chemical formula	Purity	Manufacturer
Zinc phosphate	Zn ₃ (PO ₄) ₂	>99%	Sinopharm Group Co., Ltd.
Potassium dihydrogen phosphate	KH ₂ PO ₄	>99%	Sinopharm Group Co., Ltd.
Sodium hydrogen phosphate	Na ₂ HPO ₄	>99%	Sinopharm Group Co., Ltd.
Ammonium phosphate	(NH ₄ PO ₃) _n	>98%	Taixing Chemical Co., Ltd.
Trichloroethyl phosphate	C ₆ H ₁₂ Cl ₃ O ₄ P	>99%	Chemical & Materials Co., Ltd.
Diphenyl hydrogen phosphate	C ₁₂ H ₁₁ O ₄ P	>99%	Chemical & Materials Co., Ltd.

and phosphate have been widely used in plastic industry and can help to improve the flame-retarding properties of plastics. Wang et al. used microencapsulated red phosphorus and aluminium hypophosphite to jointly inhibit the combustion of polyethylene. Based on the obtained results, they found that using P-containing compounds can reduce the heat emitted in the combustion and enhance the thermostability of polyethylene [16]. Luo et al. synthesized a kind of P-containing epoxy resin with high performance through addition reaction, showing good inflaming retarding and mechanical properties [17]. Hence, by using P-containing additives to deal with coal samples, this research studied the influence of P-containing additives on the CSC and explored the chemical inhibition mechanism of PFRs.

2. Experiments

In this study, lignite (ZT) collected from Zhaotong in Yunnan, subbituminous coal (BLT) acquired from Bulianta in Inner Mongolia, and bituminous coal (XQ) from Xiqu in Shanxi, China, were served as the coal samples. The specific parameters of these samples are shown in Table 1. To begin with, the fresh coal lump was broken into pieces to select the lumps broken with the length in a range of 0.18–0.25 mm as the specimens. Then, these specimens were dried in a vacuum drying oven at 50°C until their masses maintained unchanged. Next, six kinds of P-containing agents were used as additives (as demonstrated in Table 2) to prepare the solution with a concentration of 5%. Afterwards, 100 g of coal samples were immersed in 500 ml solution for 24 h, followed by conducting repeated drying. FTIR with the wavenumber varying from 500 to 4,000 cm⁻¹ was used to analyze the coal samples before and after the treatment. Meanwhile, experiments were carried out using TG/DSC to analyze the thermal change of the coal samples in the combustion process in the air at a heating rate of 10°C/min. In addition, a temperature programming device (as illustrated in Figure 1) was used to test the generation of CO in the coal samples before and after the treatment with P-containing agents, as

well as to evaluate the inhibition effects. Air was flowed at 20 ml/min into this device with the temperature ranging from 60°C to 200°C at a heating rate of 1°C/min.

3. Results and Discussion

3.1. Infrared Spectroscopic Analysis. As demonstrated in Figure 2, the absorption peaks of the infrared absorption spectrum for the BLT coal mainly included the out-of-plane stretching vibration induced in case heteroatoms at 508–872 replaced C-H, the C-O vibration between 1077 and 1374, the vibration of aromatic-ring C=C band at 1591–1601 cm⁻¹, 2851 cm⁻¹, and the vibration of -CH₂- at 2921 cm⁻¹, as well as the vibration of OH-stretching bands at 3006–3537 cm⁻¹. For the infrared absorption spectrum of the XQ coal, the stretching vibration of heteroatoms between 555 and 914 cm⁻¹, the C-O vibration at 1008 cm⁻¹, the vibration of aromatic-ring C=C bands at 1437–1607 cm⁻¹, and the vibration of -CH₂- at 2847–2919 cm⁻¹ were primarily contained. In addition, the following absorption peaks were observed in the infrared spectrum for the ZT coal: the absorption peak of heteroatoms at 561–795 cm⁻¹, the stretching vibration of C-O at 1003–1342 cm⁻¹, and the vibration of OH-stretching bands at 3025–3697 cm⁻¹. After the treatment using P-containing additives, obvious changes happened to the infrared absorption spectra of these three coal samples. For example, the absorption peak for the OH structure of the ZT coal at 3464 cm⁻¹ was enhanced to varying degrees, while the content of the C-O was apparently reduced. As to the BLT coal, the number of -CH₂- and C-O structures was obviously lowered. As to the XQ coal, new absorption peaks representing the OH structure occurred at 3349 cm⁻¹; meanwhile, the absorption peaks for the stretching vibration of C-O were weakened at 1054 cm⁻¹. In general, the C=C structures in these three coal samples exhibited moderate variation, while the content of the C-O structure reduced. The C-O structure is the critical structure influencing the low temperature oxidation of coal [18], which revealed that phosphorous flame retardants can

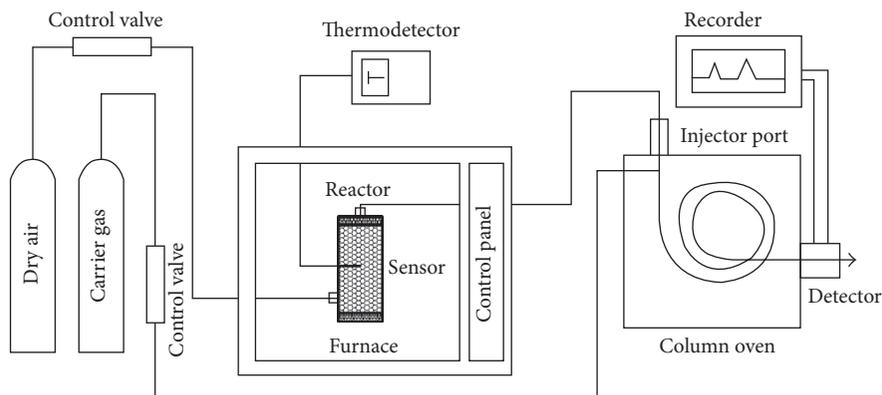


FIGURE 1: The experimental setup.

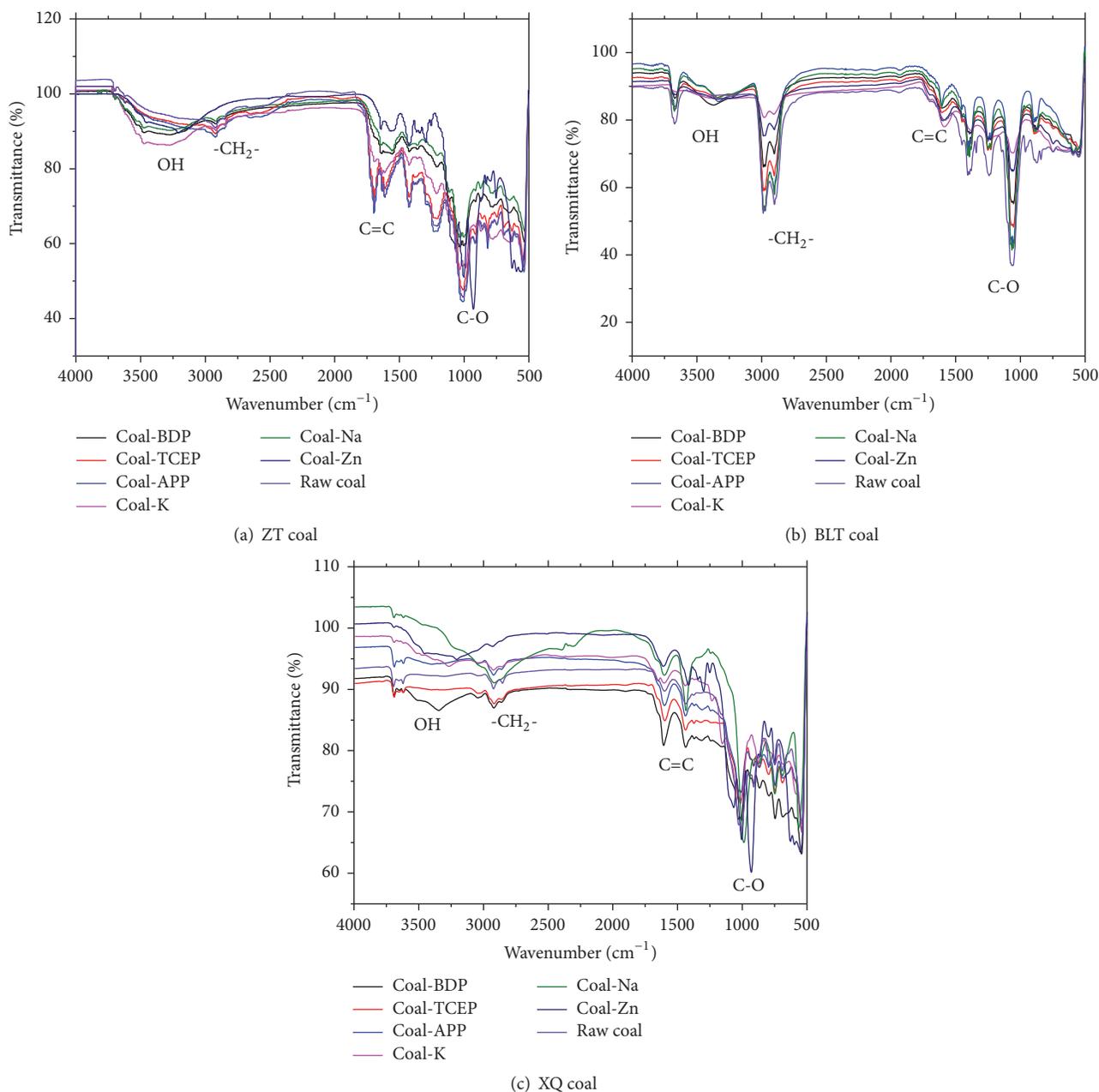


FIGURE 2: The FTIR of coal samples before and after treatment.

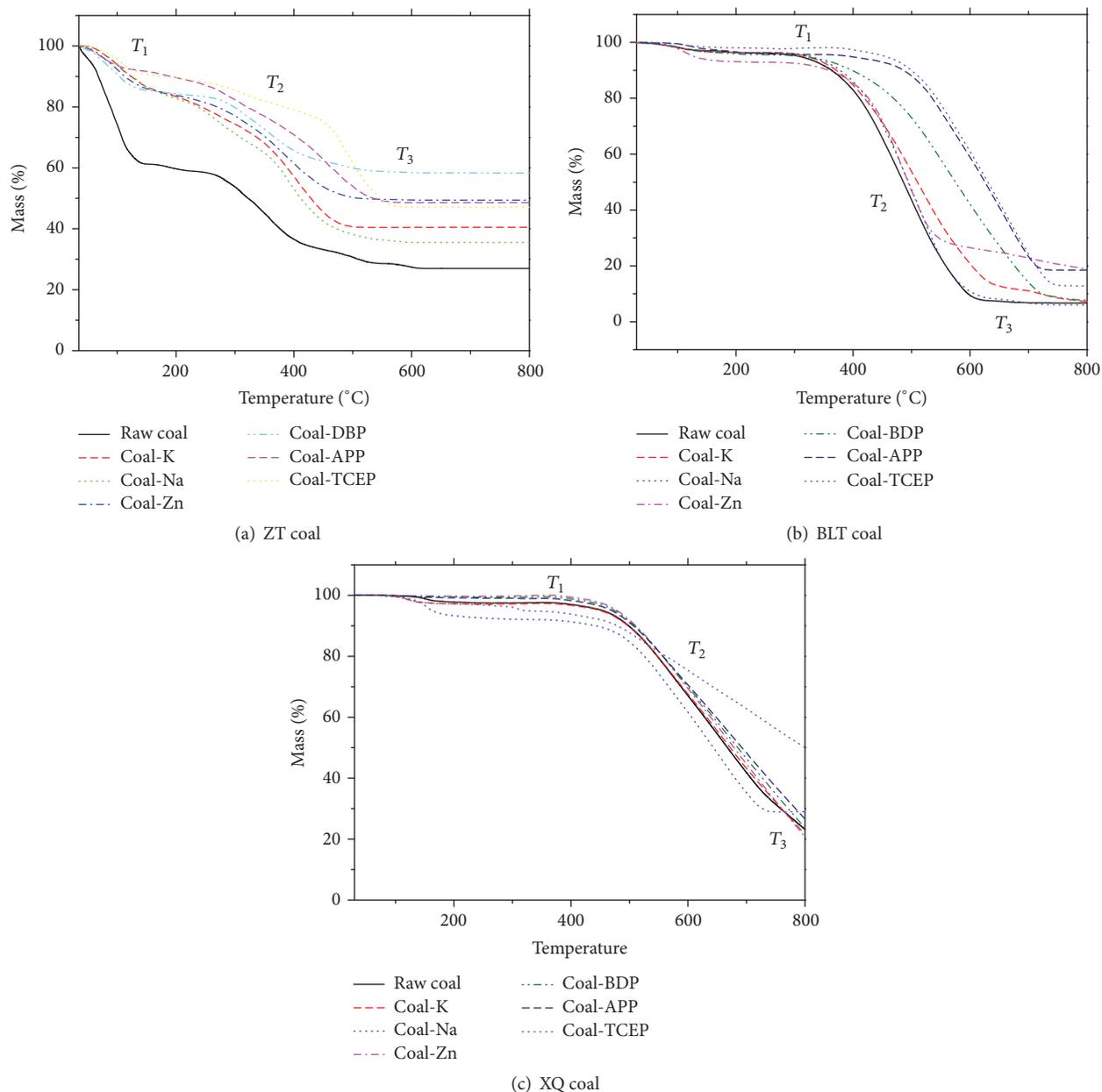


FIGURE 3: The TG curves of coal samples before and after treatment.

weaken the active structures including oxygen-containing functional groups in coal, thus affecting the low temperature oxidation of coal.

3.2. Thermal Analysis. Based on the thermal analysis, it was found that, after the treatment using P-containing additives, the thermogravimetric curves of the coal samples varied in different degrees. According to Figure 3, the combustion of coal can be divided into three stages: precombustion, combustion, and stabilization. Before 200°C, all three coal samples show similar trend in TG and DSC curves. The P-containing inhibitors play a significant role on the controlling of low temperature oxidation. And this phenomenon

remains with the temperature increasing. For the ZT brown coal, raw coal was gradually oxidized with the increasing temperature before 200°C, while it was rapidly combusted and decomposed when the temperature varied from 250°C to 300°C. After the temperature reached 600°C, the combustion basically stopped and the mass of the coal maintained stable. After the addition of the P-containing inhibitors, the coal was slowly burned and it can be found that both the critical temperature T_1 and combustion temperature T_2 of the coal were obviously postponed and the mass loss rate of the coal was also slowed down. Similarly, as shown in Figure 4, the differential scanning calorimetry (DSC) curve of the ZT coal indicated that the heat emitted by the treated coal sample

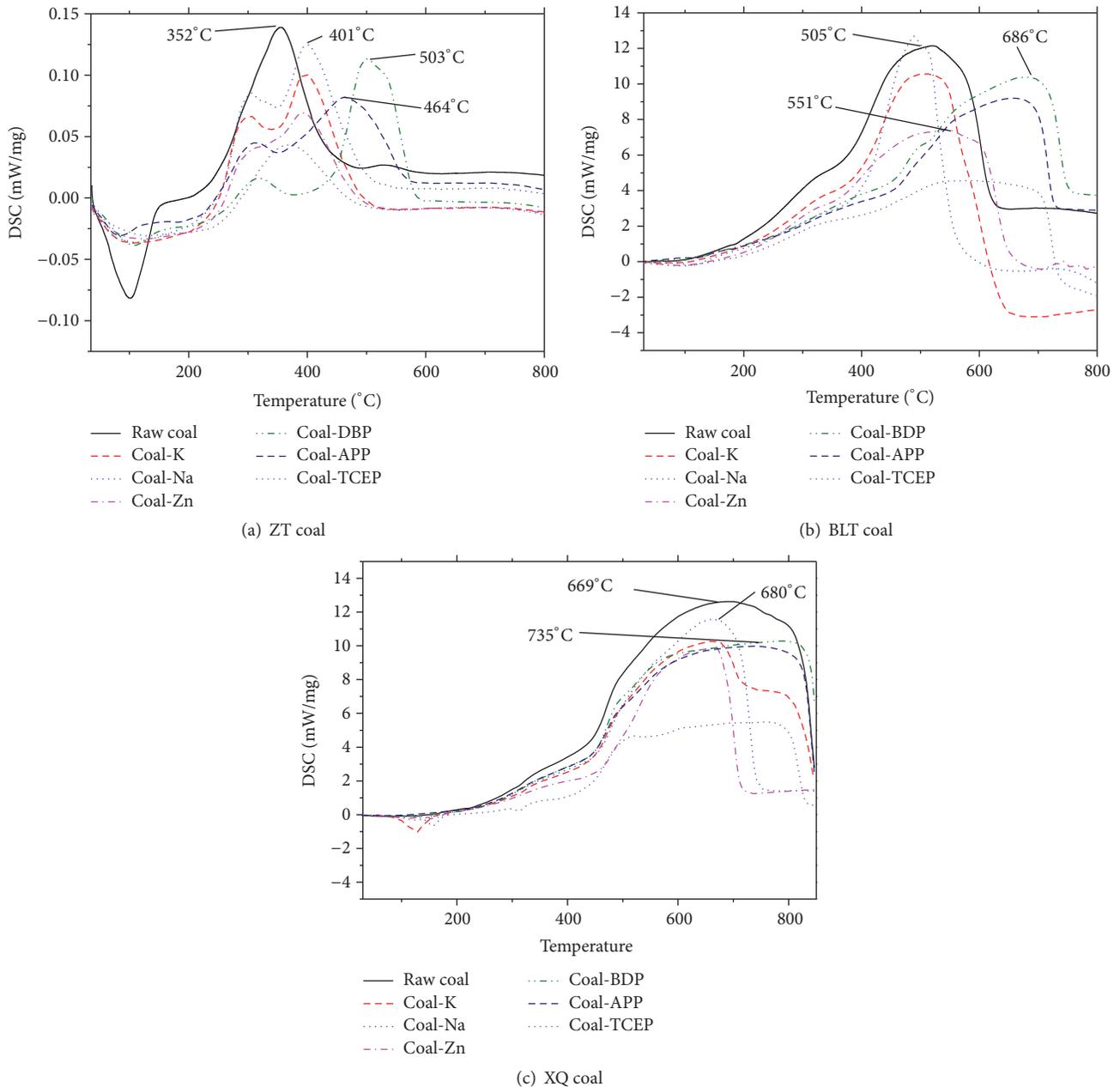


FIGURE 4: The DSC curves of coal samples before and after treatment.

was also changed: not only the heat released reduced, but also the temperature at which the greatest exothermic peak delayed occurred. In contrast, the BLT and XQ coal also showed similar rules, that is, the heat released by the coal after the treatment was significantly lowered. For example, the exothermic peak of ZT raw coal in DSC curve is 352°C. After the treatment by BDP, this temperature postpones to 503°C. The masses of these two kinds of coal samples were slightly changed owing to the addition of P-containing flame retardants before 200°C. Between 200 to 400°C, this tendency has been further strengthened. At 300°C, the heat flux of XQ raw coal is 1.486 mW/mg, while the date of coal treated by TCEP is only 0.263 mW/mg. However, after the temperature

reaches 400°C, the coal samples were burned and therefore remarkable difference was shown to the mass loss rates of the coal samples before and after the treatment.

This suggested that PFRs can be used to effectively control the combustion of coal.

The oxygenolysis of coal was a typical gas-solid reaction. Assuming that reaction order of coal was 1, according to chemical reaction kinetics, the activation energy of the coal was calculated by adopting the Coats-Redfern integral formula [19]:

$$\ln \left[\frac{g(a)}{T^2} \right] = \ln \left[\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) \right] - \frac{E}{RT}, \quad (1)$$

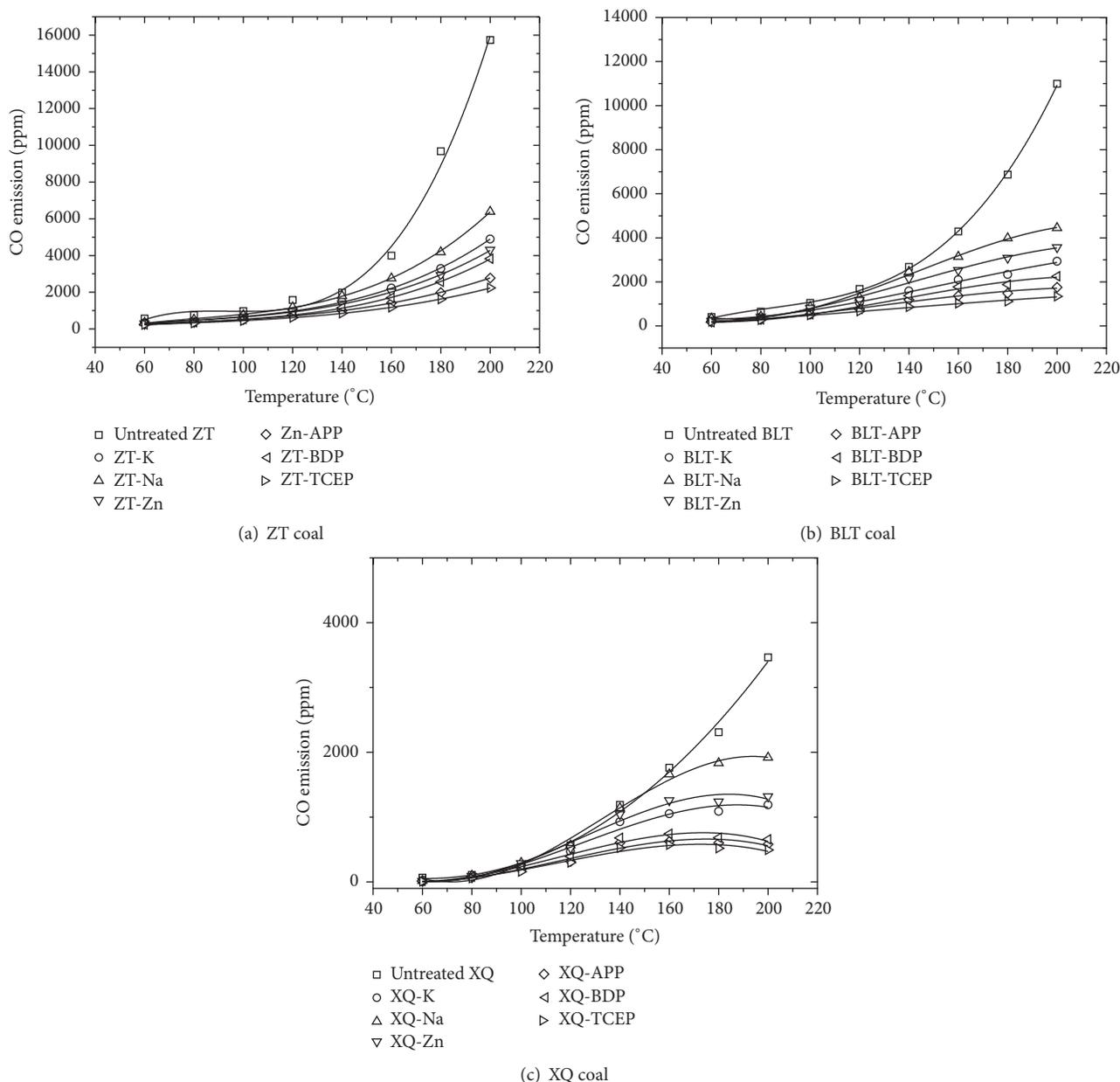


FIGURE 5: The CO emission of coal samples before and after treatment.

where a represented transformation percentage of coal in oxygenolysis process, β represented heating rate, and $g(a)$ was integral formula of function model, which reflected mechanism of oxidation reaction of coal. $g(a) = -\ln(1 - a)$. Meanwhile, t was reaction time, T was reaction temperature, A was preexponential factor, E_a was activation energy induced by oxygenolysis of coal, and R represented gas constant. Based on mechanism of the chemical reaction kinetics, the construction on $1/T$ was performed by utilizing $\ln(-\ln(1 - a)/T^2)$. Besides, according to the obtained slope, activation energy E_a of the reaction was expected to be calculated. According to Table 3, the activation energy of the coal samples after the treatment was improved to different degrees when the temperature varied from 50°C to 150°C

in comparison with those before the treatment. After the treatment using inorganic phosphorus agents, the coal dealt with zinc phosphate showed a significant change to the activation energy. In contrast, the optimal effects were found to the coal treated with the organic phosphorus agent tris(2-chloroethyl) phosphate (TCEP). The improvement of the activation energy indicated that the higher the energy needed for the low temperature oxidation of coal is, the more difficult the reaction happens.

3.3. Oxidation Products. As seen in Figure 5, as an index gas of CSC, the CO released in the oxidation of coal samples presented increased concentrations with the temperature. However, after the treatment using PFRs, the concentrations

TABLE 3: Activation energy of the coal samples before and after treatment.

Coal samples	Activation energy/(kJ·mol ⁻¹)						
	Raw coal	Coal-K	Coal-Na	Coal-Zn	Coal-BDP	Coal-APP	Coal-TCEP
ZT	74.6	76.4	77.3	75.7	98.1	81.4	114.6
BLT	76.1	83.2	78.3	80.5	82.1	90.6	115.2
XQ	119.8	130.1	124.7	126.5	131.9	142.6	178.9

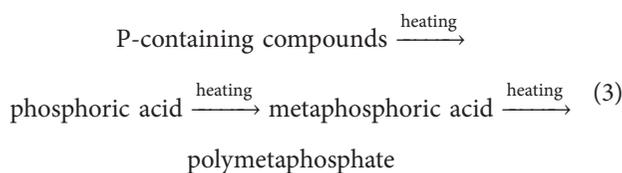
of CO caused by the combustion of coal samples apparently varied. For the XQ coking coal before the treatment, 259 ppm of CO was generated in the oxidation process at 100°C. However, after the treatment, the concentration of CO produced reduced to 156 ppm at minimum. With the increasing temperature, the coal samples treated with TCEP generated 493 ppm of CO at 200°C. Similar rules were also shown to the BLT and ZT coal. At 200°C, the concentrations of CO released by the BLT coal before and after the treatment were 10,994 ppm and 1345 ppm, separately, while those emitted by the ZT coal were 15,732 ppm at maximum and 2240 ppm at minimum. The inhibiting efficiency is expressed as shown in the following formula:

$$E = \frac{Cr - Ct}{Cr} \times 100\%, \quad (2)$$

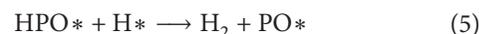
where E is the inhibiting rate of the inhibitor to the coal sample; Cr denotes the amount of CO released from the raw coal in the experiment with the unit of 10^{-6} ; Ct shows the amount of CO released from the coal treated with the inhibitor under the same condition with the unit of 10^{-6} .

According to the results calculated using formula (2), the maximal inhibiting rates of the phosphorous flame retardants to the ZT, BLT, and XQ coal were shown to be 53.5%, 52.9%, and 39.6% at 100°C, respectively. While these values changed to 85.7%, 87.1%, and 86.4% at 200°C, separately. This revealed that, compared with the combustion at a temperature lower than 100°C, the phosphorous flame retardants show more obvious inhibition effects on the CSC at a high temperature. Besides, comparing with the CO production, the CO₂ and C₂H₄ emission show the similar performance after the treatment of PFRs (Figures 6 and 7). For example, the ZT coal treated by TCEP has only 5527 ppm CO₂ emission at 200°C, while the raw coal peaks at 39343 ppm. At 200°C, the C₂H₄ yield of BLT coal climbs to 432 ppm, but the coal treated by ammonium phosphate (APP) only reaches 141 ppm.

3.4. Flame-Retardant Mechanism. With the application of PFRs, phosphorus compounds were decomposed in the combustion process of polymers with P-containing flame retardants owing to the effect of heat, accompanying with the following changes [20]:



Polymetaphosphate, as a nonvolatile stable compound, covers on the surface of the polymer, thus forming a charring layer. Since no flaming evaporative combustion or decomposition combustion would happen to simple substance carbon, polymetaphosphate can inhibit the combustion. In addition, since phosphoric acid and polymetaphosphate show strong dehydration properties, carbonized films were formed on the surface of the polymer, thus inhibiting the combustion. This is the flame-retardant mechanism of PFRs in the condensed phase of polymers. PFRs are also a kind of radical scavengers. The mass-spectrometric technique revealed that PO was generated in any P-containing compounds in the combustion of polymers. It can combine with the hydrogen atoms in the flaming area, thus restraining the flaming [21]. The specific action is expressed as



The phosphorus could inhibit the self-ignition of coal efficiently. Superabundant phosphorus in coal also work against the clean and efficient utilization of coal. When the coal was adopted as boiler fuel, P-containing compounds in coal will decompose at high temperature and then form sediments which are difficult to clear on the heating surface of boiler. Moreover, during the iron-making and steel-making process, the existence of phosphorus element will influence the quality of iron and steel. As the results, the content of phosphorus in coal is strictly limited around the world. Considering safety factors, phosphorus flame retardants could be widely applied in the abandoned area of colliery, such as gob, goaf, and coal waste heap. However, we still need comprehensively assessment before being utilized in storage and transportation of coal.

4. Conclusions

It is essential to use effective flame retardants for the prevention of CSC so as to further guarantee the mine safety. Although PFRs have played a significant role in the industrial production of polymers, more exploration is still needed in its role in the inhibition of CSC. Laboratorial research was attempted to explore the inhibition mechanism of PFRs on the organic functional groups in coal molecules. The experimental results revealed that phosphorus could effectively inhibit CSC at a high temperature interval. Although certain effects could also be emerged at a low temperature range, they were less obvious compared with that at a high temperature with a maximal inhibiting rate above 80%.

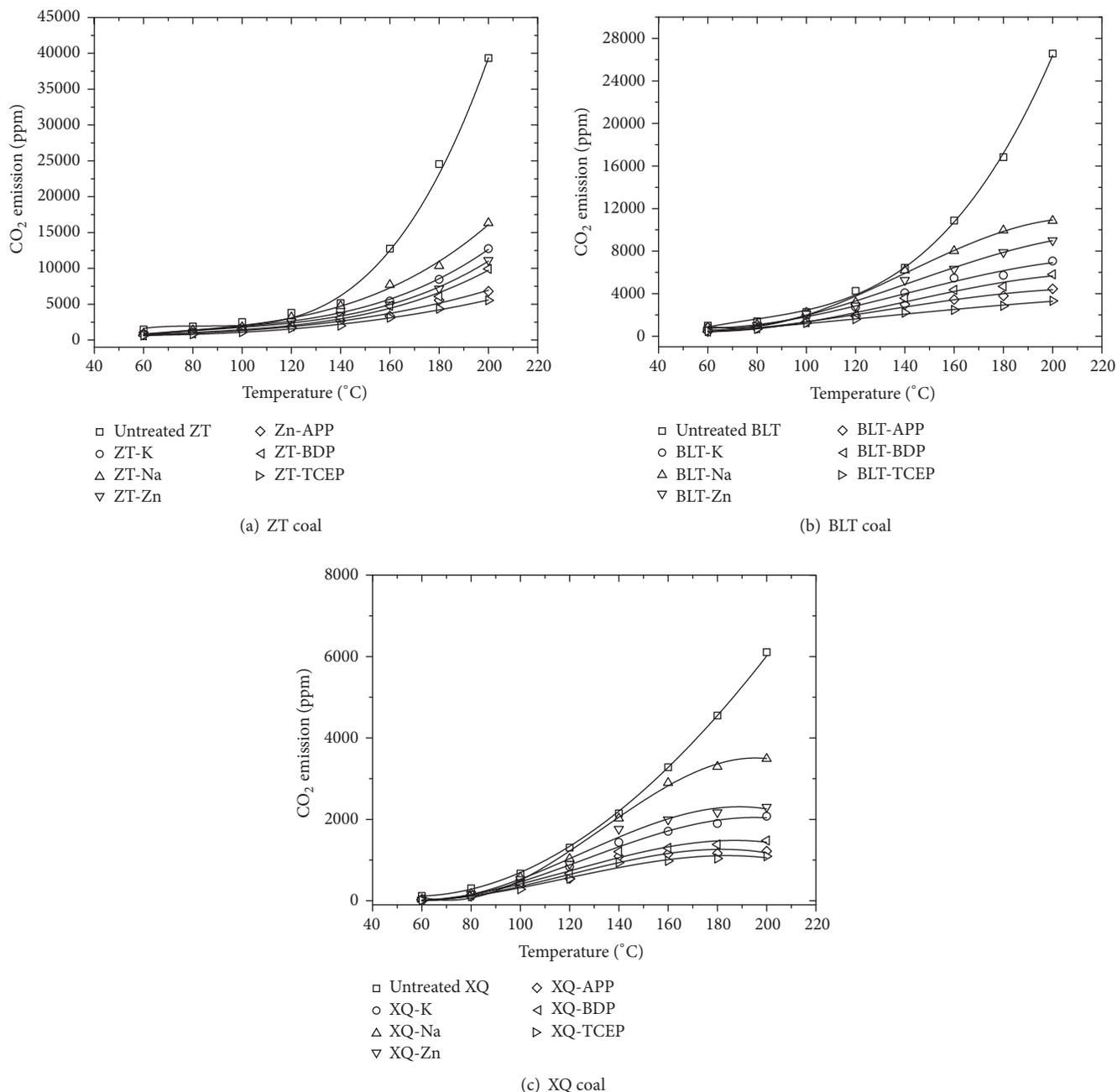


FIGURE 6: The CO₂ emission of coal samples before and after treatment.

The results obtained using the FTIR indicated that, for the coal samples with different coal ranks, the C-O structures in the coal after the treatment were obviously weakened. Similar results were also obtained in the thermal analysis and temperature programming experiment: using P-containing compounds can reduce the heat released in the combustion of coal and increase the difficulty in the reaction between coal and oxygen. This research provides a favorable reference to the application of P-containing inhibitors.

Competing Interests

The author declares that they have no competing interests.

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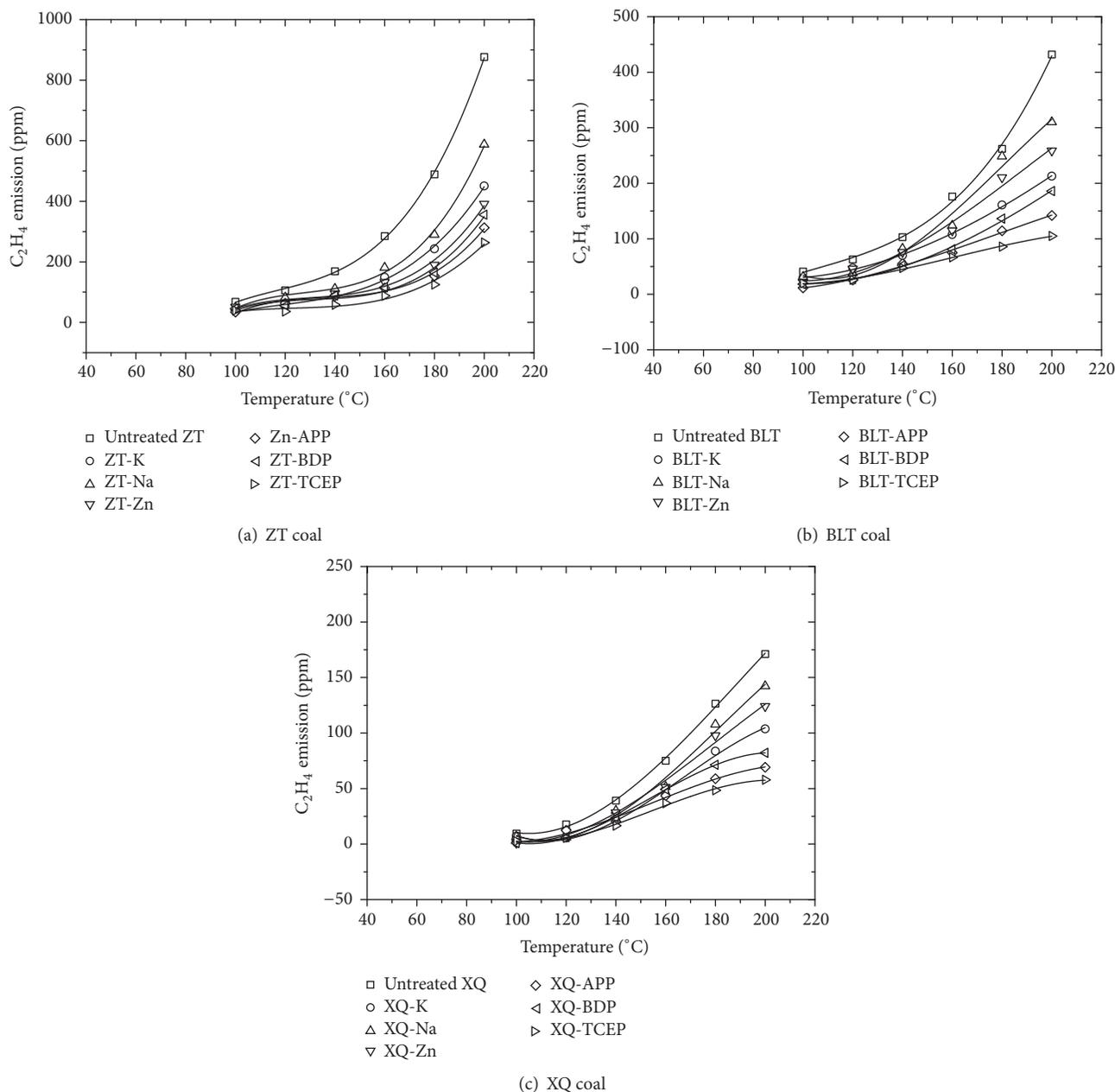


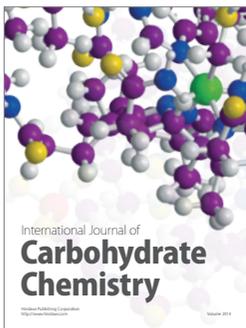
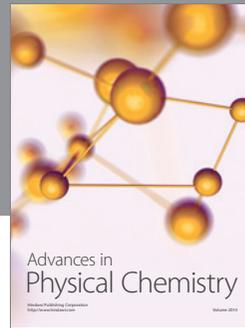
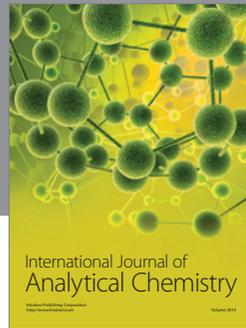
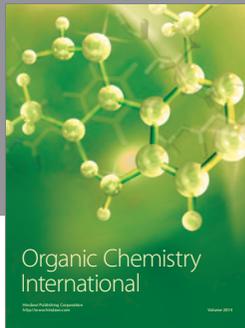
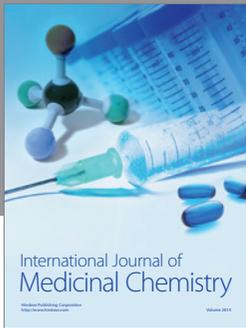
FIGURE 7: The C_2H_4 emission of coal samples before and after treatment.

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