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Experimental Study on the Inhibition Effect of the Inhibitor on Coal Spontaneous Combustion Under Critical Temperature

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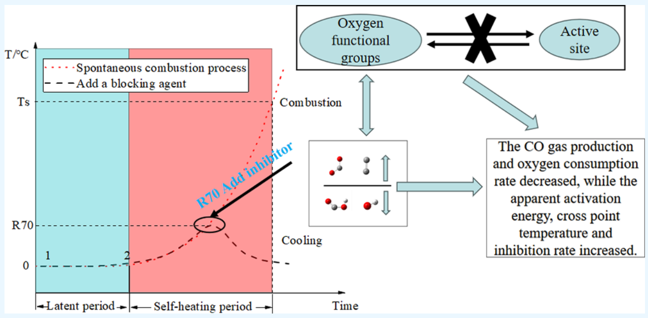
ABSTRACT: At present, related research on inhibitors has been gradually improved, but there is still a lack of research on the inhibition characteristics at specific release temperatures and the mechanism of inhibiting coal spontaneous combustion. Based on this, In this study, the inhibition characteristics of adding inhibitor to coal under critical temperature (R70) are studied in depth. In the experiment, lignite was selected as the research object, and four different types of inhibitors, $MgCl_2$, triphenyl phosphite (TPPI), Phytic acid (PA), and melatonin, were applied to coal samples at room temperature and 70 °C, respectively. The temperature-programmed-gas chromatography test and Fourier infrared spectroscopy experiment were carried out, and the oxidation kinetic parameters were calculated to study the oxidation characteristics and micromechanism of the coal samples in the process of spontaneous combustion. The experimental results show that the amount of CO gas release and oxygen consumption rate are lower, and the inhibition rate and apparent activation energy are higher when the inhibitor is added under R70 than at room temperature. Under R70, the content of oxygen-containing functional group −COOH with higher activity of inhibitor is reduced, the generation of active sites is inhibited, the concentration of active center is reduced, the path of mutual transformation between active sites and oxygen-containing functional groups is blocked, and the active groups are promoted to form a relatively stable inert oxygen-containing ether bond, which reduces the spontaneous combustion tendency of coal.



1. INTRODUCTION

Coal, being a major fossil fuel, contributes significantly to global energy consumption.[1,2] The active functional groups in coal react with oxygen and release heat during the mining and storing processes. If not regulated in time, the accumulating heat will cause coal to spontaneously burn, resulting in massive resource loss environmental devastation, and even casualties.[3−6] For the effective control of the spontaneous ignition of coal, domestic and foreign industry scholars have developed various types of inhibitor products to suppress coal spontaneous combustion

Existing research generally considers coal oxidation temperatures below 70 °C to be the critical stage of coal spontaneous ignition. Adiabatic oxidation tests are frequently used to investigate the spontaneous ignition tendency of coal during the heating stage of 40 to 70 °C. This stage's oxidation of active sites causes the production of CO and CO_2 to be far more than that of raw coal.[7] Based on the cross-point temperature method, Li et al. measured the critical temperature of Xinfeng lean coal as 83.4 °C, and the critical temperature of large long flame coal as 78.2 °C.[8] Zhang[9] studied the No.15 coal in Wangtaipu Mine by using a large coal pile test bench and found that the oxygen consumption rate gradually increased at 80 °C ∼ 110 °C, and the reaction gradually accelerated. Zhong et al.[10] measured the critical temperature points of coal with different metamorphic degrees by different experimental methods. Deng et al.[11] found that the CH_4 concentration production rate was very small when the coal temperature was lower than 90 °C. When the temperature was higher than 90 °C, the gas concentration began to increase continuously, and the chemical reaction of coal began to accelerate. Qu and Zheng[12] through the temperature programming and infrared functional group test of Hegang and Tangshan coal samples, the critical temperature of the Hegang coal stage is 65 °C respectively. The critical temperature of the Tangshan coal stage is 75 °C. The research of scholars shows that the R70 value is an important reference for evaluating the tendency of coal spontaneous combustion. Taking 70 °C as the dividing line, the self-thermal oxidation of coal samples shows linear and exponential laws, respectively.

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Table 1. Industrial and Elemental Analyses of Coal Samples

	industrial analysis (wt %)				elemental analysis (wt %)				
sample	Vad	Mad	Aad	FCad	C%	H%	O%	N%	S%
Ping-Zhuang	17.67	13.14	26.88	42.31	57.62	2.34	14.12	1.13	1.32

To better explore the optimal temperature of the inhibitor for coal inhibition, this paper selects the critical temperature of 70 °C and normal temperature coal for comparison.

Li et al.[13] found that using the temperature temperature-programmed oxidation method and the Fourier infrared method, the effect of sodium persulfate inhibitor with a mass fraction of 5% was the best in the low-temperature stage. Gao and Ran[14] found that by using a temperature-programmed approach, a certain proportion of CaCl2 and tea polyphenols could increase the inhibition rate. Li et al.[15] proved that using thermal analysis, infrared spectroscopy, low-temperature oxidation studies, and cross-point temperature, the metal chelating agent EDTA can suppress coal spontaneous combustion and have a good inhibitory impact on diverse coal samples. Guo et al.[16] found that the primary component of TP, VCH15, or H48 of epigallocatechin gallate, may easily scavenge oxygen-containing free radicals and limit the synthesis of active groups in coal. Li et al.[17] proved that experiments show that TEMPO has a significant inhibitory effect on coal spontaneous combustion, and believed that the simultaneous combustion of TEMPO and alkyl radicals in the process of coal spontaneous combustion reduces the activity of free radicals and the concentration of active free radicals, thereby reducing the chain reaction of free radicals. Zhang and co-workers[18] inorganic salt inhibitors magnesium chloride and calcium chloride were coupled with free radical scavengers N, N-dibenzyl hydroxylamine (DBHA), and 2,6-di*tert*-butyl-4-methylphenol (BHT) to generate a composite inhibitor that inhibits coal spontaneous combustion continuously and efficiently. Deng et al.[19] introduced the aerosol inhibitor atomization performance test system and selected different concentrations of $NH_4H_2PO_4$, $NaHCO_3$, and $MgCl_2$ solutions for atomization. It was concluded that 3% $NaHCO_3$ solution had the best atomization effect and 25% $MgCl_2$ solution had the strongest stability. Hou et al.[20] found that phytic acid can effectively chelate Ca, Fe, Mg, Mn, and other metal elements in coal to promote spontaneous combustion. The higher the concentration, the more obvious the chelating effect. At room temperature, various inhibitors are added, and the longer the time, the more serious the inhibitor failure. Some inhibitors have problems such as low efficiency and a short life. Given the above problems, some scholars have studied the temperature-sensitive composite inhibitor to prolong the life of the inhibitor and release the inhibitor at a specific temperature.[21] Zhang[22] developed the formula for AB-type temperature-sensitive gel by controlling variables, orthogonal compounding experiments, and material optimization, comprehensively investigated the inhibition effect of the gel, and analyzed the inhibition mechanism. Cui et al.[23] proposed a technology of encapsulating high water-containing physical inhibitors with temperature-sensitive materials, which improved the shortcomings of strong fluidity, short inhibition time, and strong corrosivity of inhibitors. Bai[24] proposed a composite inhibitor of magnesium chloride-melatonin coated with a phase change material mixture of chlorinated paraffin and used a series of techniques of microcapsules to prepare it called microcapsule inhibitor. Yu et al.[25] used konjac glucomannan (KGM) and expandable graphite (EG) as raw materials to prepare a new type of irreversible temperature-sensitive composite gel for the prevention and control of coal spontaneous combustion disasters. Yang and Zhang[26] using sodium alginate and carboxymethyl cellulose as the matrix, poly(vinyl alcohol), and *N*-isopropylacrylamide as monomers, a biobased super-absorbent temperature-sensitive hydrogel was prepared by graft copolymerization. Some achievements have been made in the research of temperature-sensitive inhibitors, but there is still a lack of research on the inhibition characteristics and inhibition mechanism of coal spontaneous combustion at specific temperature nodes.

Based on this, this study carried out in-depth research on the inhibition characteristics of coal by adding inhibitors at the critical temperature(R70). In the experiment, lignite was selected as the research object, and four different types of inhibitors, triphenyl phosphite (TPPI), phytic acid (PA), and melatonin, were applied to coal samples at room temperature and 70 °C, respectively. The inhibition effect and mechanism of different inhibitors on low-grade coal at critical temperatures were studied by testing and comparing the macroscopic indexes such as gas emission, CO inhibition rate, oxygen consumption rate, apparent activation energy, and change of surface active groups in the process of low-temperature oxidation of inhibited coal. It lays a theoretical foundation for accurate and efficient inhibition of coal spontaneous combustion.

2. EXPERIMENT

2.1. Coal Sample Preparation. *2.1.1. Sample Preparation for Raw Coal.* The low-metamorphic Pingzhuang brown coal was used in the experiment. Table 1 displays the industrial and elemental analyses of the coal samples. A 10 g coal sample was added with a concentration of 10% inhibitor solution at room temperature. The ratio of coal to inhibitor solution was 3:1, and the sample was placed for 36 h.

2.1.2. Sample Preparation of Inhibited Coal. In this experiment, four kinds of physical inhibitors, anhydrous magnesium chloride (MgCl2), metal chelating agent-phytic acid (PA), antioxidant-triphenyl phosphite (TPPI), and free radical scavenger-melatonin (melatonin), were selected (see Table 2). The 10 g raw coal was placed in the oven to rise to 70 °C. When the coal temperature rose to 70 °C, a 10% inhibitor solution was added, and the ratio of coal to inhibitor solution was 3:1, which was placed for 36 h. The contrast coal

Table 2. Inhibitor Solution Ratio

inhibitor category	drug name	use level	solvent	concentration
physical inhibitor	$MgCl_2$	3 g	water-27 mL	10%
antioxidant	TPPI	2.22 mL	absolute alcohol-30 mL	10%
metal chelator	PA	1.1 mL	absolute alcohol-30 mL	10%
free radical catching agent	melatonin	2.63 g	absolute alcohol-30 mL	10%

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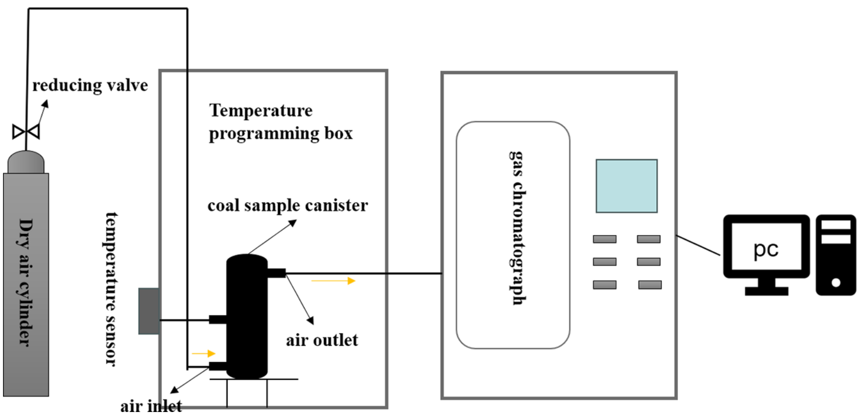

Figure 1. Programmed temperature rise device.

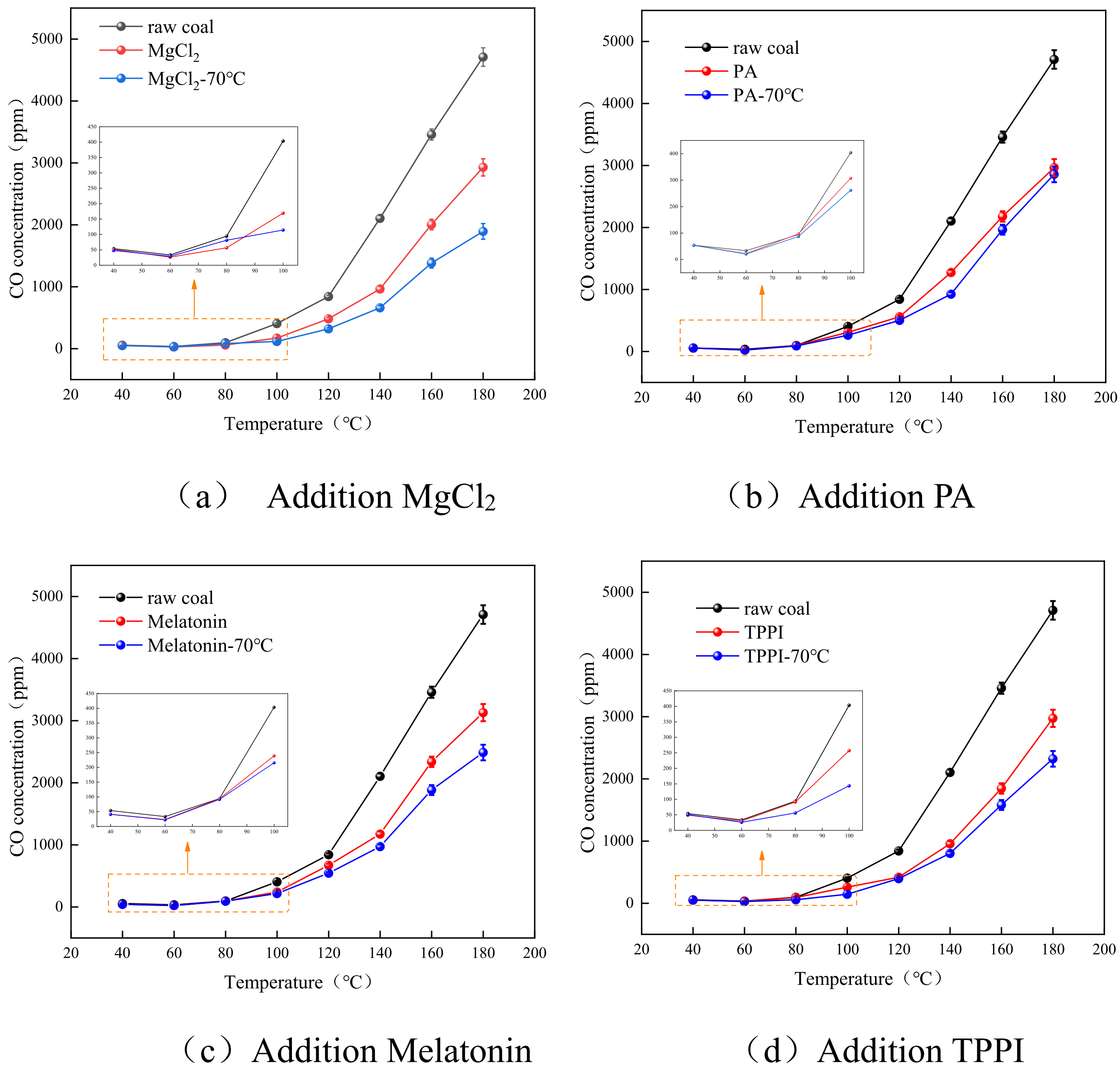

Figure 2. Comparison of the CO curves of raw coal and coal with inhibitor added at different temperatures.

samples are coal samples and raw coal samples added with the same dose and concentration of inhibitor solution at room temperature. The coal samples were vacuum-dried at 40 °C for 24 h before being placed in vacuum bags.

2.2. Macroscopic Characteristics Test of Coal Low-Temperature Oxidation. During the experiment, the ZRD-II coal spontaneous combustion characteristic tester was combined with a GC7008 gas chromatograph (Figure 1),

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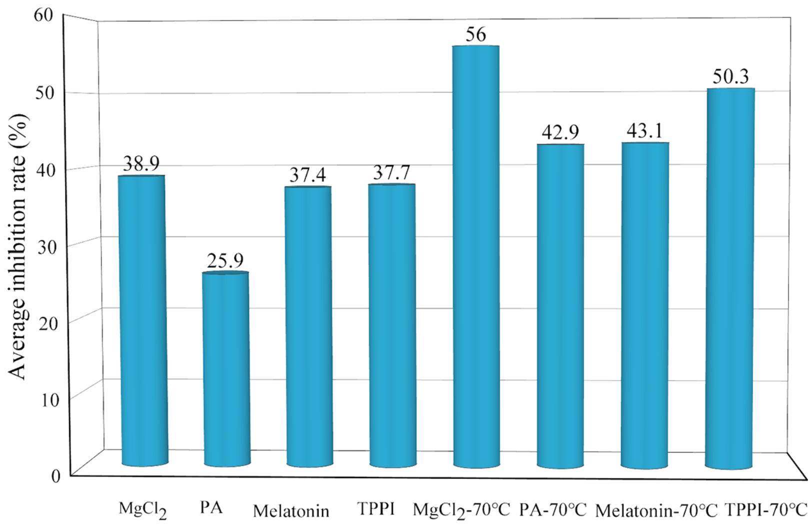

Figure 3. Comparison of the average inhibition rate of each inhibitor on lignite at different temperatures.

and the prepared coal sample was placed in a 10 g sample tank. The airflow rate was 30 mL/min. After checking the gas path, the programmed heating experiment was started, at a heating rate of 1 °C/min. In the temperature range of 40 to 180 °C, the gas is collected once for every 10 °C increase in temperature, and the generated gas is transferred to the gas chromatograph by pressing the start sample key. The gas composition and concentration at the outlet are calculated, and the operation parameters are recorded in real-time by the data acquisition system until the cross-point temperature occurs. When the coal temperature surpasses the furnace temperature, the system shuts down.

2.3. Determination of Active Functional Groups on the Coal Surface. In the experiment, a German TENSOR27 Fourier infrared spectrometer was selected. The infrared spectrometer was turned on and preheated for 10 min to scan the background 32 times, and then, the pressed sample was put into the infrared instrument to scan the sample 32 times. The coal sample and potassium bromide were in a ratio of 1:180 in the mortar, ground with a grinding rod, rotated the mortar during the grinding process to achieve full mixing of the coal sample and potassium bromide, and ensured uniform grinding, and then, the HY-15 tableting machine was used to tablet, press to 10 MPa, and press for 30 s. In the experiment, the tablet with good transmittance and uniformity was selected for measurement.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Characteristics of CO Formation. Once the coal is heated, it will produce CO. There is good correspondence between the amount of CO produced and the temperature of the coal, and the repeatability is good. Therefore, CO is often selected as the index gas to divide the different stages of the coal low-temperature oxidation process. The comparison diagram of CO concentration produced in the process of oxidation and heating is shown in Figure 1 when different inhibitors are added to lignite at room temperature and 70 °C. As the temperature rises, the CO concentration also increases, and the overall trend is on the rise. The CO gas concentration of each coal sample is small and unchanged between 40 and 60 °C. When the coal temperature rises above 70 °C, the CO concentration begins to rise slowly at first and then exponentially as the temperature rises, showing that the coal sample has begun to oxidize slowly.

The CO generation curves of raw coal and inhibited coal samples during low-temperature oxidation are shown in Figure 2. It can be seen that the yield of CO added by the inhibitor at different prefabrication temperatures is lower than that of the raw coal sample, and the yield of CO added at the prefabrication temperature of 70 °C is the smallest, indicating that the four inhibitors can significantly inhibit the oxidation reaction of coal and the addition of the inhibitor at 70 °C has the best inhibitory effect. The coal-oxygen reaction depends on the reactivity. At 70 °C, the macromolecular structure and active groups in coal are in an active state.[27] At this time, the inhibitor is added to react with it. The reaction speed is faster; the reaction activity is larger, and a large number of active functional groups are consumed. The main path of the reaction is cut off, and the coal activity is reduced in a clifflike manner at low temperatures. The reaction is not the direct oxidation reaction of C and O in coal,[28] but rather the oxidation or decomposition reaction of functional groups in coal. The production of CO is due to the decarboxylation of −COOH. With the increase of the coal temperature, the addition of inhibitor leads to the continuous decrease of −COOH content and the inhibition of active sites, resulting in a small amount of CO production when the inhibitor is added to the coal at 70 °C. Spontaneous combustion tendency decreases. Therefore, the inhibitor achieves a good inhibition effect. This is checked in Section 3.6, employing the infrared spectrum scanning test.

3.2. Inhibition Rate. To measure the inhibiting effect of inhibitors on spontaneous coal burning, the CO inhibition rate is a commonly used evaluation index. The inhibition ratio is the ratio of the difference between the amount of CO emitted by untreated and inhibited coals to the amount of CO emitted by treated coals under the same conditions. The calculation is shown in eq 1:

$$E_T = \frac{A - B}{A} \times 100\% \quad (1)$$

where E_T is the inhibition rate at a certain temperature point; A is the total release of CO gas from raw coal samples, mol; B is the total release of CO gas from inhibited coal samples, mol.

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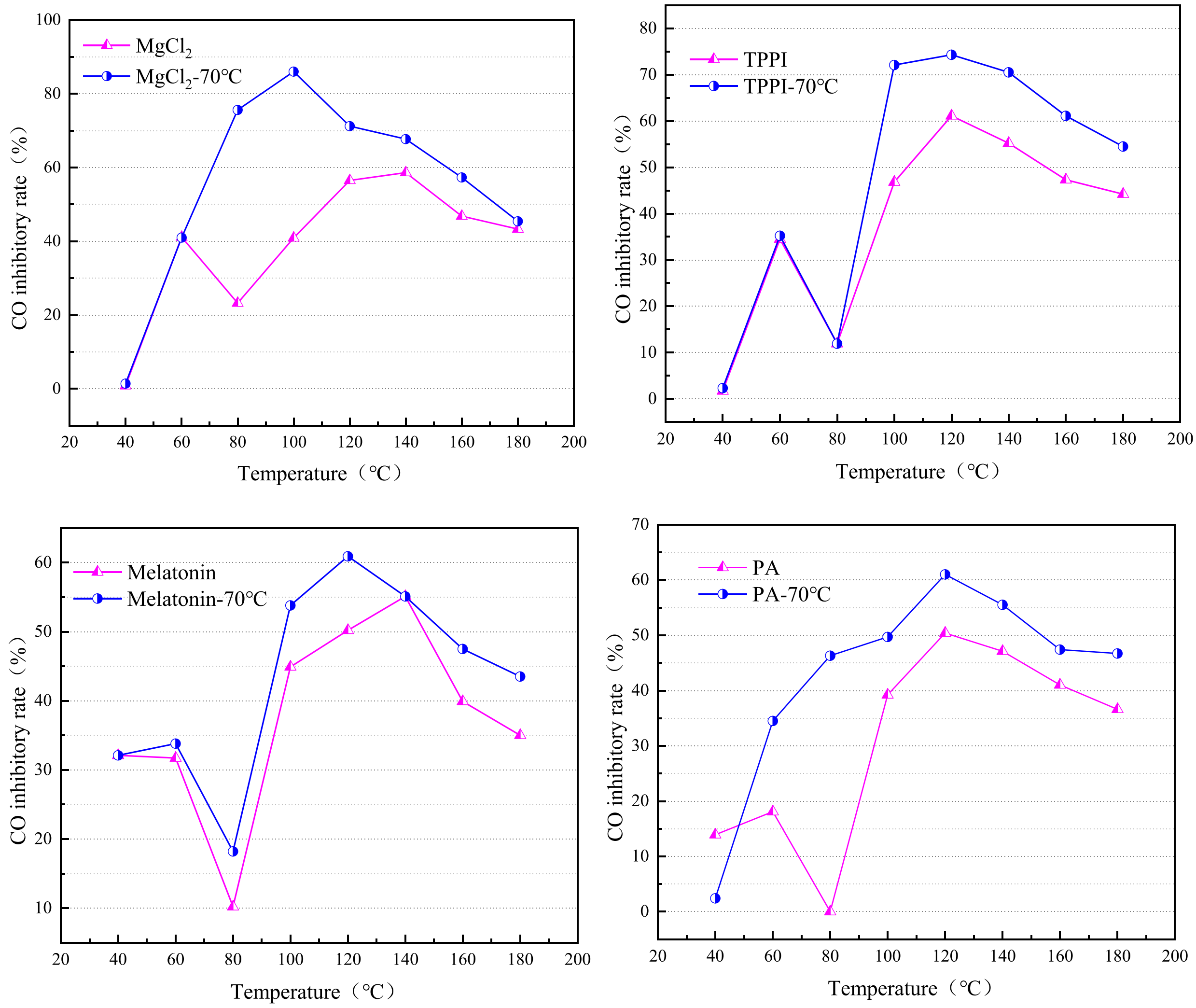

Figure 4. Inhibition rate of adding inhibitor at room temperature and critical temperature.

The average inhibition rate corresponding to all temperature points is called the average inhibition rate. The comparison of the CO inhibition rate of lignite under different temperatures and different inhibitors is shown in Figure 3. The inhibition rate of $MgCl_2$, PA, melatonin, and TPPI on R70 coal is much higher than the average inhibition rate of these inhibitors on coal at room temperature. Compared with the addition of raw coal at room temperature, the inhibition rate increased by 17, 12.9, 5.7, and 12.5% respectively. It shows that as the temperature of the coal sample increases, the inhibitor is added and the inhibition effect is on the rise.

To further clarify the effect of adding an inhibitor under R70 on the inhibition effect of varied temperature phase in the oxidizing under low-temperature condition process of coal, the inhibition rate changes with temperature at R70, and the room temperature was compared. As shown in Figure 4, the inhibition rate changes with temperature and can be divided into four phases. In the temperature range of 40∼60 °C and 80∼120 °C, the inhibition rate increases with the increase of temperature, while in the temperature range of 60∼80 °C and 120∼180 °C, the inhibition rate decreases. When the prefabricated temperature rises to R70, the inhibition rates of PA and $MgCl_2$ rise sharply before 120 °C. It can be seen that these two inhibitors inhibit coal under R70, and the result is the same as the average inhibition rate. After 80 °C, the inhibition rate of samples with R70 added inhibitor was considerably higher than for room temperature samples. It shows that the temperature at which the inhibition performance of the four types of inhibitors plays a role is about 80 °C. The inhibition rate of PA, melatonin, and TPPI reached the maximum at about 120 °C, while the inhibition rate of $MgCl_2$ added at 100 °C under R70 reached the maximum. The maximum inhibition rate temperature was increased from 140 to 100 °C compared to room temperature, and the maximum inhibition rate increased from 58.6 to 86%, an increase of 1.47 times, indicating that adding inhibitors below R70 has a significant inhibiting effect on low-temperature coal oxidation. The number of active groups in coal is small, and the oxygen supply required for coal oxidation is sufficient in the early stages of coal oxidation. As the temperature rises, the coal is accelerated to oxidize, and the system is in the state of active group.[16] Therefore, the addition of inhibitor R70 has a better effect on the consumption of active groups in coal than that at room temperature.

3.3. Consumption Characteristics of O_2. The oxygen consumption rate refers to the molar number of oxygens consumed by a certain volume of coal samples in unit time, which can indirectly indicate the strength of coal oxidation. Coal reacts with oxygen to produce heat during combustion. The faster the heat produced, the faster spontaneous

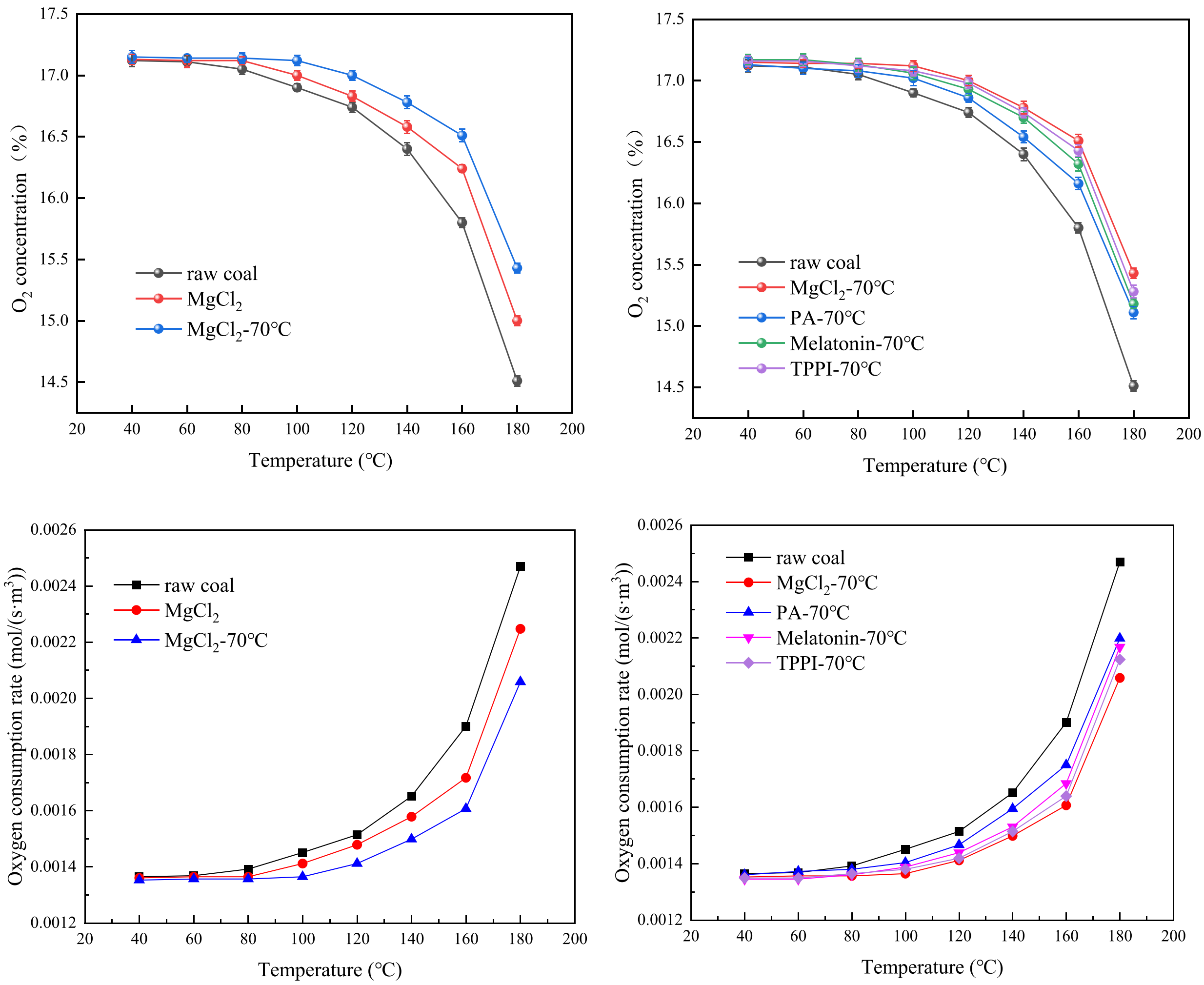

Figure 5. Comparison of oxygen concentration and oxygen consumption rate of raw coal with different inhibitors at room temperature and the critical temperature range.

combustion will occur, and the heat produced is positively correlated with oxygen consumption. Therefore, the oxygen consumption rate can reflect the tendency of coal to spontaneous combustion.

From the oxygen concentration at the gas outlet of the coal sample tank, the oxygen consumption rate can be calculated. The calculation formula is shown in eq 2:

$$V_{O_2}(T) = \frac{QC_{in}}{SL}\ln\frac{C_{in}}{c_{out}} \tag{2}$$

where $V_{O_2}(T)$ is the rate of oxygen consumption of coal at a certain temperature, mol/(s m^3); Q is the airflow required in the experiment, m^3/s; In this experiment, the airflow rate is $5 \times 10^{-7} m^3$ /s; S is the area of the cross-section of the coal sample, which is about 6.84×10^{-4} m^2; L is the height of the sample container for the coal, which is about 2.3×10^{-2} m; C_{in} is oxygen concentration at the coal sample tank inlet, the oxygen concentration in the air is 21%; c_{out} is outlet oxygen concentration, %.

The oxygen concentration comparison diagram and oxygen consumption rate comparison diagram of raw coal added with different inhibitors at room temperature and R70 are shown in Figure 5. At low temperatures, there is no consumption of oxygen in the coal sample tank, and the oxygen consumption rate is very low. This indicates that in the low-temperature stage, coal is in a relatively inert state with low activity of various groups and it is almost impossible to combine with oxygen for the oxidation reaction. After 70 °C, we can see that the concentration of O_2 is rapidly decreasing and that the rate of oxygen consumption of the coal is gradually increasing. This shows that the different groups in the coal gradually begin to be activated as the temperature of the coal gradually increases and the oxidation reaction begins when oxygen is encountered. This means that the oxidation reaction of the coal has reached the stage of accelerated oxidation, and more oxygen is consumed by the coal.[29] Raw coal consumes a lot of oxygen in the whole temperature range and has the lowest oxygen concentration. The coal sample with the inhibitor added at 70 °C has the highest oxygen concentration and the lowest oxygen consumption rate, and the coal-oxygen composite reaction is delayed. This shows that R70 coal is harder to ignite after the addition of the inhibiting agent, and the inhibiting effect of the inhibiting agent on R70 coal is better than that on normal-temperature coal.

3.4. Cross Temperature Point Analysis. The temperature in the temperature-controlled box was increased by 1 °C/min. The temperature of the coal sample was below the temperature in the programmed heating box at the start of the test. However, the temperature of the coal progressively

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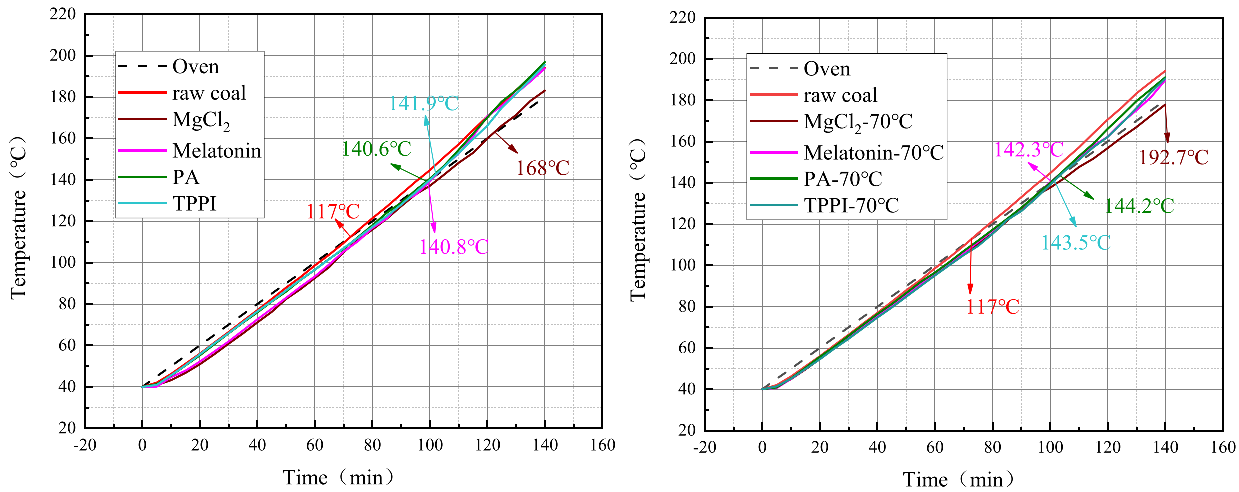

Figure 6. Cross-point temperature diagram.

increased and ultimately exceeded that of the temperature control box due to the automated response to heat liberation and heat diffusion. Therefore, there is a point where the temperature curve intersects. The temperature that corresponds to this point of intersection is called the intersection temperature. The greater the ability of the coal to produce heat when oxidized, the quicker the temperature will rise and the lower the temperature of the intersection will be. Therefore, the spontaneous combustion tendency of coal can also be assessed by using the cross-point temperature. The temperature of the intersection point of the inhibitor and its raw coal at room temperature and R70 is shown in Figure 7.

As shown in Figure 6, taking the addition of $MgCl_2$ to lignite as an example, the intersection temperature of lignite raw coal is 117 °C. After adding $MgCl_2$ solution to lignite at room temperature, it is 51 °C more than for raw coal. When the temperature rises to 70 °C, the addition of $MgCl_2$ solution is 75.7 °C higher than that of raw coal, and 24.7 °C higher than the intersection temperature of $MgCl_2$-inhibited coal samples at room temperature. This shows that the inhibition efficiency is considerably increased with the increase of the prefabrication temperature. The addition of an inhibitor below R70 weakens the oxidation performance of coal and reduces the tendency of coal to spontaneously combust. In comparison with the four types of inhibitors, the physical inhibitor $MgCl_2$ has the best inhibition effect.

3.5. Apparent Activation Energy analysis. Activation energy is the energy required to convert ordinary molecules into activated molecules. The activation energy of oxidizing under the low-temperature reaction of coal is negatively correlated with the possibility of coal spontaneous combustion disasters. During the oxidation and heating process of coal, gases such as CO and CO_2 are generated:

$$\text{coal} + O_2 \rightarrow x\text{CO} + y\text{CO}_2 + \text{Other products} \tag{3}$$

According to the reaction rate formula and Arrhenius equation, the coal oxygen reaction rate at any temperature is

$$v(T_i) = \frac{v(\text{co})}{m} = Ac_{O_2}^{n}\exp(-E/RT_i) \tag{4}$$

where v is the reaction rate; T_i is the thermodynamic temperature of coal, K; A is the pre-exponential factor; $c_{O_2}^{n}$ is the content of oxygen in the reaction gas, mol/m^3; n is the order of reaction; E is the activation energy, J/mol; and R is the molar gas constant, 8.314J/(mol K).

In the process of the temperature-programmed simulation of coal oxidation, it is assumed that the airflow is only along the axial direction of the coal sample container. The coal sample CO formation rate at dx along the axial direction of the coal sample container is

$$Sv(\text{CO})\text{d}x = kv_g\text{d}c \tag{5}$$

where S is the cross-sectional area of the coal sample container, m^2; v(CO) is the rate of formation of CO, mol/(m s); k is the unit conversion coefficient used to convert, 22.4×10^9; $v_g$is the air-flow rate, m^3 /s; c is the amount of CO generated by oxidizing coal., 10^{-6}.

It should be ensured that there is sufficient air during the reaction of the coal sample and that the initial consistency of oxygen in the reaction is constant at all temperatures during the coal-oxygen reaction. Bring eq 5 into eq 4 to obtain

$$ASmc_{O_2}^{n}\exp\left(-\frac{E}{RT_i}\right)\text{d}x = kv_g\text{d}c \tag{6}$$

The pair (eq 6) is integral at both ends.

$$\int_0^L ASmc_{O_2}^{n}\exp\left(-\frac{E}{RT_i\text{d}x}\right) = \int_0^{c_{out}} kv_g\text{d}c \tag{7}$$

where L is the length of the coal sample container, m; c_{out} is the calculated CO concentration at the outlet of the coal sample container.

The pair (eq 7) is obtained by taking the natural logarithm on both sides.

$$\ln c_{out} = -\frac{E}{RT_i} + \ln(ASLmc_{O_2}^{n}/kv_g) \tag{8}$$

It can be seen from eq 8 that there is a linear parabolic equation relation between $\ln c_{out}$ and $1/T$ when the ventilation flow rate is constant. By calculating the slope, the apparent activation energy of different stages of the coal oxygen reaction can be obtained. After 120 °C, the combustion state of the hindered coal sample gradually stabilized. Therefore, linear fitting is carried out for all coal samples in the temperature range of 120 °C ∼ 180 °C, and the fitting calculation results are shown in Figure 7. After the addition of different types of

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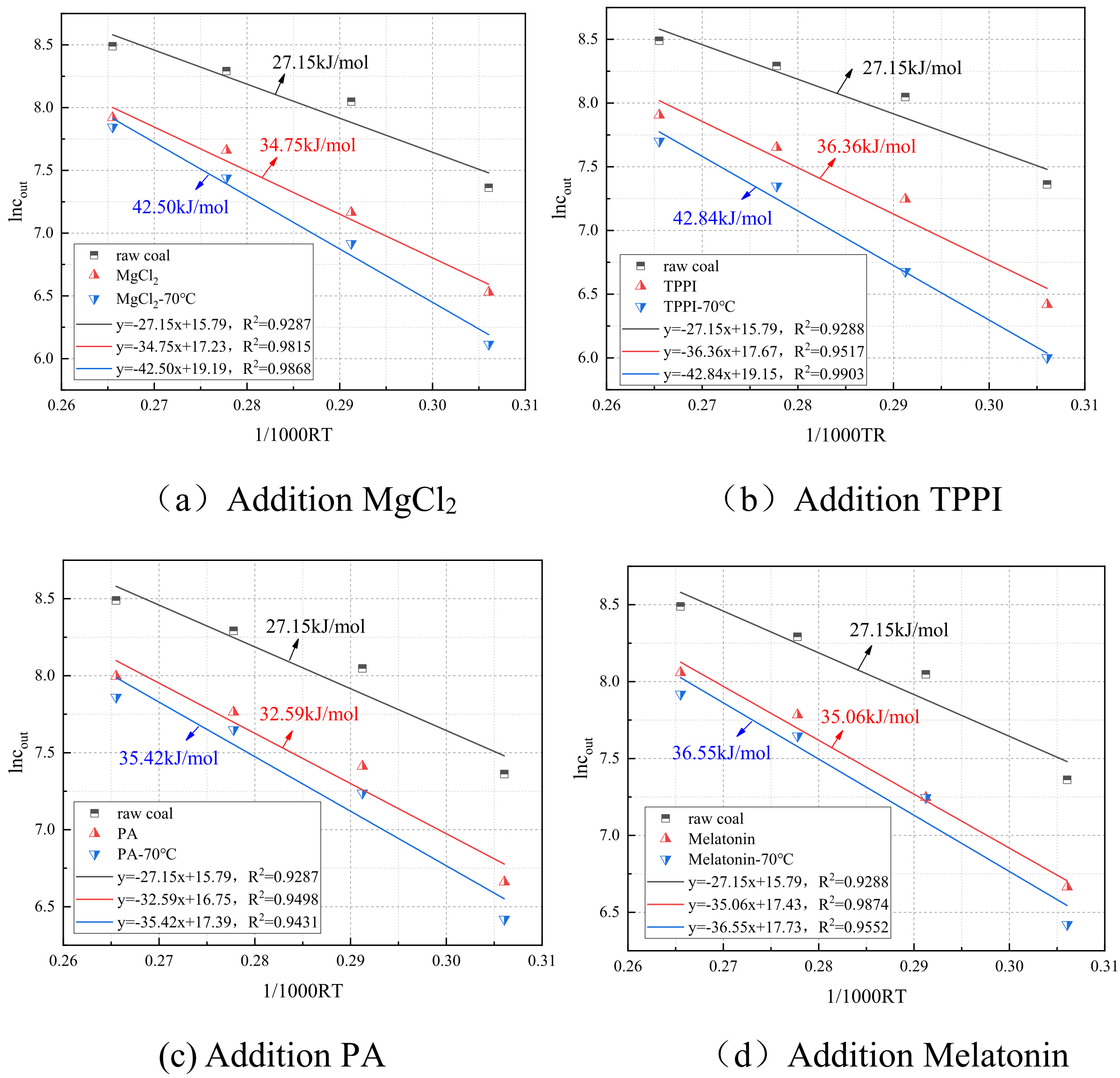

Figure 7. Apparent activation energy of raw coal and coal after adding inhibitor.

inhibitors, the apparent activation energy was higher than that of raw coal, indicating that the inhibitors effectively inhibited the process of coal spontaneous combustion. The diagram shows that as the preheating temperature is increased, the preheating time decreases and the apparent activation energy gradually increases. Taking $MgCl_2$ as an example, the apparent activation energy of $MgCl_2$ added under R70 increases from 34.75 to 42.50 kJ/mol, an increase of 7.75 kJ/mol, indicating that the addition of inhibitor under R70 is significantly improved compared with the conventional addition of inhibitor.

3.6. Changes of Surface Functional Groups of Coal.

The content of surface functional groups of coal can be reflected in the results of infrared spectrum scanning. To analyze the influence of inhibitors on surface functional groups at critical temperatures, infrared spectrum experiments were carried out on samples of coal that had been treated at different temperatures. The research results of lignite are shown in Figure 8. It reflects the change of active group content and absorption peak intensity of raw coal and lignite after adding an inhibitor at a critical temperature. The vibration intensity of the absorption peak of lignite is the strongest at 900 cm^{-1} ∼ 1800 cm^{-1}. After the coal is blocked in the critical temperature range, the intensity of the vibration peak at 900 cm^{-1} ∼ 1800 cm^{-1} is significantly reduced, and the content of oxygenated functional groups with the highest proportion and activity in coal. analogous absorption bands and particular absorption peaks are found in the IR of different coal samples added with inhibitors at different temperatures. However, the addition of inhibitors at higher temperatures will not transform the construction of the coal but changes the concentration of functional groups, as the absorbance of dissimilarity peak positions changes noticeably. Studies have shown that functional groups containing oxygen are key in the promotion of spontaneous combustion of coal. PeakFit1.12 software was used to fit the peak of the spectral curve to precisely quantify the effect of temperature on radicals in the R70 As shown in Figure 9.

Oxygen is an important part of coal. It is mainly present in the form of water, inorganic compounds that contain oxygen,

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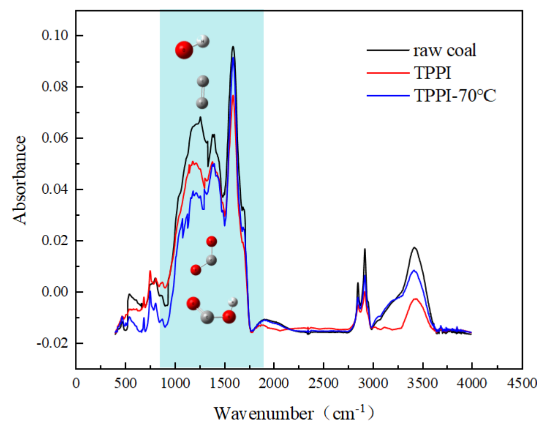
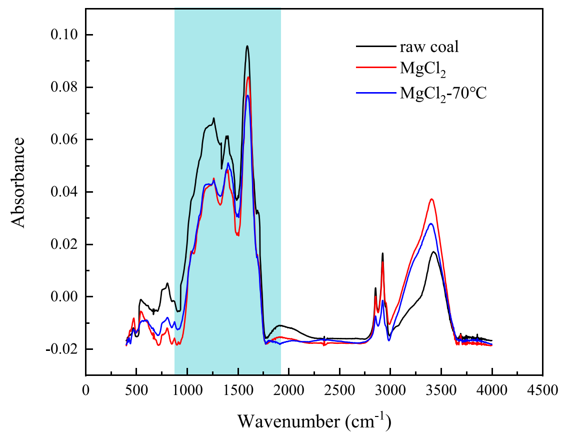
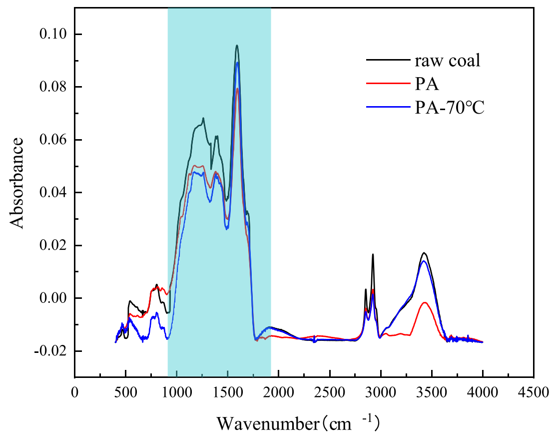


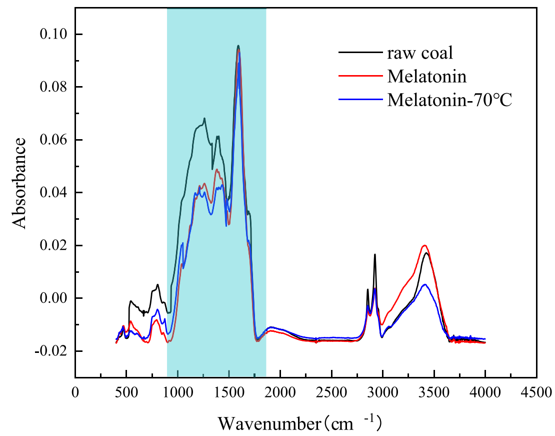
(a) Addition TPPI



(b) Addition $MgCl_2$



(c) Addition PA



(d) Addition Melatonin

Figure 8. Infrared spectra of a lignite added inhibitor heated to 110 °C.

and functional groups in coal that contain oxygen. Among them, Oxygen has the greatest influence on the properties of coal in the form of oxygen-containing functional groups. It is directly related to the reaction characteristics of coal and largely determines the properties of coal. The oxidized functional group in the molecular structure of coal is mainly located in the wavenumber range of 900 cm^{-1} ~ 1800 cm^{-1}, including −COOH, C═O, alkyl ether and phenolic alcohol ether, C═C, phenolic−OH bond, etc. From the infrared spectrum of this experiment, it can be observed that the vibration intensity of the absorption peaks at 500 cm^{-1} ~ 700 cm^{-1} and 2700 cm^{-1} ~ 3000 cm^{-1} and their group content are relatively stable and unchanged.

It can be seen from Figure 10 that the level of the phenolic hydroxyl group and the carboxyl group is much lower than that of the raw coal after the addition of an inhibitor. The decrease is more pronounced with the increase of the prefabrication temperature. With the progress of low-temperature oxidation of coal, when the temperature reaches 70 °C, a large number of alkyl radical active centers are formed by the decomposition of oxygen-containing functional groups, accompanied by the formation of CO and CO_2. At this time, the inhibitor is added to reduce the content of −COOH, achieving a good effect in inhibiting coal spontaneous combustion by reducing the formation and oxidation of its active sites, blocking the mutual conversion path between its active center and oxygen-containing functional groups.[30] The addition of an inhibitor under R70 makes the content of easily oxidized−OH decrease.[31] After the addition of the inhibitor, the content of ether bond is much higher than that of coal, and it shows an increasing trend with the increase of prefabrication temperature. The number of stable ether bonds increased, indicating that the addition of inhibitors under R70 presents good inhibitory action, which could help active groups in coal form relatively stable ether bonds, thereby inhibiting the oxidation of coal. The content of C═C tends to be stable and increases slightly. This is because the core structure of coal molecules is an aromatic group, and the basic structural units are aromatic rings and a small amount of alicyclic and heterocyclic rings. When the temperature is small, it is difficult to destroy the C═C double bond structure of the aromatic hydrocarbon skeleton, which does not participate in the oxidation reaction. After the addition of the inhibitor to R70, the C═C increases slightly, which may be due to the decrease of the content of other aliphatic hydrocarbons and oxidized functional group, which affects the content of aromatic hydrocarbons so that the proportion of aromatic hydrocarbons shows a slight increase.

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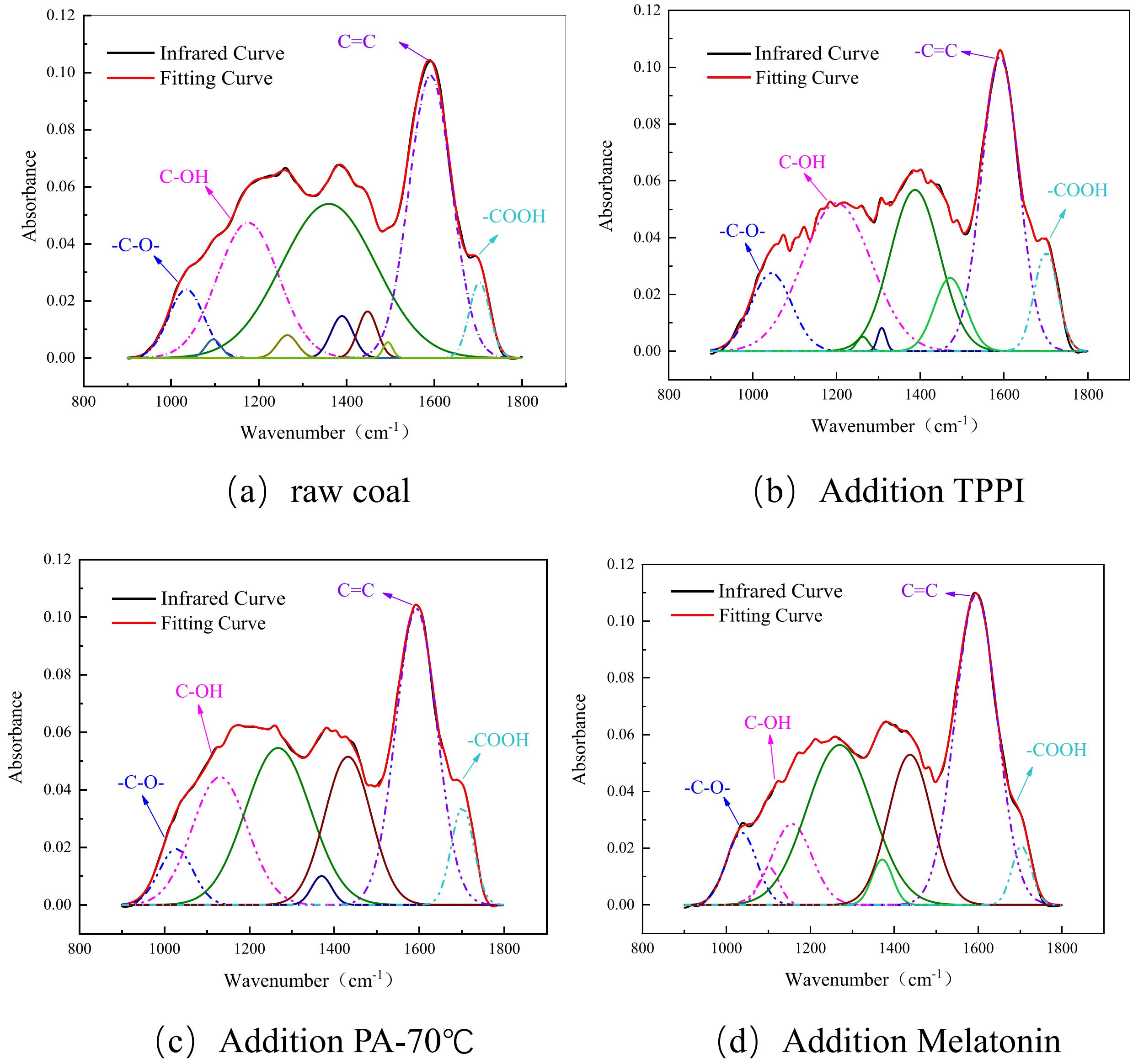

Figure 9. Peak fitting diagram of some samples.

3.7. Mechanism Analysis. From the above experiments and analysis results, it can be inferred that the mechanism of adding an inhibitor under R70 has a significant inhibiting effect on spontaneous coal burning, as shown in Figure 11.

Macroscopic experiments show that the addition of inhibitors at R70 reduces the amount of CO produced, the oxygen consumption rate decreases, the intersection temperature and its apparent activation energy show an increasing trend, and the inhibition rate of adding inhibitors is also higher than that of adding at room temperature. From a macroscopic point of view, the addition of inhibitors under R70 has a better inhibition effect. Microscopically, in the process of coal oxidation at low temperatures of coal, the oxidation of active centers and the pyrogenic decomposition of oxygenous groups will inevitably occur. After pyrolysis, huge amounts of free radical active centers are generated. Some of the radical reactive centers can exist stably under indifference conditions. As soon as they are in contact with oxygen, an oxidizing reaction can occur at once. The temperature at which active functional groups begin to decompose is usually 70 °C.[32] When the temperature of coal reaches the liminal of heat decomposition of these groups, coal begins to coalesce, and these groups are resolved to produce active sites and a small amount of gas products, such as CO and CO_2. Then, the active sites can be oxidized to produce an oxidized functional group, releasing a large amount of CO, CO_2, and heat.[33−35] The thermal decomposition of oxidized functional groups in coal is the key to spontaneous combustion. The thermal decomposition of oxidized functional groups during coal oxidation produces alkyl radical active sites. These active sites are oxidized under certain conditions and converted into new oxidized functional groups.[36−39] Subject to certain conditions, oxidized functional groups and active centers can undergo a reciprocal transformation, increasing the concentration of their active centers, increasing the concentration of active centers, and their continuous transformation with an oxidized functional group leads to the accumulation of coal thermal and the persistent increase of coal temperature. At R70, water began to evaporate, and the active sites covered by water began to appear. The evaporation of water not only leads to the exposure of the active center but also exposes the pores and fissures of the coal surface reacting with oxygen.[40,41] At this

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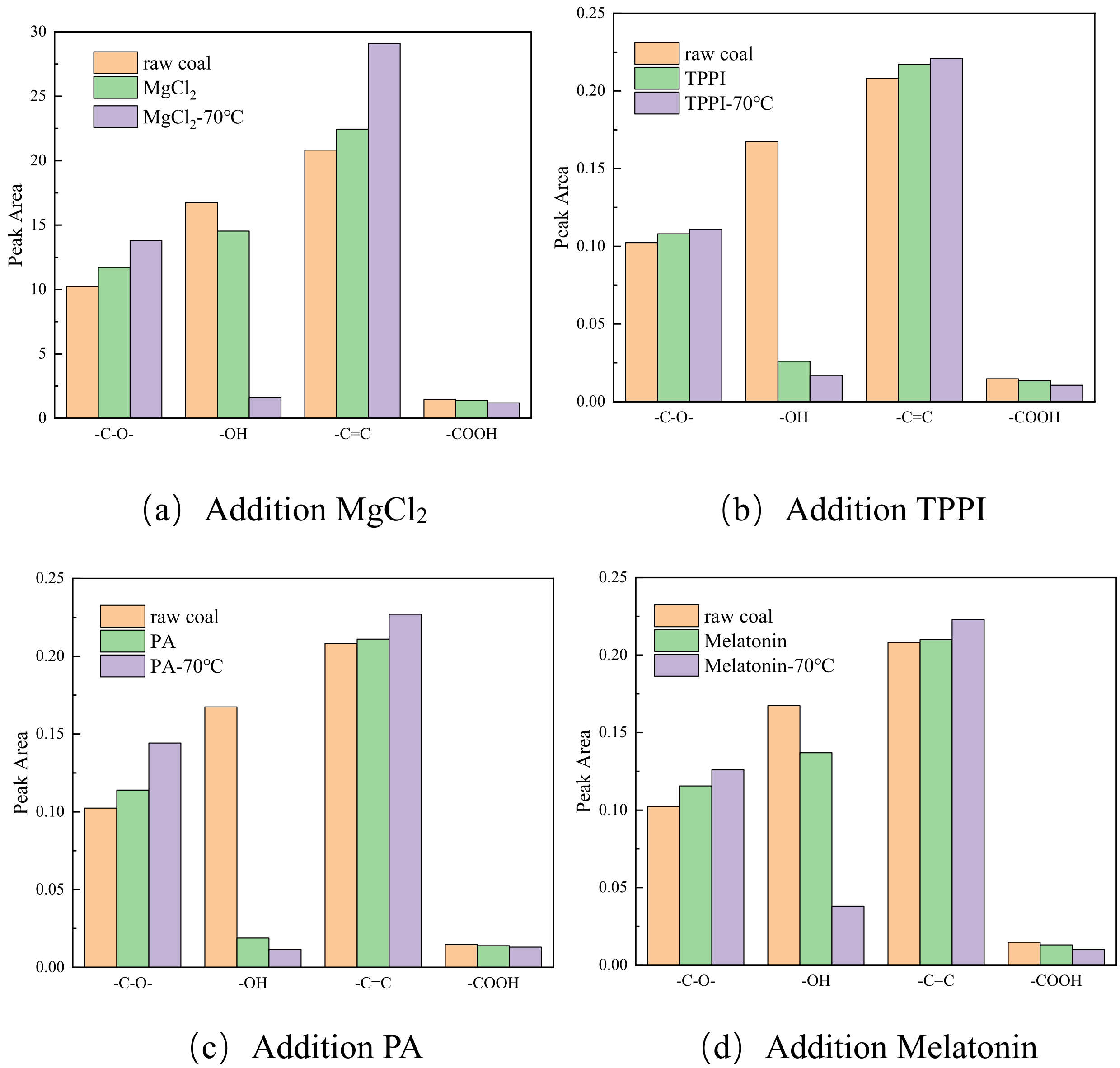

Figure 10. Peak area ratio of lignite was increased to 110 °C by adding an inhibitor.

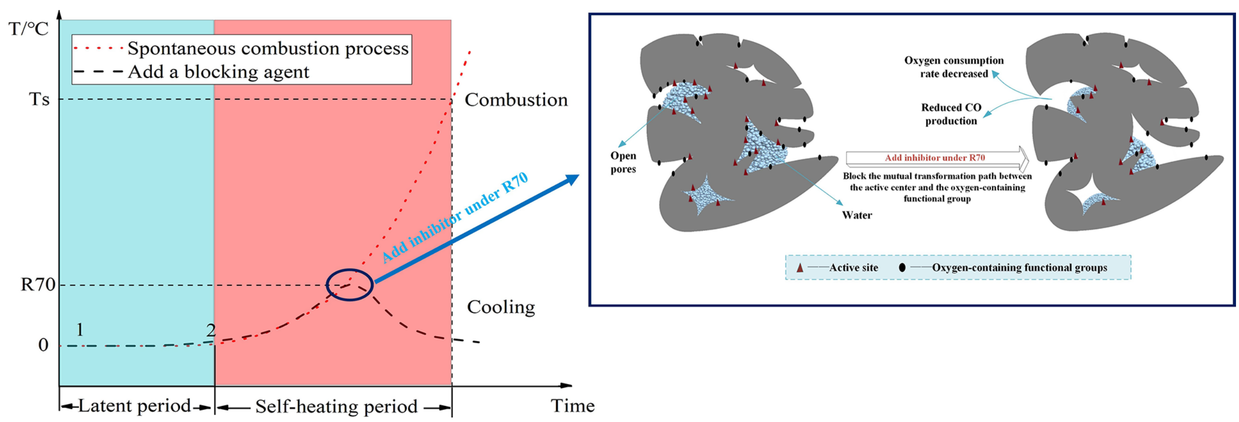

Figure 11. Mechanism of inhibiting coal spontaneous combustion by adding inhibition under R70.

time, it can be seen from the infrared spectrum experiment, the addition of an inhibitor makes the content of oxygen-containing functional groups with higher activity decrease, reduces the oxidation of its active sites, delays the oxidation process of coal, blocks the reciprocal transformation path between the active center and the oxidized functional group,

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and also promotes the formation of relatively stable inert oxygen-containing ether bonds, thereby inhibiting the spontaneous combustion of coal.

4. CONCLUSIONS

In this study, in order to study the inhibition characteristics of adding inhibitors to coal at the critical temperature of coal oxidation, the temperature-programmed-gas chromatography experiment and Fourier transform infrared spectroscopy experiment were used to analyze the lignite at room temperature and 70 °C. After the addition of four different types of inhibitors, $MgCl_2$, PA, TPPI, and melatonin, the macroscopic spontaneous combustion characteristics and microstructure changes of the inhibited coal samples and their inhibition mechanism were analyzed. The main conclusions are as follows:

1. Based on the temperature-programmed gas chromatography experiment, the macroscopic characteristics of the oxidation spontaneous combustion stage at room temperature and R70 coal after adding the inhibitor were clarified. After adding four kinds of inhibitors to coal under R70, the intersection temperature increased significantly. After adding inhibitors to R70, the CO production decreased and the inhibition rate increased, indicating that the addition of inhibitors under R70 effectively inhibited the process of low-temperature oxidation of coal spontaneous combustion.
2. Through the analysis of the oxidation thermodynamic parameters of different inhibited coal samples, it is concluded that after adding four inhibitors to coal at room temperature and R70, the oxygen consumption rate and activation energy of the inhibited coal samples in the oxidation and spontaneous combustion stage are different. After adding an inhibitor under R70, the oxygen consumption rate decreased significantly and the activation energy increased significantly. The activation energy of coal added with inhibitor under R70 increased by 1.49 kJ/mol ~ 7.3 kJ/mol compared with that of the coal sample at room temperature. Therefore, the spontaneous combustion ability of coal is significantly reduced after adding an inhibitor under R70, and the inhibition effect is enhanced.
3. The change trend of microstructure and functional group content of coal added with four kinds of inhibitors at room temperature and the critical temperature was clarified. The addition of inhibitor under R70 reduces the content of oxygen-containing functional groups with high activity, to reduce the generation and oxidation of active sites, blocks the mutual transformation path between active functional groups and active sites, and promotes the formation of relatively stable group ether bonds, thus inhibiting the oxidation process of coal.

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Notes

The authors declare no competing financial interest.

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