INTRODUCTION

Coal is likely to combust spontaneously in various stages such as mining, transportation, and storage. Coal spontaneous combustion (CSC) can not only produce lots of toxic and harmful gases, but also cause casualties.\textsuperscript{1-4} Therefore, CSC prevention is of great significance for the safe production of coal.\textsuperscript{5} Many methods have been proposed to inhibit CSC in underground coal mines. At present, a wide range of inorganic salts such as NaCl, MgCl\textsubscript{2}, and CaCl\textsubscript{2} has been considered for use in this role.\textsuperscript{6-8} These inorganic salts can absorb water to wrap the coal, thereby preventing its spontaneous combustion by cutting off its contact with oxygen. They are both useful and cheap for CSC inhibition. Lu et al\textsuperscript{9} used inhibition foam for fire extinguishment in the underground goaf. Nevertheless, while these inorganic salts can well inhibit CSC by covering coal surface, their inhibitory effects weaken with the evaporation of water because they are mixed with distilled water for the inhibition. To address the problem, Cui et al\textsuperscript{10,11} proposed thermo-responsive inhibitors and a thermo-responsive secundine inhibitor. In addition, some chemical inhibitors prevent CSC by changing...
functional groups in coal. Li et al.12,13 studied the inhibitory effect of ethylenediaminetetraacetic acid (EDTA) on CSC. EDTA can inhibit CSC by altering active groups in coal, but its inhibitory effect is not obvious.

As green organic solvents, ionic liquids can be adopted for VOCs or CO₂ separation.14 Wang et al.15,16 investigated the effects of two ionic liquids with [HSO₄]⁻ on oxidative desulfurization of coal. Ionic liquids can not only enhance the oxidation of -OH, aliphatic -CH₂⁻, and aromatic -CH to generate the -COOH group, but also enable organic sulfur structures, that is, -S-S- and -SH, to be removed more efficiently. They are nonflammable and nonvolatile with good solubility and high thermal and chemical stability.16,17 The ionic liquids proposed by Jiang et al.18-20 for CSC inhibition have achieved excellent effects. Deng et al.21 explored the effect of imidazole ionic liquid on macro-parameters and microstructure of bituminous coal during low-temperature oxidation.

According to previous studies, imidazolium ionic liquids such as [HOEtMIm][BF₄], [BMIm][AC], and [AΟEMIm][BF₄] can be used to inhibit CSC, because they can change some functional groups of coal and retard coal oxidation to varying extents.18-20 After coal is pretreated with ionic liquid [BMIm][BF₄], the weak covalent bond in coal structure gets destroyed.22 [AMIm]Cl has a good swelling effect of cellulose, while [HOEmim][BF₄] possesses relatively strong polarity.23,24 Zhang et al.25 proposed that ionic liquids are applicable to CSC prevention and control. Besides, ionic liquids can effectively destroy hydroxyl-associated hydrogen bonds in coal and suppress the activity of coal oxidation.

However, the concentrations of above ionic liquids are up to 98% when they are used to control CSC, and they are extremely expensive. Many ionic liquids are soluble in water which is able to isolate coal from oxygen by forming a liquid film on coal surface. In addition, since water resources are abundant and cheap, the dilution of ionic liquid with pure water can reduce the cost of CSC inhibition. In this paper, five ionic liquids were mixed with water to form ionic liquid solutions at the mass ratios of 0:1, 1:2, 1:5, 1:10, 1:25, and 1:50, respectively. It is noteworthy that the ionic liquid mixed with distilled water at the mass ratio of 0:1 is named as Add water. Finally, they were sealed and stored for use.

### 2.1 | Materials

#### 2.1.1 | Coal sample preparation

In this study, the raw coal (bituminous coal) supplied by Longdong Coal Mine in Xuzhou City, China, was crushed, grounded, and sieved to specific particle sizes (75-96 μm). Then, it was dried under vacuum at 40°C for 48 hours and stored in an airtight bag for later use. The technical parameters of Longdong coal are listed in Table 1.

#### 2.1.2 | Preparation of different concentrations of ionic liquids

Five kinds of ionic liquids, namely [HOEtMIm][BF₄], [BMIm][BF₄], [AMIm]Cl, [BMIm][NTf₂] with purity of 99%, and [AΟEMIm][BF₄] with purity of 98%, were prepared. They were bought from Lanzhou Institute of Chemical Physics. The above ionic liquids were briefly marked as HB, BB, AC, BN, and AB, respectively. Each of them was fully mixed with distilled water at mass ratios of 0:1, 1:2, 1:5, 1:10, 1:25, and 1:50 to obtain each ionic liquid with five different concentrations, respectively.

### 2.2 | FTIR test

Each ionic liquid solution was uniformly mixed with 2 g of dried raw coal and sealed for 24 hours at room temperature, after which the samples were repeatedly washed with distilled water until they were neutral. To eliminate the interference of water on the spectrum, the samples were dried in vacuum for 48 hours. In this way, the experiments were performed 10 times for each kind of ionic liquid solution. Fourier-transform infrared spectroscopy (FTIR) is widely employed to characterize the chemical structure of coal chemical functional groups, while temperature-programmed experiments are often performed to analyze CO₂ production and O₂ consumption during CSC. They laid a foundation for exploring a kind of suitable and economical green material for CSC inhibition. In order to find out the optimal concentration of ionic liquid solution with low cost and good effect, the effect of ionic liquid solution concentration on CSC was investigated through FTIR and temperature-programmed experiments.

### 2.3 | EXPERIMENT

#### 2.3.1 | Coal sample preparation

In this study, the raw coal (bituminous coal) supplied by Longdong Coal Mine in Xuzhou City, China, was crushed, grounded, and sieved to specific particle sizes (75-96 μm). Then, it was dried under vacuum at 40°C for 48 hours and stored in an airtight bag for later use. The technical parameters of Longdong coal are listed in Table 1.

| Proximate analysis (%) | Ultimate analysis (%) |
|------------------------|-----------------------|
| Mₐd                    | A_d                   | V_daf | FC_daf | Odaf | C_daf | H_daf | N_daf | St.d |
| 2.38                   | 25.32                 | 40.96 | 43.04  | 13.42 | 78.49 | 5.10  | 1.45  | 1.15 |

**TABLE 1** Technical parameters of Longdong coal
4 cm⁻¹. Spectral peak separation and quantitative calculation were performed by the curve fitting program of OMNIC 8.0 software. A linear line was selected as the baseline, and the position and number of spectral peaks were established based on the second derivative. Spectral smoothing was performed before fitting. The shape, height, and width of the spectrum were obtained by the Gaussian/Lorentz combination.³⁹

Figure 1 shows the FTIR spectra of raw coal and some samples treated with different kinds of ionic liquids at various concentrations. According to the FTIR spectra, the ionic liquid treatment does not alter the types of main functional groups in coal, but it alters their vibrational intensities in ranges of 3000-2800 cm⁻¹ (CH₂ and CH₃ stretching vibration), 1800-1000 cm⁻¹ [ν(C = C), ν(C = O), and ν(C = C) stretching vibration], and 900-700 cm⁻¹ [γ(C-H)].

The parameter CH₂/CH₃ represents the length of t aliphatic side chain and can be obtained by Equation (1):

\[
\text{CH}_2/\text{CH}_3 = \left( \frac{A_{2852\text{cm}^{-1}} + A_{2924\text{cm}^{-1}}}{A_{2957\text{cm}^{-1}}} \right)
\]

A larger value of CH₂/CH₃ means that longer aliphatic chains are bound to the aromatic rings, while a smaller value indicates shorter aliphatic chains, smaller spaces between aromatic clusters, and more compact structure of coal.⁴⁰ FTIR spectra were fitted to the ranges of 3000-2800 cm⁻¹ (aliphatic νC-H stretching vibration) and 900-700 cm⁻¹ (aromatic γC-H bending vibration). The parameter \( A_{\text{al}}/A_{\text{ar}} \) which represents the aromaticity and metamorphic grade of coal is estimated by Equation (2):

\[
A_{\text{al}}/A_{\text{ar}} = A_{900-700\text{cm}^{-1}} / A_{3000-2800\text{cm}^{-1}}
\]  

The parameter \( A_{\text{al}}/A_{\text{hy}} \) which indicates the relative content of hydrogen bonds,⁴¹ is estimated by the ratio of the total area of hydrogen bonds in the range of 3600-3100 cm⁻¹ to the total area of aromatic C-H vibration in the range of 900-700 cm⁻¹, as shown in Equation (3).

\[
A_{\text{al}}/A_{\text{hy}} = A_{3600-3100\text{cm}^{-1}} / A_{900-700\text{cm}^{-1}}
\]  

The condensation degree ‘B’ of aromatic ring can be estimated by Equation (4) which denotes the relation between the vibrational intensity of aromatic C=C and the area \( A_{1624\text{cm}^{-1}} \) of the spectrum peak at 1624 cm⁻¹.

\[
'B' = A_{900-700\text{cm}^{-1}} / A_{1624\text{cm}^{-1}}
\]  

The structural parameter ‘C’ of oxygen-containing group indicates the change in the ratio of the oxygen-containing functional group C=O to C=C in aromatic or fused rings, and it is used to demonstrate the coal maturity. ‘C’ is estimated by Equation (5).

\[
'C' = A_{1800-1650\text{cm}^{-1}} / (A_{1800-1650\text{cm}^{-1}} + A_{1624\text{cm}^{-1}})
\]  

**FIGURE 1** FTIR spectra of coal samples in the range of 4000-600 cm⁻¹
The parameter ‘D’ in Equation (6) which shows the intensity of aliphatic peak relative to the aromatic peak is used to indicate the degree of coal deterioration.44,45

\[
D' = A_{3000-2800 \text{ cm}^{-1}} / (A_{3000-2800 \text{ cm}^{-1}} + A_{1624 \text{ cm}^{-1}}) \tag{6}
\]

### 2.3 Temperature-programmed experiment

The production of index gases such as CO and CO\textsubscript{2} during the heating of coal sample can be directly monitored in the temperature-programmed experiment. In this study, temperature-programmed experiments were performed on HB-tc, BB-tc, AC-tc, BN-tc, and AB-tc, at different concentrations and temperatures, respectively, to obtain the inhibitory effects of ionic liquids on CSC. In the experiments, 3 g of raw coal sample and 1.8 g of ionic liquid solution were fully mixed and placed in the coal reaction vessel. The experimental system diagram is shown in Figure 2. While the dry air was injected into the coal reaction vessel at a rate of 20 mL/min, the mixture was heated from 30°C to 200°C at a rate of 2°C/min. In the heating process, the data acquisition device collected the data once every 1 minute.

The inhibition index calculated by Equation (7) represents the inhibitory effect of an inhibitor on coal oxidation during the heating process, and a larger inhibition index plays a positive role in CSC inhibition. \(E\) is the inhibition index of an inhibitor for a coal sample; \(A\) is the amount of CO released from the raw coal sample in the experimental process, ppm; \(B\) is the amount of CO released from a treated coal sample under the same test conditions, ppm.

\[
E = \frac{(A - B)}{A} \times 100\% \tag{7}
\]

Equation (8) shows the oxygen consumption rate.46

\[
V_{O_2}^0(T) = \frac{Q}{M} \times \ln \left(\frac{C_i}{C_{i+1}}\right) \tag{8}
\]

where \(V_{O_2}^0\) is the oxygen consumption rate of coal at temperature \(T\), mol/(cm\textsuperscript{3} s); \(Q\) is the volume of air passing through the furnace, cm\textsuperscript{3}/s; \(M\) is the mass of coal, g; \(C\) is the initial molar concentration of oxygen in the injected air, mol/cm\textsuperscript{3}; \(C_i\) and \(C_{i+1}\) are the molar concentrations of oxygen in the gas at the inlet and outlet of the furnace, respectively, mol/cm\textsuperscript{3}.

According to the Arrhenius formula, taking the reaction order of 1, the apparent activation energy calculation Equation (9) can be derived to calculate the apparent activation energy of each coal sample.47-49

\[
\ln \frac{f(c)}{T^2} = \ln \frac{AR}{\alpha A_a} - \frac{E_a}{RT} \tag{9}
\]

where \(E_a\) is the apparent activation energy, J/mol; \(R\) is the gas constant, \(R = 8.314\) J/(K mol); \(T\) is coal temperature, K; \(C\) is the oxygen content in the mixed gas, mol/cm\textsuperscript{3}; \(A\) is the prefactor; \(\alpha\) is the heating rate constant at \(\omega = dT/dt\).

### 3 RESULTS AND DISCUSSION

#### 3.1 FTIR spectral characteristics of coal samples

In order to quantitatively analyze the functional group structure of coal, a series of parameters were used to represent the structural changes in coal based on Figures 3 and 4. The FTIR spectral parameters \((CH_2/CH_3, A_{ar}/A_{al} \text{ and } A_{hy}/A_{ar})\) were obtained from Equations (1)-(3), and the parameters ‘B’, ‘C’, and ‘D’, which represent the relative maturity of coal, were obtained by Equations (4)-(6). Their specific values are listed in Table 2.

#### 3.1.1 Evolution of aliphatic structures

Oxygen adsorbs on aliphatic C-H structures initially\textsuperscript{26} to generate intermediate products such as peroxides and hydroperoxides which further oxidize into oxygen-containing
functional groups. Thus, CH$_2$, whose content is a key index of CSC, oxidizes easily under low temperature. According to Figures 1 and 5, both the aliphatic C-H stretching vibration intensity and the CH$_2$ content are significantly reduced. The CH$_2$ contents of 1:2, 1:5, 1:10, 1:25, and 1:50 HB-tc undergo the largest reductions, accounting for 12.60%, 10.28%, 6.34%, 8.42%, and 12.34% of that of raw coal, respectively. Similarly, the CH$_2$ content of 1:2 AC-tc also drops to about 20% of that of raw coal. Nevertheless, the CH$_2$ content of 1:2 BB-tc remains high, probably due to the existence of a small amount of ionic liquid residue in it.

The change in CH$_2$/CH$_3$ ratio can be observed in Figure 5C. The CH$_2$/CH$_3$ ratios of 1:10, 1:25, and 1:50 AC-tc coal samples are all lower than that of raw coal. With the decrease in HB concentration, the CH$_2$/CH$_3$ ratios in coal rise gradually. The CH$_2$/CH$_3$ ratios of 1:25 and 1:50 HB-tc even exceed that of raw coal. For BB-tc, AB-tc, and BN-tc, the CH$_2$/CH$_3$ ratios are not linearly related to the concentration of ionic liquids, but they all undergo turning points at the concentration of 1:10. The comparison between different concentrations of the same ionic liquid suggests that CH$_2$/CH$_3$ ratios of 1:10 BB-tc and 1:10 AB-tc are the smallest, while that of 1:10 BN-tc is the greatest. On the whole, AB-tc, 1:10 BB-tc, and 1:50 BB-tc have relatively short aliphatic side chains and relatively stable aromatic cluster structures, while 1:2 HB-tc and 1:10 HB-tc boast better aliphatic side-chain structures and lower CH$_2$ and CH$_3$ contents which are conducive to CSC prevention.

For the raw coal, the CH$_2$ peak area is 11.84, while the CH$_3$ area is 3.57; the value of CH$_2$/CH$_3$ aliphatic side chain is 3.30. According to Figure 5, HB-tc has less CH$_2$ and CH$_3$, and 1:2 HB-tc, 1:5 HB-tc, and 1:10 HB-tc have smaller CH$_2$/CH$_3$ ratios. BB-tc has higher contents of CH$_2$ and CH$_3$, while AC-tc contains less CH$_2$ and more CH$_3$, so the aliphatic side...
chain remains at a lower level. BN-tc aliphatic side-chain CH$_2$/CH$_3$ shows a greater value at 1:10, while other IL-tc has a smaller relative value at 1:10. It shows that at 1:10, HB-tc, BB-tc, AC-tc, and AB-tc can reduce the spatial structure and enhance the structural stability of aromatic clusters in coal, and IL-tc can effectively reduce the contents of CH$_2$ and CH$_3$ in coal.

### 3.1.2 Evolution of aromatic structure and hydrogen bond

$A_{ar}/A_{al}$ and $A_{hy}/A_{ar}$ were used to characterize the aromatic structure of coal and the relative content of hydrogen bonds, respectively. Ionic liquids serve to weaken the reactivity of hydrogen bonds (OH annular closely-associating type, OH…ether O type and OH self-associating type) to some extent.\textsuperscript{18,19}

The IL-tc samples exhibit obvious vibration at 850 cm$^{-1}$, so the value of parameter $A_{ar}/A_{al}$ grows. The unstable side-chain structure of flammable coal tends to be destroyed by ionic liquids, and the shortening of aliphatic side chains enhances the stability of aromatic structure. In addition, the relative content of hydrogen bonds decreases, indicating that the ionic liquid can somewhat dissolve hydrogen bonds in coal.\textsuperscript{25,27}

As can be seen from Figure 6, the $A_{ar}/A_{al}$ value of raw coal is the smallest. The $A_{ar}/A_{al}$ values of HB-tc and AB-tc increase first and then decrease with the rise of concentration, both reaching the maximum at the concentration of 1:10. As the concentration rises, the $A_{ar}/A_{al}$ value of BB-tc decreases slowly, while that of AC-tc increases; besides, that of BN-tc decreases first and then increases. Figure 7 shows that the $A_{hy}/A_{ar}$ value of raw coal outnumbers those of all samples except 1:25 HB-tc and 1:50 HB-tc. The comparison between Figures 6 and 7 suggests that with the rise of concentration, the $A_{hy}/A_{ar}$ values of samples exhibit opposite variation trends with the $A_{ar}/A_{al}$ values. This shows that the treatment of coal with ionic liquids raises the $A_{hy}/A_{ar}$ value and reduces the $A_{ar}/A_{al}$ value. It can be concluded that ionic liquid solutions are able to increase the aromaticity and metamorphic grade of coal, thus enhancing the stability of coal. Meanwhile, ionic liquids lower the content of hydrogen bonds in coal, which proves that they can destroy hydrogen bonds.

### TABLE 2 Structural parameters derived from the FTIR spectra

| Sample   | Ratio | $CH_2/CH_3$ | $A_{ar}/A_{al}$ | $A_{hy}/A_{ar}$ | $B'$ | $C'$ | $D'$ |
|----------|-------|-------------|-----------------|-----------------|------|------|------|
| Raw coal |       | 3.301       | 0.036           | 46.634          | 0.216 | 0.500 | 0.857 |
| HB-tc    | 1:2   | 1.635       | 0.127           | 41.668          | 0.172 | 0.500 | 0.576 |
|          | 1:5   | 2.925       | 0.197           | 35.315          | 0.269 | 0.500 | 0.495 |
|          | 1:10  | 2.278       | 0.899           | 25.022          | 0.305 | 0.500 | 0.433 |
|          | 1:25  | 3.694       | 0.520           | 49.758          | 0.248 | 0.500 | 0.367 |
|          | 1:50  | 5.341       | 0.408           | 58.670          | 0.166 | 0.500 | 0.288 |
| BB-tc    | 1:2   | 3.180       | 0.186           | 24.551          | 0.538 | 0.523 | 0.743 |
|          | 1:5   | 3.906       | 0.278           | 31.378          | 0.398 | 0.520 | 0.682 |
|          | 1:10  | 1.217       | 0.136           | 40.096          | 0.264 | 0.532 | 0.661 |
|          | 1:25  | 1.925       | 0.290           | 29.010          | 0.279 | 0.528 | 0.580 |
|          | 1:50  | 1.797       | 0.334           | 25.997          | 0.389 | 0.538 | 0.538 |
| AC-tc    | 1:2   | 1.059       | 0.635           | 10.732          | 0.519 | 0.523 | 0.450 |
|          | 1:5   | 1.025       | 0.585           | 18.530          | 0.452 | 0.538 | 0.432 |
|          | 1:10  | 1.084       | 0.509           | 23.221          | 0.437 | 0.518 | 0.462 |
|          | 1:25  | 1.998       | 0.496           | 35.234          | 0.348 | 0.512 | 0.468 |
|          | 1:50  | 1.269       | 0.473           | 37.867          | 0.317 | 0.522 | 0.401 |
| BN-tc    | 1:2   | 2.264       | 0.416           | 25.938          | 0.278 | 0.507 | 0.401 |
|          | 1:5   | 3.292       | 0.360           | 33.560          | 0.283 | 0.509 | 0.458 |
|          | 1:10  | 4.318       | 0.230           | 35.553          | 0.182 | 0.522 | 0.442 |
|          | 1:25  | 3.452       | 0.598           | 16.621          | 0.562 | 0.563 | 0.472 |
|          | 1:50  | 3.458       | 0.899           | 8.896           | 0.756 | 0.528 | 0.457 |
| AB-tc    | 1:2   | 4.660       | 0.154           | 37.575          | 0.230 | 0.524 | 0.592 |
|          | 1:5   | 4.582       | 0.260           | 32.271          | 0.291 | 0.524 | 0.563 |
|          | 1:10  | 2.806       | 0.349           | 26.919          | 0.340 | 0.521 | 0.505 |
|          | 1:25  | 3.624       | 0.313           | 29.179          | 0.287 | 0.560 | 0.491 |
|          | 1:50  | 4.664       | 0.235           | 32.709          | 0.305 | 0.533 | 0.463 |
3.1.3 | Evolution of oxygen-containing groups

Most of the oxygen-containing groups in coal structure have certain reactivity, and the 1750-1000 cm\(^{-1}\) spectral band represents oxygen-containing functional groups with different changes in various IL-tc samples. Although the content of -COO- increases at 1570 cm\(^{-1}\) peak, the C=O structure appears at 1690 cm\(^{-1}\), and the carbonyl group is more stable than the carboxyl group,\(^{51}\) so that the parameter ‘C’ which characterizes the maturity of coal changes little. At the same time, the C=C content of aromatic nucleus increases at 1624 cm\(^{-1}\) and the C-H content of aliphatic compound decreases, which is also the reason for the decrease in parameter ‘D’.

It can be observed from Figures 8, 9, and 10 that the ‘B’ value of raw coal is generally smaller than those of other samples. In addition, the ‘B’ values of HB-tc and AB-tc first increase

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**FIGURE 5** Changes of methyl and methylene contents in IL-tc: (A) CH\(_2\); (B) CH\(_3\); (C) CH\(_2\)/CH\(_3\)

**FIGURE 6** Value of parameter \(A_{ar}/A_{al}\) among different samples

**FIGURE 7** Value of parameter \(A_{hy}/A_{ar}\) among different samples
and then decrease with the rise of ionic liquid concentration, reaching the maximum values at the ionic liquid concentration of 1:10. However, the ‘B’ values of BB-tc and BN-tc first decrease and then increase with the rise of ionic liquid concentration and reaching the minimum values at 1:10. The ‘B’ value of AC-tc increases with the rise of ionic liquid concentration. From Figure 9, it can be known that the ‘C’ value of raw coal is smaller than those of all samples except HB-tc. Besides, the ‘D’ value of raw coal is the largest, and the ‘D’ values of all samples grow with the rise of ionic liquid concentration, except BN-tc.

3.2 | Results of temperature-programmed experiments

CO is an important index gas to characterize CSC. Figure 11 shows the variation curve of CO with temperature in the heating process. Besides, a control experiment was carried out to measure the CO production of water-treated coal (hereafter referred to as Add water).

3.2.1 | Changes in CO production with temperature

As can be seen from Figure 11, the CO concentration generally goes up with the rise of temperature in the range of 30-200°C. The CO concentration of raw coal reaches 3645 ppm at 200°C. In the heating process, both Add water (raw coal and water mixed control experiment) and IL-tc experience a platform period in the range of 98-125°C where the CO concentration ceases to increase and maintains a relatively stable state. The CO concentration just increases slightly before 98°C, and it starts to grow rapidly after 125°C, that is, beyond the platform period. The CO concentrations of raw coal, Add water, and IL-tc demonstrate notable changes after 125°C. The CO concentrations of 1:2 HB-tc and 1:5, 1:10, and 1:25 AC-tc are significantly lower than that of raw coal, and their CO concentrations at 200°C are only 65%, 55.6%, 42%, and 43.3% that of raw coal, as shown in Figure 12. In Figure 11, the CO concentration of 1:2 AB-tc becomes higher than that of raw coal at about 150°C and reaches 6787 ppm at 200°C.

During the platform period, 98-112°C, the CO concentrations of Add water and IL-tc remain higher than that of raw coal until the temperature steps into the range of 112-125°C where their CO concentrations become lower than that of raw coal. This is because of the better thermal conductivities of Add water and IL-tc before the platform period. Therefore, before 112°C, the treated coal samples undergo faster temperature growths and thus generate more CO than raw coal. When the water reaches the boiling point 98°C, it evaporates at a higher rate and takes away a lot of heat, which is why the CO concentrations of treated coal samples begin to enter the platform period. The ionic liquid equipped with the function of CSC inhibition will play the main role in CSC inhibition after the moisture has evaporated, so most of the CO
concentrations of IL-tc samples become lower than that of raw coal sample at 125°C.

Figure 13 intuitively displays the changes in CO concentration with the concentration of ionic liquids. According to Figure 13, the CO concentration in AC-tc is kept at a relatively low level at 140°C, 160°C, 180°C, and 200°C; the CO concentration in HB-tc with mass concentration ratios of 1:2 and 1:10 are also lower, which is consistent with the changes in Figure 12. Under several temperature conditions, it can be seen that HB-tc has a better inhibitory effect on CO.
production, and its inhibitory effect decreases with the drop of concentration. With the rise of temperature, the effect of concentration on the inhibition of CO production gradually weakens at 180°C and 200°C. In AC‐tc, CO production exhibits a U‐shaped variation trend. Under all four temperature conditions, a smaller value appears at 1:10 mass concentration ratio, indicating that the ionic liquid AC‐tc has an optimum inhibition concentration near 1:10 mass concentration ratio. The inhibitory effects of the other three kinds of ionic liquids are not very obvious, but the inhibitory effect of AB increases and then tends to stabilize with the drop of concentration, which has a strong guiding significance for the application of ionic liquids to inhibit CSC.

3.2.2 | Inhibition index and oxygen consumption rate

The change curves of inhibition index are presented in Figure 14. The same variation rule can be observed from the five pictures in Figure 14. The inhibition indexes of samples change gently before the temperature reaches 80°C. However, they fall first and then climb after 80°C, reaching the minimum and maximum values at 98°C and
125°C, respectively. Then, they decline gradually when the temperature rises from 125°C to 140°C. Specifically, as can be observed from Figure 14A, in the range of 80-140°C, 1:2 AB-tc has a smaller inhibition index than other AB samples, while 1:10 AB-tc has a relatively greater inhibition index. After 140°C, the inhibition indexes of all AB-tc samples generally become smaller than 0.2, indicating their poor inhibitory effects of different concentrations of AB ionic liquid after 140°C. As displayed in Figure 14B, the inhibition indexes of AC-tc samples gradually decrease and tend to stabilize after 125°C. Among them, 1:10 AC-tc always keeps a greater inhibition index (around 0.6) than the other samples, suggesting its excellent CSC inhibitory effect. It is followed by 1:25 AC, 1:50 AC, and 1:5 AC in turn. Figure 14C-E show that BB, BN, and HB all have rather poor CSC inhibitory effect, because their inhibition indexes are all smaller than 0.2 after the treatment.

Before 140°C, O₂ consumption is a very slow process. In contrast, after 140°C, the coal samples enter the accelerated oxidation stage where they oxidize rapidly to produce a large amount of CO and CO₂ quickly. At the same time, after 140°C, the inhibitory effects of ionic liquids on coal samples tend to stabilize. Figure 15 exhibits the change curves of oxygen consumption of 4 treated coal samples and raw coal sample with temperature. From Figure 15, the O₂ consumption is closely correlated with the CO production: The more the O₂ consumed, the more the CO produced. Under the same temperature condition, 1:2 HB-tc, 1:5 AC-tc, 1:10 AC-tc, and 1:25 AC-tc have lower oxygen consumption rates.

It is worth noting that the inhibition index shows a negative value between 80°C and 112°C, which may be related to the increase in CO production caused by water evaporation. Our research team will further explore the specific causes of this phenomenon in subsequent experiments. Despite the negative inhibition index at the initial stage, the short-term rise of CO concentration just exerts a very weak effect on CSC, that is, |A-B| < 30 ppm. After passing the platform period, the coal samples enter the accelerated oxidation stage, in which the amount of CO produced increases rapidly. Despite the low inhibition indexes of IL-tc samples, the value of |A-B| exceeds 60 ppm after 125°C, for example, the CO concentration of 1:2 HB-tc is reduced by 720 ppm compared with that of raw coal sample.
3.2.3 Apparent activation energy analysis

\[ \ln\left(\frac{f^2}{T^2}\right) \] is linearly related to \( 1/T \). According to the functional relationship between them, the apparent activation energy of coal oxidation can be calculated by fitting the linear relationship diagram. Table 3 shows the apparent activation energy \( E_a \) of coal sample in the temperature range of 125-200°C. It can be seen that the \( E_a \) values of coal samples and the treated coal samples lie in the range of 5.84-8.5 kJ mol\(^{-1}\), and the \( E_a \) values of most of the treated coal samples are around 7 kJ mol\(^{-1}\) without obvious differences. In this range, the \( E_a \) value of raw coal sample (7.71 kJ mol\(^{-1}\)) is slightly greater than that of Add water.
Most of the IL-tc samples have greater \( E_a \) values than the raw coal sample in this range, indicating that certain concentrations of ionic liquid can increase the apparent activation energy and reduce the oxidation activity of coal samples. The \( E_a \) value of 1:2 AC-tc reaches 8.50 kJ mol\(^{-1}\), and the results show that 1:2 HB-tc, 1:10 AC-tc significantly increase the \( E_a \) values of coal samples. However, there is no obvious change for other concentrations of IL-tc, which still requires further study.

### 4 CONCLUSIONS

Fourier-transform infrared spectroscopy was used to study the changes in CH\(_2\), CH\(_3\), and hydrogen bonds in IL-tc and to characterize the structural parameters of coal. The quantitative parameters were obtained from the spectral fitting curves. The FTIR results show that the intensity of aliphatic C-H stretching vibration of IL-tc drops obviously and that IL-tc effectively reduces the CH\(_2\) and CH\(_3\) contents in coal. Among the IL-tc samples, HB-tc samples undergo the largest drops in their CH\(_2\) content, while HB-tc and AC-tc also boast relatively good effects in reducing the aliphatic side chains. Moreover, the inhibitory effect of HB-tc decreases with the decrease in concentration.

According to the temperature-programmed experiments, the CO concentrations of coal samples grow with the rise of temperature. In the heating process, both Add water and IL-tc experience a platform period in the range of 98-125°C where the CO concentration ceases to grow with the rise of temperature. After the platform period, the CO concentration increases rapidly with increasing temperature in the accelerated oxidation stage. The CO concentrations of 1:2 HB-tc and 1:10 AC-tc are lower than that of raw coal, demonstrating that 1:2 HB and 1:10 AC boast excellent inhibitory effects. HB-tc and AC-tc are both effective in reducing CO concentration. Moreover, among the samples, AC-tc achieves an optimum inhibitory effect near 1:10 mass concentration ratio.

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