Characterization and Performance Testing of an Intumescent Nanoinhibitor for Inhibiting Coal Spontaneous Combustion

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ABSTRACT: Considering disadvantages such as the low thermal stability and environmental pollution of existing gel inhibitors, a green and stable intumescent nanoinhibitor (INI) was prepared and tested. First, polyacrylamide (PAM), nano-silica, and intumescent flame retardant (IFR) were selected as raw materials. The INI was prepared by nanoparticle modification and cross-linking polymerization. Then, the structure and physical properties of INI were tested by Fourier transform infrared spectroscopy, scanning electron microscopy, and rheological experiments. Meanwhile, the inhibition performance of INI was studied through thermogravimetric analysis-Fourier transfer infrared spectroscopy (TGA-FTIR) analysis. The results suggest that the nano-modification improved the dispersibility of INI particles. The addition of modified nano-silica (MNS) and IFR enhances the strength of the reticular structure, thereby improving the transport convenience and covering ability of the INI gel. At high temperatures, IFR can generate a porous foamed carbon layer that further coats the coal. After INI inhibition treatment, the characteristic temperature and activation energy of coal were significantly improved, and the production of carbon monoxide and carbon dioxide decreased. Hence, irrespective of physical properties, physical inhibition performance, or chemical inhibition performance, INI performed well. Research results can provide valuable references for the preparation and performance study of a coal spontaneous combustion inhibitor.

1. INTRODUCTION

Coal is closely related to economic development and people’s lives and is a primary energy source globally. However, coal mines have long been plagued by various disasters, of which, coal mine fires are the most serious. When a coal mine fire occurs, it not only causes massive casualties and losses but also leaves behind intractable pollution, which continues to affect the coal mining environment. Among coal mine fires, 90% are caused by the spontaneous combustion of coal.

To prevent coal spontaneous combustion, various coal mine fire-prevention technologies have been developed. Among them, gel fire-prevention technology has been widely used in coal mine fire-fighting due to its high water absorption, strong permeability, and high inhibition performance. In recent years, many studies have tried to develop gels with improved properties. Nie et al. prepared a new type of dust suppression gel and studied its water absorption and retention. Zhang et al. combined the gel with a foaming agent and N2 to prepare a foam gel for inhibiting coal spontaneous combustion. The above research has strongly promoted the development of gel fire-prevention technology. However, there are still problems that need to be improved, such as poor water retention and thermal stability of the gel, as well as the generation of irritating gases. Therefore, to ensure high inhibition performance, it is of great significance to develop a green and stable composite gel inhibitor. As a hot spot in the research of environmentally friendly inhibitors, chemical intumescent flame retardant (IFR) systems and inorganic nanoparticle flame retardant systems are feasible solutions.

IFR is a green and environmentally friendly flame retardant with many advantages such as being halogen-free, having low toxicity, and causing smoke suppression. IFR is widely used in plastics, rubber, coatings, and other fields. When the temperature reaches approximately 150 °C, the IFR decomposes to form a porous carbon foam layer, which plays a role in heat insulation and acts as an oxygen barrier. Qi et al. found that the addition of an intumescent flame retardant system...
effectively improved the flame retardancy and thermal stability of the inhibitor. Bhoite et al. used the IFR to treat expanded polystyrene beads to improve their fire resistance. Shiu et al. compounded the IFR with raw lacquer to improve the fire resistance and thermal stability of the raw lacquer.

Although IFRs have many advantages, they also have disadvantages, such as low flame retardant efficiency and high consumption. The addition of nanomaterials can make up for these disadvantages. Bao, Ali, and Kahraman studied the influence of different nanomaterials on IFR, and all concluded that nanomaterials and IFR have a good synergistic flame retardant effect. Nano-silica is a nanomaterial with good antioxidation properties, which can be used in the preparation of anticorrosion coatings. However, it has the problems of easy agglomeration and uneven distribution in application, which needs to be solved by methods such as modification. In addition, materials composed of nanomaterials and IFRs are rarely used in the field of coal spontaneous combustion prevention. Therefore, this study examines the relative research in this field to prepare an intumescent nano inhibitor.

In this study, polyacrylamide/modified nano-silica (PAM/MNS) was prepared by in situ polymerization using polyacrylamide (PAM) as the hydrogel and modified nano-silica (MNS) as the nanomaterial. Subsequently, PAM/MNS and IFR (melamine/polyethylene glycol/ammonium polyphosphate) were mixed to prepare the intumescent nano inhibitor (INI). First, to study the preparation mechanism of the inhibitor, the molecular structure of the product in the preparation process was characterized by infrared spectroscopy. Then, the microstructures of inhibitor particles and the INI gel were observed by scanning electron microscopy. Next, the rheological properties of the INI gel and the PAM gel were compared by rheological experiments. Meanwhile, thermogravimetric analysis-Fourier transfer infrared spectroscopy (TGA-FTIR) analysis was used to analyze the influence of INI on coal characteristic temperature, activation energy, and gas products. Finally, combined with the experimental results, the application advantages and inhibition performance of INI were analyzed. The research results may provide a new method for the prevention of coal spontaneous combustion and a reference for the preparation mechanism of inhibitors.

### 2. EXPERIMENTAL SECTION

#### 2.1. Chemicals and Coal Samples

The reagents for the preparation of the INI are listed in Table 1. The coal samples used in the experiment were Yangguan lignite (Shanxi, China). Table 2 summarizes the basic properties of the coal samples.

#### 2.2. Preparation of INI

##### 2.2.1. Preparation of MNS

First, 10 g of dried nano-silica was added to 240 mL of 75% ethanol solution, fully stirred by a magnetic stirrer, and heated to 70 °C. Then, 2 mL of KH-570 was added to the solution, and the pH was adjusted to 4 with 10% acetic acid. The solution is fully reacted in a water bath for 90 minutes. Then, the system was cooled to room temperature and centrifuged to obtain a nano-silica gel. After the unreacted KH-570 hydrolysate was washed away by absolute ethanol, the MNS gel was dried and stored for later use.

##### 2.2.2. Preparation of PAM/MNS

A total of 10 g of acrylamide and 0.4 g of MNS were dissolved in 150 mL of water. The solution was stirred vigorously for 1 h, and 0.07 g of KPS was added during the stirring. Then, the solution was sealed for polymerization under a constant-temperature water bath at 75 °C for 4 h to form a PAM/MNS gel. During the polymerization reaction, slight stirring was carried out until the solution was uniform and stable. Next, deionized water was used to wash away unreacted substances in the PAM/MNS gel. Finally, the PAM/MNS gel was dried and stored for later use.

##### 2.2.3. Preparation of INI

First, ammonium polyphosphate, polyethylene glycol, and melamine were configured in a mass ratio of 21:5:4 to obtain the IFR. Then, the PAM/MNS and IFR were mixed in a mass ratio of 3:1. When the powder was fully mixed, the INI was prepared.

The overall preparation process of the INI is shown in Figure 1.

#### 2.3. Chemical Structure Characterization of MNS

In this study, the experimental instrument was an iSS0 FTIR Fourier infrared spectrometer, and KBr was mixed with the samples to make a tablet. Nano-silica, unwashed MNS, and MNS washed with absolute ethanol were used as samples to study the removal of impurities in MNS and the modification of nano-silica. The experimental parameters are as follows: the resolution was 4 cm⁻¹, and the spectral wavenumber range was 400–4000 cm⁻¹ with 32 scans.

#### 2.4. Chemical Structure Characterization of Composite Gels

In this study, by analyzing the infrared spectra of PAM, PAM/MNS, and INI, the combination of each component of the INI was studied. The experimental method and experimental parameters are the same as in Section 2.3.

#### 2.5. Microstructure Characterization of Nano-Silica

The experimental instrument was a LEO 1450 scanning electron microscope. The nano-silica, MNS, and INI were dried and ground into powder for sample preparation. The morphology characteristics of nano-silica, MNS, and INI were observed under 1000 times magnification.

#### 2.6. Microstructure Characterization of the INI Gel

The experimental instrument was a LEO 1450 scanning electron microscope. The PAM and INI gels were dried in a constant-temperature oven at 300 °C for 1 h to prepare sheet samples. Then, the samples were treated with a gold spray. At 100 times magnification, the microstructure of the surface and sides of the gels was observed.

### Table 1. Reagents for Preparation of the Composite Inhibitor

| reagent name | specification | source |
|-------------|---------------|--------|
| nano-silica |              | Shanghai Meryl Chemical Technology Co., LTD, China |
| anhydrous ethanol |              | Beijing Honghu United Chemical Products Co., LTD, China |
| 3-(methacryloyl) propyl trimethoxy silane (KH-570) | CP | Beijing Yinoki Technology Co., LTD, China |
| acrylamide | CP | Beijing Honghu United Chemical Products Co., LTD, China |
| potassium persulfate (KPS) | CP | Beijing Honghu United Chemical Products Co., LTD, China |
| melamine | AR | Beijing Honghu United Chemical Products Co., LTD, China |
| poly(ethylene glycol) |              | Beijing Honghu United Chemical Products Co., LTD, China |
| ammonium polyphosphate | AR | Shanghai Meryl Chemical Technology Co., LTD, China |

### Table 2. Properties of Coal Samples

| sample | proximate analysis (air-dried basis) (%) |
|--------|-----------------------------------------|
|        | M_d | A_d | V_d | F_Cd |
| lignite | 9.55 | 9.76 | 32.12 | 48.57 |
2.7. Rheological Property Analysis of the INI Gel. The instrument used in the experiment was a Brookfield RST-SST rheometer. The fluid properties of the PAM gel and the ING gel were tested by two experimental methods. Each experiment was performed three times to verify the repeatability and reliability of the experimental results, and then, the final results were obtained by fitting.

2.7.1. Relationship between Gel Viscosity and Shear Rate. In this experiment, the shear rate gradually increased from 0 to 290 s\(^{-1}\), the increase rate was fixed to 1 s\(^{-1}\), and the experimental data were taken every 1 s.

2.7.2. Effect of Shear Rate Mutation on Gel Viscosity. In this experiment, the shear rate was first held at a low rate (0.5 s\(^{-1}\)) for 50 s, then increased instantaneously to a high rate (100 s\(^{-1}\)), and returned to a low shear rate after 100 s. The experimental data was taken every 1 s.

2.8. Analysis of Inhibition Performance. In this study, TGA-FTIR analysis was used to analyze the inhibition performance of INI against coal spontaneous combustion. After grinding to a particle size of 0.125–0.180 mm, the coal was mixed with inhibiting materials and dried to obtain the inhibited coal samples. Meanwhile, a coal sample mixed with water was set as a control. By studying the mass changes, kinetic parameters, and gas generation of each inhibited coal sample during the heating process, the inhibition performance of INI was verified. The amounts of reagents for each sample are shown in Table 3. The experiments were carried out in a synthetic air (21% O\(_2\)/79% N\(_2\)) environment. Each sample was tested at four heating rates (2, 10, 15, 20 \(^\circ\)C/min), and the heating range was 30–400 \(^\circ\)C. The amount of sample required for the experiment was 10 mg. Before the experiment, synthetic air was used for ventilation at room temperature for 5 min at the rate of 50 mL/min to replace the entire reaction atmosphere of the thermogravimetric analyzer.

3. RESULTS AND DISCUSSION

3.1. FTIR Results of MNS. By analyzing and comparing the infrared spectra of the samples, the changes in the chemical structure of the samples can be studied.\(^\text{31}\) However, there were overlaps between peaks in the directly obtained infrared spectrum, which affected the analysis of the results. Therefore, the infrared spectra peak of each sample was fitted by PeakFit software, as shown in Figure 2. To visually show the change of functional groups in the samples, the infrared spectrum after fitting was remapped, and the result is shown in Figure 3.

After the modification, new absorption peaks appeared in the infrared spectra of the MNS. The absorption peak at 1880 cm\(^{-1}\) can be attributed to the stretching vibration of the C=O double bond in KH-570. The absorption peak at 2947 cm\(^{-1}\) can be attributed to the stretching vibration of C–H. This is because the combination of KH-570 and nano-silica introduced C=O double bonds and C–H bonds. The Si–OH produced by the hydrolysis of KH-570 and the –OH on the surface of the nano-silica condensed to form Si–O–Si, making the KH-570 chemically bond to the nano-silica surface. As a result, the surface of the nano-silica changed from hydrophilic to hydrophobic.\(^\text{32}\) In addition, the coupling agent on the surface of the nano-silica blocked the agglomeration of particles, improving the dispersibility of the material, as shown in Figure 4. Moreover, asymmetric stretching vibration absorption peaks of the –OH bond appeared at 3421 and 3600 cm\(^{-1}\) in the spectrum of the washed MNS. This occurred because unreacted KH-570 was washed off the surface of the MNS by absolute ethanol, resulting in a relative increase in –OH bonds.

3.2. FTIR Results of Composite Gels. In this study, the infrared spectra peaks of PAM, MNS, and INI were fitted by PeakFit software, and the result is shown in Figure 5. The infrared spectrum of PAM showed double peaks for the primary amide between 3500 and 3100 cm\(^{-1}\). The absorption

### Table 3. Amounts of Reagents for Each Sample

| sample number | types          | coal (g) | inhibitor     | deionized water (mL) |
|---------------|----------------|----------|---------------|----------------------|
| 1             | raw coal       | 15       |               | 35                   |
| 2             | PAM inhibited coal | 15   | PAM (2 g)     | 33                   |
| 3             | PAM/MNS inhibited coal | 15 | PAM/MNS (2 g) | 33                   |
| 4             | INI inhibited coal | 15       | INI (2 g)     | 33                   |
peak at 1668 cm\(^{-1}\) can be attributed to the stretching vibration of C=O. These absorption peaks are known amide features, showing that PAM contains a large number of amide groups.

This is because PAM is formed by the polymerization of acrylamide, and its polyacrylamide structure (\([-\text{CH}_2-\text{CH}-(\text{CONH}_2)]_n\)) contains a large number of amide groups.

The infrared spectrum of the PAM/MNS (Figure 5b) showed the characteristic peaks, the stretching vibration absorption peak of Si-O (505 and 1103 cm\(^{-1}\)), and the stretching vibration absorption peak of -OH (3512 cm\(^{-1}\)). These are the main characteristic peaks of MNS. This indicates that the MNS in PAM/MNS fully combines with PAM. On the one hand, the hydroxyl group in MNS is a highly water-absorbing functional group, which can effectively improve the water absorption of the gel. On the other hand, these hydroxyl groups can be combined with the highly reactive hydroxyl groups in coal via an etherification reaction. This reaction will generate stable ether bonds, which improves the molecular stability of coal. The reaction process is shown in eq 1.

\[
R_1\text{OH} + \text{MNS} \rightarrow R_1 - O - R_2 + H_2O \quad (1)
\]

where \(R_1\) and \(R_2\) represent carbon chains.

Compared with PAM/MNS, there are new absorption peaks in the infrared spectrum of INI (Figure 5c), which mainly include the flexural vibration absorption peak (885 cm\(^{-1}\)) of P-O-P in ammonium polyphosphate, the stretching vibration absorption peak of C-H in polyethylene glycol (2912 cm\(^{-1}\)), and the stretching vibration peak of C=N– in melamine (1900 cm\(^{-1}\)). Compared with PAM/MNS, the molecular structure of IFR was observed in INI, which shows that IFR and PAM/MNS are fully combined. After dissolving INI in
water, the colloidal particles of the INI sol will slowly polymerize to form a gel with a reticular structure. Due to this sol–gel process, MNS and IFR are uniformly distributed in the reticular structure. In addition, at high temperature, IFR can decompose to form a porous carbon foam layer, which provides stable oxygen barrier properties. Therefore, we can infer that the inhibition performance of INI at high temperatures improved. Figure 6 shows the molecular structure changes of INI during the preparation process.

![Figure 6. Molecular structure changes of the INI gel during the preparation process.](image)

### 3.3. Microstructure of Nano-Silica

The microstructures of nano-silica, modified nano-silica, and INI are shown in Figure 7. It can be found in Figure 7a that the nano-silica particles are of uneven size and have obvious agglomeration. In the process of dissolving the inhibitor, the agglomeration of the inhibitor particles will reduce the specific surface area of the material, thereby seriously affecting the dissolution rate and uniformity. In Figure 7b, the MNS particles are more uniform in size. The agglomeration of particles is also significantly reduced. It shows that the modification of nano-silica by KH-570 successfully improves the dispersibility of nanoparticles. Finally, as can be seen in Figure 7c, the INI particles are distinct and rarely agglomerated. It is proved that INI also has good dispersibility. When dissolving, the INI powder with good dispersibility has a larger contact area with water, so that it can dissolve in water faster and form an INI gel.

### 3.4. Microstructure of the INI Gel

After drying in an incubator at 300 °C for 1 h, the microscopic morphology of the gels is shown in Figure 8. From Figure 8a, it can be seen that the surface of the PAM gel showed obvious cracking after heating. Numerous cracks distributed on the surface reduced the oxygen barrier properties of the PAM gel. Oxygen penetrates through the cracks and oxidizes the coal. In contrast, as shown in Figure 8b, the surface of the INI gel did not crack after heating but was covered with numerous wrinkles. This is the porous carbon foam layer formed by the decomposition of the IFR at high temperature. The surface of the porous carbon foam layer is continuous and dense, which can replace the cracked gel and continue to exert the blocking performance. In Figure 8c, a large number of small pores are distributed on the cross section of the INI gel, forming a complex network structure. This is due to the decomposition of IFR at high temperatures to form a molten system and generate gases such as ammonia and water vapor. The gas formed these small pores in the molten system. These pores cause the gel to swell, compensating for the volume reduction caused by water loss, thereby enhancing the gel’s filling capacity.

### 3.5. Results of Rheological Experiment

#### 3.5.1. Relationship between Gel Viscosity and Shear Rate

The changes in viscosity and shear stress of the INI gel and the PAM gel with the increase in shear rate are shown in Figure 9. It can be found that the viscosity of the two gels exhibits typical curves of non-Newtonian pseudoplastic fluids. The change in their viscosity can be mainly divided into two stages. In the range of 1–150 s⁻¹, the viscosity of the two gels decreased rapidly with increasing shear rate, but the decreasing trend gradually slowed down. This stage is called the shear dilution region. At this stage, the gel undergoes shear thinning under continuous shearing, and the shear stress curve is close to the Herschel–Bulkey model. When the shear rate is higher than 150 s⁻¹, the viscosity of the gel hardly decreased with the increase of the shear rate. This range is called the Newton region. At this stage, the degree of shear thinning of the gel is approaching its limit. The shear stress is only affected by the shear rate, and its change curve is similar to that of the Bingham model.

When the shear rate tends to 0, the viscosity of the PAM gel is 16.96531 Pa·s, and the viscosity of the INI gel is 35.78746 Pa·s. However, at a high shear rate (350 s⁻¹), the shear stress of the PAM gel is 339.27084 Pa, and that of the INI gel is 287.28494 Pa. When the shear rate tends to 0, the viscosity of the PAM gel is 16.96531 Pa·s, and the viscosity of the INI gel is 35.78746 Pa·s. However, at a high shear rate (350 s⁻¹), the shear stress of the PAM gel is 339.27084 Pa, and that of the INI gel is 287.28494 Pa. Therefore, compared with the PAM gel, the INI gel has a higher viscosity when adhering to the coal surface (low-shear-rate environment) and less resistance in transport (high shear rate environment), which indicates that the addition of MNS and IFR significantly improves the rheological properties of the gel.

To further compare the rheological properties of the two gels, the Herschel–Bulkey model (eq 2) was used to fit the shear stress curves of the two gels in the shear dilution region.

\[
\tau = \tau_0 + C\gamma^n
\]

(2)

![Figure 7. Micromorphology of (a) nano-silica, (b) MNS, and (c) INI.](image)
where \( \tau \) (Pa) denotes the shear stress, \( \tau_0 \) (Pa) denotes the yield stress, \( C \) denotes the consistency coefficient, \( \gamma \) (s\(^{-1}\)) denotes the shear rate, and \( n \) is the flow characteristic index.

The fitting result of the PAM gel is shown in eq 3, and the determination coefficient \( R^2 = 0.99828 \).

\[
\tau = 0.82843 + 20.58804 \cdot \gamma^{0.44651} \tag{3}
\]

The fitting result of the INI gel is shown in eq 4, and the determination coefficient \( R^2 = 0.99707 \).

\[
\tau = 10.04187 + 30.45997 \cdot \gamma^{0.36772} \tag{4}
\]

The determination coefficient \( R^2 \) for both gels is close to 1, which indicates that the model fits the experiment well. From the fitting results, it can be found that the non-Newtonian exponents of the two gels are both less than 1, so it can be inferred that both the PAM gel and the INI gel are pseudoplastic fluids. In addition, the yield stress of the PAM gel is 0.82843 Pa, while that of the INI gel is 10.04187 Pa. The higher yield stress makes INI more rigid when covering the coal surface.

### 3.5.2. Effect of Shear Rate Mutation on Gel Viscosity

The effect of shear rate mutation on gel viscosity is shown in Figure 10. It can be seen from the figure that the change rules of the two gels after the shear rate mutation are basically the same. When the shear rate suddenly increased to 100 s\(^{-1}\), the viscosity of the two gels also dropped sharply. When the shear rate returned to its original state after 100 s, the viscosity increased, but it was still lower than that at the beginning of the experiment. This is because the high-speed shear destroys the network structure of the gel. Subsequently, in the low-shear-rate environment, the viscosity of the gel increased slowly and gradually returned to the initial state of the experiment. This proves that both gels have a good self-healing function, and high-speed shearing will not cause a permanent decrease in the viscosity of the gels.

### 3.5.3. Rheological Properties of the INI Gel

The thixotropy of the gel may come from the reticular structure of the gel, which is formed by the cross-linking of acrylamide in the inhibitor particles. This structure can block the movement of the fluid and increase the viscosity of the gel. Compared with the PAM gel, the viscosity of the INI gel was significantly improved, indicating that the MNS and IFR attached to the network structure improved the strength of the structure. When the fluid flows, the reticular structure is deformed and destroyed, and the blocking effect decreases, resulting in a
decrease in viscosity. This process can be regarded as the transformation of the system from gel to sol. At the same time, as the broken structures collide with each other, the reticular structure gradually recovers. Therefore, when the shearing failure rate is lower than the self-healing rate of the reticular structure, the viscosity of the gel starts to rise. This explained the reason why the viscosity increased slowly after the shear rate dropped sharply in Figure 10. Figure 11 illustrates the destruction and reconstruction of the gel reticular structure during shearing.

![Figure 11](image)

**Figure 11.** Destruction and reconstruction of the gel reticular structure.

### 3.6. Results of TGA-FTIR Analysis

#### 3.6.1. Inhibition Effect Analysis through TG/DTG

Figure 12 shows the thermogravimetry/derivative TG (TG/DTG) curves of different samples. To study the mass change of coal in the oxidation process, the water evaporation stage and the oxygen absorption stage were selected for analysis. By analyzing the TG/DTG curve, the characteristic temperature points of each sample were determined, as shown in Table 4.

As seen in Table 4, the characteristic temperatures of the inhibited coal samples were higher than those of the raw coal. It proves that the addition of inhibitors had an inhibitory effect on coal spontaneous combustion. Moreover, the characteristic temperatures of the INI inhibited coal sample were higher than other inhibited coal samples, which shows that INI’s inhibition performance was the best of those tested. It is worth mentioning the xerochasy temperature ($T_x$) and the thermal decomposition temperature ($T_d$), which reflect the water retention performance of the inhibitor in the early stage of oxidation and the inhibition performance in the late oxidation stage, respectively.

Compared with the raw coal, the $T_x$ values of the PAM inhibited coal, PAM/MNS inhibited coal, and INI inhibited coal increased by 21.54, 33.21, and 38.12 °C, respectively. The $T_d$ of the PAM inhibited coal increased. On the one hand, this is because the PAM gel has strong water absorption and water retention, which slows the evaporation of water from the coal. On the other hand, the gel covering the coal prevents the desorption of gas in the coal. The $T_x$ of the PAM/MNS inhibited coal and the INI inhibited coal further increased because the addition of MNS increased the strength and thermal stability of the gel and provided oxidation resistance. The addition of MNS increases the strength and thermal stability of the gel, thereby slowing the rate of water loss. Additionally, the added nanoscale particles increased the contact area between the gel and the coal, increasing the oxygen barrier performance. As the temperature increased, the PAM gel with low thermal stability gradually deactivated and began to crack. That is why the $T_d$ of the PAM inhibited coal only increased by 0.28 °C compared to that of the raw coal. In contrast, the $T_d$ of the PAM/MNS inhibited coal increased by 4.43 °C. This is because the MNS in the PAM/MNS continued to exert antioxidation properties at high temperatures. Finally, the $T_d$ of the INI inhibited coal increased by 7.50 °C. This is because the porous carbon foam layer formed by IFR exerts stable oxygen barrier properties even at high temperatures, which allow the INI to maintain a good inhibition performance in the late oxidation stage.

#### 3.6.2. Inhibition Effect Analysis through Oxidation Kinetics

In this experiment, the low-temperature oxidation process of coal was divided into two parts: the water evaporation and desorption stage and the oxygen absorption and weight gain stage. The activation energy of coal can be calculated using the Starink method based on the multiple scan rate method, as shown in eq 5.

\[
\ln \left( \frac{\beta}{T^{1.8}} \right) = C_S - \frac{BE}{RT} = C_S - 1.0037 \cdot \frac{E}{RT}
\]

where $\beta$ (K min$^{-1}$) denotes the programmed heating rate, $C_S$ is a constant, $B = 1.0037$, and $R$ (8.314 KJ·mol$^{-1}$·K$^{-1}$) is a kinetic constant.

The water evaporation and desorption stage starts at a temperature of 30 °C and ends at $T_a$. The oxygen absorption and weight gain stage starts at $T_a$ and ends at $T_b$. The activation energies of different samples are shown in Figure 13.

As seen in Figure 13, the change law of the activation energy of the coal samples was nearly the same. As the conversion rate increased, the activation energy of raw coal first decreased in the water evaporation and desorption stage and then increased in the oxygen absorption and weight gain stage. The activation energies of different coal samples had the following order: INI inhibited coal > PAM/MNS inhibited coal > PAM inhibited coal > raw coal. It indicates that the addition of inhibitors had a significant inhibitory effect on coal spontaneous combustion, and the INI had the best inhibitory effect. It is worth noting that, during the oxygen absorption and weight gain stage, the increase in the activation energy of the INI inhibited coal was significantly higher than that in the previous stage. This may be due to the oxygen barrier effect of the porous carbon foam layer. Therefore, as the temperature increases, the gel with the IFR exhibits a better inhibition performance.

In summary, INI had a significant and stable inhibitory effect on the spontaneous combustion of coal samples, whether in the water evaporation and desorption stage or in the oxygen absorption and weight gain stage.

#### 3.6.3. Inhibition Effect Analysis through Gas Production

The amount of CO and CO$_2$ gases produced in the oxidation process reflects the oxidation of coal samples and the difficulties associated with coal spontaneous combustion. By analyzing the influence of inhibitors on gas production in the coal oxidation process, the inhibitor performance can be studied. Figure 14 shows the three-dimensional infrared spectra of the gas products of different samples. For further study, the infrared spectra at characteristic temperature points of each coal sample were separated, as shown in Figure 15.

As seen in Figure 15, the characteristic peaks in the infrared spectrum of the samples mainly included CO$_2$, CO, and –OH. CO and CO$_2$ were the main reaction products of coal oxidation. In this study, CO and CO$_2$ were selected, and the 2115 cm$^{-1}$ (CO) and 2350 cm$^{-1}$ (CO$_2$) absorbances (with the most obvious changes) were analyzed (Figure 16). It can be seen that the amount of CO and CO$_2$ produced by the raw
Figure 12. TG/DTG curves of (a) raw coal, (b) PAM inhibited coal, (c) PAM/MNS inhibited coal, and (d) INI inhibited coal.

Table 4. Characteristic Temperatures of Different Samples

| samples              | critical temperature ($T_1$) | xerochasy temperature ($T_2$) | activity temperature ($T_3$) | growth temperature ($T_4$) | thermal decomposition temperature ($T_5$) |
|----------------------|-----------------------------|-------------------------------|-------------------------------|---------------------------|------------------------------------------|
| raw coal             | 37.25                       | 93.71                         | 127.19                       | 242.15                    | 270.34                                   |
| PAM inhibited coal   | 41.57                       | 115.25                        | 152.91                       | 244.97                    | 270.62                                   |
| PAM/MNS inhibited coal | 43.37                    | 126.92                        | 159.31                       | 245.69                    | 274.77                                   |
| INI inhibited coal   | 44.65                       | 131.83                        | 161.31                       | 247.58                    | 277.84                                   |
coal during the oxidation process gradually increased as the temperature rose. The CO and CO₂ production of the PAM inhibited coal increased rapidly after 275 °C, which may be due to the cracking of the gel. However, the gas generation of the INI inhibited coal decreased slightly after about 260 °C, which proved the oxygen barrier performance of the porous carbon foam layer. The CO and CO₂ gases were produced in the following order: raw coal > PAM inhibited coal > PAM/MNS inhibited coal > INI inhibited coal. Therefore, INI significantly retards the oxidation reaction of coal, and its inhibition performance is the best among the three inhibitors.

3.7. Application Advantages and Inhibition Mechanism of INI Gel. 3.7.1. Application Advantages of the INI Gel. Similar to the commonly used gel inhibitors, the application method of the INI gel is mainly the pressure injection gel method. As shown in Figure 17, drill holes in the three directions indicated in the figure at the section where the support of the mine tunnel is located. A casing pipe with multiple holes drilled in the pipe wall is embedded in each drill hole. The prepared INI gel is transported into the casing and enters the coal seam through the borehole on the casing. The advantages of INI gels in applications are analyzed as follows.

The modification of nano-silica improves the dispersion of the INI inhibitor, makes it more difficult to agglomerate when dissolved in water, and improves the configuration efficiency of the gel. In the injection process, the thixotropy of the gel reduces its viscosity after passing through the gel pump and reduces the resistance in pipeline transportation. This allows the gel to travel farther in the pipeline, helping to adapt to the complex terrain in coal mines. As the gel flows out of the pipe
from the borehole, it is thought to have a sudden drop in the shear rate at the borehole. During the self-healing period, the viscosity of the INI gel decreases, which facilitates the flow of the gel in the coal seam before it solidifies. Then, the viscosity of the gel will gradually recover until it adheres firmly to the coal surface. This improves both the ease of shipping and the coverage of the gel. In the process of coal oxidation, the INI gel can exert good physical resistance and antioxidation properties and significantly delay the oxidation of coal. After the temperature rises, the porous carbon foam layer formed by the reaction of the expansion inhibitor will further coat the coal. In addition, compared with the gel, the porous carbon foam layer is less affected by temperature and moisture and can

Figure 15. Infrared spectra of thermally decomposed gas at characteristic temperature points. (a) Raw coal, (b) PAM inhibited coal, (c) PAM/MNS inhibited coal, and (d) INI inhibited coal.

Figure 16. Changes in the quantities of (a) CO and (b) CO₂ produced at various temperatures.

Figure 17. Pressure injection gel method.
exert oxygen barrier properties for a longer time, which significantly improves the service life of the inhibitor.

3.7.2. Inhibition Mechanism of the INI Gel. Due to the combination of gel, nanomaterials, and intumescent flame retardants, the efficiency of INI inhibitors in preventing coal spontaneous combustion has been significantly improved.

Figure 18 shows the inhibition mechanism of INI, which mainly includes three aspects.

1. The polyacrylamide reticular structure and the attachment of MNS enhanced the water absorption, fluid properties, and toughness of INI gels. The gel can coat the coal to prevent it from coming into contact with oxygen while at the same time lowering the temperature of the coal by evaporation of moisture, thereby delaying the oxidation of the coal.

2. The molecular structure of nano-silica contains a large number of hydroxyl groups. These hydroxyl groups can be combined with the hydroxyl groups (R-OH) with a higher oxidation activity in coal to form relatively stable ether bonds (R−O−R).42,43 Thereby, the stability of the coal molecular structure is improved and the oxidation reaction of the coal is inhibited.

3. As the temperature rises, the gel will gradually crack and lose the function of oxygen barrier and water retention. When the temperature rises to 150 °C, the IFR will decompose into a large amount of incombustible gas. These gases foam the molten expansion agent to form a porous foamed carbon layer that coats the coal surface. It can effectively prevent the coal−oxygen contact that occurs after the gel cracks, thereby further enhancing the plugging performance of the gel.

4. CONCLUSIONS

In this study, the INI inhibitor was prepared and characterized. Then, the preparation mechanism and rheological properties of the gel were studied by FTIR and rheological experiments. Furthermore, the inhibition performances of INI, PAM, and PAM/MNS were compared using TGA-FTIR analysis. The main conclusions are summarized as follows.

1. The FTIR and SEM results of nano-silica indicate that the MNS produced new Si−O−Si, meaning that KH-570 bonded to the surface of the nano-silica. This makes the surface of nano-silica hydrophobic due to alkylation, thereby enhancing its dispersibility.

2. The FTIR and SEM results of composite gels showed that PAM, MNS, and IFR were fully combined. The addition of MNS not only improved the water absorption but also increased the antioxidant properties of MNS to the inhibitor. At the same time, the porous carbon foam layer formed by IFR enabled the INI to maintain good inhibition performance in the late oxidation stage.

3. Due to the reticular structure formed by the cross-linking reaction of acrylamide, the INI gel and the PAM gel exhibited shear thinning during the shearing process and could gradually recover the viscosity after the shear rate was reduced. The addition of MNS and IFR improved the fluid properties, thereby enhancing the transport convenience and covering ability of the gel.

4. The results from the TGA-FTIR analysis indicate that the characteristic temperature increase for the INI inhibited coal was the most significant compared with the other inhibited coal samples. Additionally, the INI inhibited coal had the highest activation energy and the lowest carbon monoxide and carbon dioxide emissions. Thus, the INI gel exerts significant antioxidant properties and effectively delays the oxidation reaction of coal.

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Notes

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NOMENCLATURES

- \( R_1 \) carbon chains
- \( R_2 \) carbon chains
- \( C \) consistency coefficient
- \( \tau_0 \) yield stress (Pa)
- \( n \) flow behavior index
- \( R^2 \) determination coefficient
- \( \tau \) shear stress (Pa)
- \( \gamma \) shear rate (s\(^{-1}\))
- \( \beta \) programmed heating rate (K/min)
- \( C_s \) constant
- \( B \) constant, 1.0037
- \( R \) kinetic constant (KJ/mol\(^{-1}\cdot K^{-1}\)), 8.314

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