The Effect Mechanism of Fe on Coal Pyrolysis to NO_\textsubscript{x} Precursors: Quantum Chemical Calculations and Mass Spectrometry Experiments

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ABSTRACT: Density functional theory is adopted to thoroughly analyze the influence mechanism of Fe on the formation of NH_3 and HCN. The structure of Fe adsorbed on the surface of seven-membered zigzag coal containing pyridine nitrogen is selected as the Fe-containing coal model. The effect of Fe on the nitrogen distribution during Zhundong coal pyrolysis is further studied by thermogravimetry–mass spectrometry. The theoretical calculations show that Fe increases the Mulliken charge density on the N5 surface, which increases the rate-determining step energy barrier value of NH_3 generated from coal pyrolysis and inhibits the NH_3 formation. On the other hand, Fe significantly enhances the bonding energy between σ N5–C6 and π N5–C6, increases the activation energy required for N stripping from the pyridine ring (about 69.14 kJ/mol higher than that without Fe), and inhibits HCN formation. The experimental results show that Fe catalyzes the precipitation peaks of NH_3 and CH_3CN about 20 K ahead of time and has no obvious catalytic effect on HCN and HNCO. In terms of the nitrogen distribution, Fe significantly promotes the CH_3CN formation and shows a significant inhibitory effect on NH_3, HCN, and HNCO. Kinetic results show that Fe reduces the precipitation rates of NH_3 and HCN, and the inhibitory effect on HCN is more significant.

1. INTRODUCTION

Coal predominates primary energy consumption in China\textsuperscript{1,2} and nitrogen oxides (NO\textsubscript{x}) emitted during coal combustion are one of the main types of atmospheric pollutants.\textsuperscript{3,4} NO\textsubscript{x} lead to the generation of acid rain and acid mist, damage the ozone layer, and worsen climate change. An in-depth understanding of the transformation mechanism of nitrogen-containing compounds during coal combustion will help reduce NO\textsubscript{x} emissions. Pyrolysis is an important stage of the coal combustion process, and the nitrogen-containing components such as HCN, NH\textsubscript{3}, and CH\textsubscript{3}CN generated during this stage are directly oxidized to NO\textsubscript{x}.\textsuperscript{5} Therefore, it is of great significance to study the changes in nitrogenous compounds during coal pyrolysis to improve the understanding of the NO\textsubscript{x} generation mechanism and control NO\textsubscript{x} emissions.

Minerals in coal catalyze pyrolysis and affect the generation of small nitrogen-containing gases such as NH\textsubscript{3} and HCN.\textsuperscript{6,7} Fe is abundant in coal and has a very important effect on the release characteristics of nitrogen during coal pyrolysis.\textsuperscript{8,9} Previous studies have shown that iron changes the distribution of nitrogen-containing products in volatiles through two mechanisms.\textsuperscript{10} One mechanism was the nitrogen fixation of iron, which promoted the retention of more nitrogen in coke, and the other was the catalytic effect of iron, which promoted the conversion of volatile nitrogen to N\textsubscript{2} via a secondary reaction. Studies have found that Fe had different effects on the precipitation characteristics of various nitrogen-containing compounds (those with pyrrole nitrogen, pyridine nitrogen, quaternary nitrogen, etc.).\textsuperscript{11} The presence of Fe allowed more nitrogen to enter the aromatic skeleton of coke, decreasing the release of nitrogen-containing gases (NH\textsubscript{3}, HCN, etc.) during pyrolysis. Guan et al.\textsuperscript{9} showed that the addition of an Fe-containing compound to coke can significantly reduce the formation of NH\textsubscript{3} and HCN. The reason was attributed to the ability of Fe to combine with the generated NH\textsubscript{3} and HCN to form nitrogen- and iron-containing compounds and promote the decomposition of NH\textsubscript{3} and HCN (eqs 1–4).\textsuperscript{8,9} Liu et al.\textsuperscript{2} found that iron catalysts promoted the formation of NH\textsubscript{3} but inhibited HCN formation. The reason for this was that amine nitrogen-containing compounds reacted to form nitriles and other nitrogen-containing heterocyclic rings during catalytic
pyrolysis in the presence of Fe, accompanied by a large amount of NH₃. On the other hand, Fe terminated the cracking of nitriles and amides to HCN, resulting in less HCN precipitation. Hou et al. studied the effect of Fe catalysts on the precipitation characteristics of NH₃ and HCN during the pyrolysis of sludge using thermogravimetry–mass spectrometry (TG–MS) and found that Fe fixed the generated NH₃ in the coke and inhibited its precipitation. Moreover, the presence of Fe inhibited the decomposition of nitriles and nitrogen-containing heterocycles to HCN and promoted the transformation of HCN to NH₃ via a secondary reaction.

\[
2\text{NH}_3 + 8\text{Fe} = 2\text{Fe}_3\text{N} + 3\text{H}_2
\]

\[
2\text{Fe}_3\text{N} = 8\text{Fe} + \text{N}_2
\]

\[
2\text{HCN} + \text{Fe} = \text{Fe}(\text{CN})_2 + \text{H}_2
\]

\[
\text{Fe}(\text{CN})_2 = \text{FeC}_2 + \text{N}_2
\]

The above studies found that the presence of Fe changed the distribution of nitrogen-containing gases in volatiles, but there was no consistent conclusion on how it affected the release characteristics of NH₃, HCN, HNCO, and CH₃CN. In addition, most of the existing studies are limited to experimental research, and it was difficult to determine the effect mechanism of Fe on the conversion of N in volatiles during pyrolysis. With the rapid development of computers, the theoretical calculation method of quantum chemistry has been widely applied and has become a feasible alternative to laborious experiments. The calculations can reveal microscopic mechanisms that cannot be determined through experiments. Liu et al. studied the pyrolysis of nitrogen-containing char to HCN and NH₃ using density functional theory (DFT) and compared the intermediates and transition states that may appear in different reaction paths. Chen et al. calculated the conversion characteristics of N during coal pyrolysis in the presence of demineralized coal and Ca and revealed how Ca influenced the formation of NH₃ and HCN from the microlevel.

So far, no studies have combined experimental and theoretical studies on the effects of Fe on the nitroge distribution characteristics during coal pyrolysis, particularly the mechanism studies concerning the effect of Fe on the release of NOₓ precursors. In this paper, DFT is used to calculate the formation paths of NH₃ and HCN in the presence of Fe and determine how Fe influences the nitrogen migration characteristics from a microscopic perspective. Furthermore, TG–MS is used to study the influence of Fe on the transformation of NOₓ precursors during coal pyrolysis to clarify the effect of Fe on the nitrogen distribution characteristics. The combination of theoretical calculations and experimental analysis is of great significance to improve and perfect the NOₓ generation mechanism and control NOₓ emissions.

2. THEORETICAL CALCULATIONS

2.1. Methodology. The DFT of Gaussian 09 software package is conducted to study the thermodynamic and kinetic generation processes of NH₃ and HCN during the pyrolysis of coal model with Fe in Figure 1. Chen and Yang calculated and compared graphite models with different structures and found that using a seven-ring zigzag structure to simulate char could explain experimental phenomena or reproduce experimental results. Moreover, Li et al. and Chen et al. successfully simulated the reaction of gas on a carbon-based surface using a seven-ring zigzag char structure. Previous studies have shown that nitrogen in coal mainly exists as pyridine nitrogen. Jiao et al. and Zhang adopted a model containing pyridine nitrogen at the edges to simulate the heterogeneous reaction of nitrogen-containing char with CO and NO and obtained satisfactory results. Therefore, to study the migration and transformation characteristics of N during the pyrolysis of coal in the presence of Fe, the structure of Fe adsorbed onto a seven-membered zigzag coal containing a pyridine nitrogen surface is constructed to model Fe-containing coal. The atoms involved in the reaction are labeled with corresponding serial numbers in their optimized structures (see Figure 1).

In this study, the unrestricted M06-2X method and 6-311g(d) are used to calculate the generation process of NH₃ and HCN via the pyrolysis of the Fe-containing coal model. This method is chosen because M06-2X has demonstrated good performance for describing reactions involving metals. This combination method is typically used to calculate reactions with weak interaction forces, and the obtained thermodynamic and kinetic results are more accurate. Zhao et al. and Chen et al. also suggested using this combination method to study the adsorption process or chemical reactions of carbonaceous surfaces with metal participation. A frequency scale factor (0.970) is added in the calculations to better characterize the thermochemical properties of the reactants, transition states, intermediates, and products. The energy distributions of other stable structures and products are expressed based on the energy of the reactants, and the minimum energy paths of the transition states and corresponding intermediates are verified by IRC calculations.

The traditional transition state theory (TST) is adopted to calculate the release rates of NH₃ and HCN during coal pyrolysis from 298 to 1200 K. By comparing the generation rates of NH₃ and HCN with and without Fe, the influence of Fe on nitrogen distribution is revealed from a kinetic point of view. The specific rate calculation formula is shown in eq 5, and the tunneling correction coefficient can be calculated by eq 6.

\[
k_{\text{TST}} = \Gamma \times \frac{k_B T}{h} \times \frac{Q_{\text{FS}}(T)}{Q_{\text{A}}(T)Q_{\text{B}}(T)} \times \exp\left(-\frac{E_a}{RT}\right)
\]

\[
\Gamma = 1 + \left(\frac{1}{24}\right) \times \left(\frac{h \nu_{\text{F}}}{k_B T}\right)^2
\]

2.2. Results and Discussion. 2.2.1. The Formation Characteristics of NH₃ in the Presence of Fe. Figure 2 shows the generation path of NH₃ during coal pyrolysis in the presence of Fe, and Figure 3 shows the energy change during the formation of NH₃. The black line represents the theoretical calculation of the coal (R*) pyrolysis to NH₃ without Fe.
the red line is the energy change during coal (R) pyrolysis with the generation of NH3 in the presence of Fe.

In the presence of Fe, the pyrolysis of R begins with the stripping of N from the pyridine ring (see Figure 2, R → 1-IM1), which causes the electrons to be rearranged during the ring opening of the pyridine ring (see Table 1). As can be seen from Table 1, the valence electrons of C3 decrease from 4.24 (R) to 4.00 (1-TS1), while the valence electrons of C4 increase from 3.84 (R) to 3.90 (1-TS1); the valence electrons of N5 decrease from 5.46 (R) to 5.32 (1-TS1), while the valence electrons of C6 increase from 3.83 (R) to 3.84 (1-TS1). This indicates that after the cleavage of the C4-N5 bond in the pyridine ring, C3 provides electrons to the receptor C4, and N5 provides electrons to the receptor C6, which weakens the force between C4 and N5, strengthens the covalent bond between C3 and C4 and between N5 and C6, and increases their binding energy. Further analysis of the Mulliken charge distribution of R (see Figure 4) shows that C4 and N5 show strong gravitational action, so their fracture needs to overcome certain activation energy. From the energy change of NH3 generated in Figure 3, it can be seen that this process must overcome an energy barrier of 186.92 kJ/mol and consume 134.08 kJ/mol of heat. 1-IM1 to 1-IM2 in Figure 2 is the N atom migration, which is manifested by a gradual increase in the N5-C6 bond length (from 1.26 to 1.34 to 1.63 Å) and a decrease in the N5-C7 bond length (from 1.56 to 1.49 Å and then to 1.27 Å). The proximity of the N5 atom and C7 atom promotes their bonding. According to Table 1, N5 and C6 in 1-IM1 have heterogeneous charges, indicating that they have large binding energies, and the migration of N5 from the C6 surface to C7 needs to overcome an energy barrier of 151.69 kJ/mol. Subsequently, the H atom is adsorbed on the N5 atom surface to form ·NH2, which is barrier-less and releases high heat of 409.08 kJ/mol, providing a thermal driving force for subsequent reactions. Finally, the desorption of ·NH2 formed on the char surface has to overcome a high energy barrier of 596.42 kJ/mol, which is the rate-determining step of the reaction, and the generated ·NH2 reacts with H free radicals in the system to release NH3.

Compared with a previous study,18 the four main processes involved in the NH3 formation during coal pyrolysis in the presence of Fe are still the stripping of N from the pyridine ring, the migration of N atom, the attack of H radical on the
nitrogen site to form ·NH₂, and the ·NH₂ desorption from the char surface. The above results show that Fe only plays a catalytic role during coal pyrolysis to NH₃ formation and does not change the coal pyrolysis process. Further analysis of the rate-limiting step that determines the speed and difficulty of the whole reaction show that the rate-determining step of NH₃ formation from demineralized coal and Fe-loaded coal pyrolysis is all ·NH₂ desorption. However, the addition of Fe increases the desorption energy barrier of ·NH₂ by about 24.34 kJ/mol, indicating that Fe inhibits the NH₃ formation. The reason can be analyzed by the Mulliken charge distribution (see Figure 5). The presence of Fe increases the surface charge density of N and enhances the Coulombic attraction between N and C, increasing the activation energy required to cleave the N-C bond.

2.2.2. The Formation Characteristics of HCN in the Presence of Fe. Figure 6 shows the generation path of HCN during coal pyrolysis in the presence of Fe, and Figure 7 shows the energy change during the HCN formation. The black line represents the theoretical calculation of the coal (R*) pyrolysis to HCN without Fe, and the red line is the energy change during coal (R) pyrolysis with the HCN generation in the presence of Fe.

In the presence of Fe, the pyrolysis to HCN begins with R → 2-IM1 and the stripping of N from the pyridine ring. From the Mulliken population distribution of the atoms on the R surface in Figure 4, it can be seen that the positive charge density on the C6 atom surface is larger than that of C4, and the binding energy between N5 and C6 atoms is stronger than that of C4-N5, so the activation energy required to cleave the N5-C6 bond is higher than 186.92 kJ/mol (the energy barrier required to cleave the C4-N5 bond to form NH₃, as shown in Figure 3). According to Figure 7, the stripping of N atom from the pyridine ring has to overcome an energy barrier of 322.58 kJ/mol, which is one of the rate-limiting steps. The following is the migration process of N atom from 2-IM1 to 2-IM2 (see Figure 6). In addition to the N atom migration, electrons on the char surface rearranged. As can be seen from Table 2, the valence electrons of C3 decrease from 4.14 (2-IM1) to 3.95 (2-TS2) and then to 3.88 (2-IM2), while the valence electrons of the C4 atom increase from 3.71 (2-IM1) to 3.84 (2-TS2) and then to 3.89 (2-IM2), and valence electrons of the N5 atom increase from 5.35 (2-IM1) to 5.44 (2-TS2) and then to 5.46 (2-IM2). This indicates that during the migration of the N5 atom, the C3 atom donates electrons to C4 and N5. Therefore, C3 and C4 atoms gradually display the same charge distribution, and the force is weakened. Simultaneously, the force between C3 and N5 atoms increase gradually, the binding energy increase, and their bonding is promoted. With the gradual approach of C4 and C6 atoms in Figure 6 (the bond length decrease from 2.65 Å (2-IM2) to 2.39 Å (2-TS2) and then to 1.39 Å (2-IM3)), the C4-C6 bond is formed to create a closed five-membered ring. The process only needs to overcome an energy barrier of 23.4 kJ/mol, and releases the heat of 310.75 kJ/mol, indicating that the formed intermediate 2-IM3 is stable and can exist in the system for a long time. 2-IM3 to 2-IM4 only need to overcome an energy barrier of 37.86 kJ/mol, and the position of 2-IM4 is 89.65 kJ/mol lower than that of 2-IM3 (see Figure 7). This suggests that 2-IM4 is a more stable intermediate, and the formation of
−CN radicals by destroying its stable six-membered ring has to overcome a high energy barrier of 252.91 kJ/mol. Finally, the desorption of −CN formed on the char surface only needs to overcome an energy barrier of 22.65 kJ/mol, indicating that −CN is more likely to desorb from the char surface, which is beneficial to the process in thermodynamics.

Compared with the literature, it is found that regardless of the presence or absence of Fe, the main processes of HCN formation during pyrolysis are as follows: the stripping of N from the pyridine ring, the migration of N, the formation of closed five-membered rings, the generation of pyrrole nitrogen, the formation of −CN free radicals, and the desorption of −CN on the char surface. This indicates that Fe only plays a catalytic role in coal pyrolysis to HCN and does not change the main HCN formation process. Comparing the reaction energy barriers of each step in coal pyrolysis to HCN in the presence of Fe (see Figure 7), it can be seen that the energy barrier of N stripping from the pyridine ring (R → 2-IM1) is higher than those of the other steps, making it the rate-determining step. Moreover, the rate-determining step of HCN formation by coal pyrolysis (R*) in the absence of metal is also the stripping of N from the benzene ring, indicating that Fe does not change the rate-determining step of coal pyrolysis to HCN.

Remarkably, comparing the rate-determining energy barrier of HCN generation in the presence of Fe (red line R → 2-IM1 in Figure 7) and in the absence of Fe (black line R* → 2-IM1* in Figure 7), it is found that the presence of Fe significantly increases the barrier energy of the rate-determining step, indicating that Fe has a significant inhibitory effect on HCN formation. The reason for this can be analyzed by the interatomic force calculated by NBO (see Table 3). According to Table 3, it can be seen that Fe significantly increases the bonding energy between σ N5-C6 and π N5-C6, making the N5-C6 bond cleavage overcome a higher activation energy, thus inhibiting the stripping of N from the pyridine ring.

In addition to the rate-determining step, the energy barrier values of other four basic reactions (2-IM1 → 2-IM2; 2-IM2 → 2-IM3; 2-IM3 → 2-IM4; 2-IM5 → P2), which are the migration of N atoms (2-IM1 → 2-IM2), the formation of defective char surfaces (2-IM2 → 2-IM3), the generation of pyrrole nitrogen (2-IM3 → 2-IM4), and the desorption of −CN radical from the char surface (2-IM5 → P2), have little difference with R* pyrolysis to HCN. This indicates that Fe has little effect on these four processes. The formation of −CN radical by R* pyrolysis does not need to overcome the energy barrier, while the formation of −CN radical in the presence of Fe (by R pyrolysis) has to overcome a high energy barrier of 252.91 kJ/mol. This indicates that Fe greatly influences the −CN formation and increases the binding energy between C3 and N5, which is not conducive to the −CN formation. The reason why the C3 atom strips from the benzene ring and combines with the N5 atom to form a −CN radical can be analyzed in Figures 8 and 9. According to the HOMO and LUMO distribution on the 2-IM4 surface in the presence of Fe (see Figure 8), it can be seen that Fe improves the reactivity of char surface, improves the contribution of N5 and adjacent C atoms to the frontier orbitals, and makes it possible for C3 stripping from the benzene ring. On the other hand, according to the Mulliken charge distribution of 2-IM4 (see Figure 9), the C3 and N5 atoms have heterogeneous charge, and the strong attraction between them is another reason for the −CN formation. Due to the high stability of the benzene ring, stripping the C3 atom from the benzene ring and

Figure 6. Process of coal pyrolysis to HCN in the presence of Fe (bond length in Å).
the reaction with N5 atom to $\text{CN}$ radical have to overcome a high energy barrier.

3. EXPERIMENTAL SECTION

3.1. Sample Preparation. The raw coal used in this paper is Zhundong coal, which is dried in a vacuum drying box at 80 °C for 12 h. To provide better contact between coal samples and the FeCl$_3$ catalyst, the coal particle size is kept within 75–μm using a previously reported screening procedure.$^{18}$ Minerals are removed by pickling, and the specific steps$^{2,31}$ are as follows. First, 50 g of Zhundong raw coal is placed into 500 mL of 6 mol·L$^{-1}$ HCl. After 12 h of oscillation, the coal is placed in a water bath at 60 °C for 4 h and then filtered with deionized water. Residual coal samples are placed into 500 mL of 40% HF, oscillated for 12 h, and placed in a water bath at 60 °C for 4 h. Subsequently, the coal samples are filtered three to five times with deionized water. Finally, 500 mL of 12 mol·L$^{-1}$ HCl is added into the residual coal sample, and then the coal sample is washed and filtered until no Cl ions are observed in the filtered solution. Finally, the coal sample filtered by deionized water is dried in an air-drying box at 60 °C.$^{32,33}$

In this study, an Fe catalyst is loaded on the demineralized coal samples by an impregnation method. First, the required mass of supported catalyst is determined according to the ratio of the mass of Fe in the air-dried coal sample at 5%. Then, they are mixed in a conical flask according to the required ratio and placed on a magnetic agitator and stirred at a constant speed for 6 h. The resulting coal samples are dried under vacuum at 60 °C.

3.2. Apparatus. The temperature-programmed pyrolysis of Zhundong coal is performed on a NETZSCH thermogravimetric analyzer and mass spectrometer. During experiments, 10 mg of demineralized coal samples and coal-supported FeCl$_3$ are placed in the alumina trioxide crucible of the thermogravi-

Figure 7. Energy change of HCN generated from coal pyrolysis.

Table 2. Natural Density of Some Important Atoms Calculated by NBO

| atom   | species | charge | valence |
|--------|---------|--------|---------|
| C3     | 2-IM1   | −0.18  | 4.14    |
|        | 2-TS2   | 0.02   | 3.95    |
|        | 2-IM2   | 0.09   | 3.88    |
| C4     | 2-IM1   | 0.24   | 3.71    |
|        | 2-TS2   | 0.12   | 3.84    |
|        | 2-IM2   | 0.08   | 3.89    |
| N5     | 2-IM1   | −0.37  | 5.35    |
|        | 2-TS2   | −0.45  | 5.44    |
|        | 2-IM2   | −0.47  | 5.46    |

Table 3. Natural Orbits of Some Important Bonds Calculated by NBO

| bond   | energy (a.u.) |
|--------|---------------|
| σ C4-N5| −0.84         |
| σ C4-N5| −0.30         |
| σ N5-C6| −0.80         |
| σ N5-C6| −0.41         |

Figure 8. HOMO and LUMO of 2-IM4 in the presence of Fe.

Figure 9. Mulliken charge distribution of 2-IM4 in the presence of Fe.

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metric analyzer, then the air in the system is replaced by injecting argon with a purity of 99.999%, and the replacement is repeated three times. After the mass spectrometer signal stabilized, the program is started. At the same time, the mass spectrometer is used to monitor the distribution of the nitrogen-containing components during pyrolysis. The flow rate of argon gas is 50 mL/min, the heating rate is 10 °C/min, and the temperature is in the range of 25–900 °C. The experimental results are normalized and corrected.

3.3. Experiment Analysis and Discussion. Figure 10 shows the precipitation characteristics of NH3, HCN, CH3CN, and HNCO during the pyrolysis of demineralized raw coal and Fe-supported coal. The precipitation intensities of NH3 and HCN are significantly higher than those of HNCO and CH3CN, indicating that NH3 and HCN are the main nitrogen-containing components in the volatile gas.

The precipitation of NH3 in both demineralized raw coal and Fe-supported coal peaks during the active pyrolysis stage and thermal polycondensation stage and NH3 begins to precipitate at about 520 K. However, the precipitation peak of NH3 in the coal samples containing Fe appears to be 20 K lower than that of demineralized coal in the active pyrolysis stage and 15 K lower during the thermal condensation stage. The reason is mainly that α-Fe and Fe-C will be formed after impregnating FeCl3 and α-Fe has a high activity, which decreases the temperature required for the cleavage of quaternary nitrogen, aromatic rings, and nitrogen-containing heterocycles to produce NH3. On the other hand, NH3 precipitation amount of HNCO is much lower than HCN.

Figure 10 shows that the presence of Fe inhibits the precipitation of NH3. There are mainly two reasons: (1) During the active pyrolysis stage, the addition of Fe promotes the conversion of quaternary amines that can generate NH3 into other nitrogen-containing compounds, and the presence of Fe retains more nitrogen in char. The added Fe reacts with the generated NH3 to form compounds containing nitrogen and iron via the reaction shown in eq 1. The above two factors cause the added Fe to inhibit the precipitation of NH3. (2) During the high-temperature polycondensation stage, the added Fe has a stronger catalytic effect on the conversion of NH3 to N2. In particular, when the temperature is higher than 970 K, the effect of iron catalyzing the conversion of NH3 to N2 is greatly improved, and the generation of NH3 during the thermal condensation stage significantly reduced. The specific catalytic process is expressed by eqs 1 and 2. Moreover, the experimental results are consistent with the theoretical calculation results of Section 2.2.1, which shows that Fe inhibits the pyrolysis of coal to NH3 and the theoretical calculations further reveal the inhibition mechanism of NH3 by Fe at the microlevel. The combination of experiments and theoretical calculations further deepens the understanding and awareness of the coal pyrolysis to NH3 in the presence of Fe.

By analyzing the precipitation characteristics of HCN, it is found that the precipitation peaks of HCN in demineralized raw coal and coal containing Fe are all around 720 K, and their pyrolysis generation curves are essentially the same, indicating that Fe does not change the chemical properties of nitriles and amides that generated HCN. However, much less HCN is produced from coal samples containing Fe than demineralized raw coal. The reason is that nitrogen fixation of iron promotes the condensation of cyclic amide compounds to form stable macromolecular char N, which requires a higher temperature to crack into HCN and inhibits the HCN formation. On the other hand, highly active α-Fe has a strong catalytic effect on the decomposition of HCN in the volatiles, thereby reducing HCN production. The process by which Fe promotes the conversion of HCN to N2 can be expressed by eqs 3 and 4. The inhibition of Fe on HCN formation in experimental results is in good agreement with the theoretical results in Section 2.2.2, and the theoretical calculation further clarifies the mechanism of Fe inhibiting HCN formation at the molecular level. The combination of theoretical calculations and experiments, on the one hand, enhances the reliability and persuasiveness of the theoretical calculation results; on the other hand, it reveals the mechanism of HCN formation from coal nitrogen migration in the presence of Fe.

Further analysis of Figure 10 shows that the precipitation curves of HNCO and HCN are basically the same, but the precipitation amount of HNCO is much lower than HCN. This indicates that HNCO may be a transition product during the conversion of tar nitrogen and volatile nitrogen to generate HCN. Similar to the inhibition of HCN, the presence of Fe decreases the generation of HNCO, which may be that the addition of Fe promotes the retention of some nitrogen in char. It is also possible that Fe changes the cleavage pathway of cyclic amides and promotes formation of other small nitrogen-containing molecules, which reduces the production of HNCO.

From the release curve of CH3CN, it can be seen that the initial release temperature of CH3CN during the devolatilization of demineralized raw coal and Fe-loaded coal samples occurs at about 620 K. The generation of CH3CN in demineralized coal mainly occurs from 620 to 1020 K, while the generation of CH3CN in Fe-loaded coal occurs from 620 to 900 K. This indicates that Fe narrows and lowers the temperature range of CH3CN generation, and the precipitation peak advances about 20 K. The reason is that α-Fe catalyzes the cleavage of long ring or long-chain nitrogen-containing heterocyclic compounds and reduces the activation energy required for its cleavage to produce CH3CN, allowing cleavage to be completed at a lower temperature, so Fe narrows the temperature range of CH3CN formation. Further analysis shows that the precipitation amount of CH3CN from the coal sample with Fe is significantly higher than that from the demineralized coal, indicating that Fe significantly promotes the CH3CN generation. The main reason for this phenomenon is the presence of α-Fe catalyzes the free radical generation, which attacks the structure of nitrogen-containing long-ring or...
long-chain macromolecules, thereby increasing the production of CH$_3$CN.

4. KINETIC ANALYSIS OF NH$_3$ AND HCN FORMATION FROM COAL PYROLYSIS IN THE PRESENCE OF Fe

A kinetic analysis can be used to intuitively reflect the rate and difficulty of a reaction. Therefore, we focus on analyzing the precipitation characteristics of NH$_3$ and HCN (see Figure 11) and plot their calculated average release rates in the histogram of Figure 12. To facilitate comparison of the experimental results and the theoretical calculations, traditional transition state theory$^{30,38}$ is used to calculate the kinetics of the pyrolysis of coal containing pyridine nitrogen without (R$^*$) and with Fe (R) for the formation of NH$_3$ and HCN (see eqs 5 and 6). The total reaction rate of NH$_3$ and HCN formation is plotted in Figure 13.

It can be known from Figure 11 that during the main release temperature range, the average release rates of NH$_3$ and HCN in demineralized coal are $1.69 \times 10^{-9}$ and $2.29 \times 10^{-9}$ eV/T, suggesting that the HCN precipitation occurs faster than NH$_3$. That is, the precipitation intensity of HCN reaches its peak within a narrow temperature range, whereas NH$_3$ needs to go through a broader temperature range before the precipitation intensity can reach the peak value. When Fe is added, the average release rates of NH$_3$ and HCN during the main release temperature range are $1.22 \times 10^{-9}$ and $1.62 \times 10^{-9}$ eV/T, respectively, indicating that the precipitation rate of HCN is still faster than NH$_3$ in the presence of Fe. It should be noted that from the histogram of the average release rate (see Figure 12), Fe reduces the precipitation rates of NH$_3$ and HCN. Further comparing the average release rates of NH$_3$ and HCN during the pyrolysis of demineralized raw coal and coal impregnated with Fe shows that Fe notably reduces the release rates of HCN and more strongly inhibits HCN generation.

According to the total rate constants of NH$_3$ and HCN (see Figure 13), within the calculated pyrolysis temperature range (285–1200 K), a higher pyrolysis temperature is more favorable for the cracking of nitrogen-containing heterocyclic rings in coal, resulting in a faster NH$_3$ and HCN generation. The theoretical calculations are consistent with previous experimental research.$^{39,40}$ By comparing the generation rates of NH$_3$ and HCN during R and R$^*$ pyrolysis in Figure 13, it is found that within the pyrolysis temperature range, the generation rate of HCN is higher than that of NH$_3$, indicating that HCN is generated faster than NH$_3$ regardless of the presence or absence of Fe. The theoretical calculation results are consistent with the experimental TG-MS results in Figure 12. In addition, the formation rates of NH$_3$ and HCN during R pyrolysis are lower than those during R$^*$ pyrolysis, indicating that Fe inhibits the formation of NH$_3$ and HCN. Further analysis shows that during the active pyrolysis stage (700–800 K), the formation rate of NH$_3$ from R is 2 orders of magnitude lower than that from R$^*$, and the formation rate of HCN from R is 6–7 orders of magnitude lower than that from R$^*$, which indicates that compared with NH$_3$, the inhibition of Fe on HCN is more significant. The theoretical calculations are in good agreement with the experimental results in Figure 12, and the theoretical calculations illustrate the degree inhibitory of Fe on HCN and NH$_3$ from the kinetic perspective.

Interestingly, in the temperature range (700–800 K) where the precipitation intensity of NH$_3$ and HCN peaks, the formation rate of HCN from R$^*$ cracking without Fe is 15–18 orders of magnitude higher than that of NH$_3$, while the formation rate of HCN from R cracking in the presence of Fe is 11–13 orders of magnitude higher than that of NH$_3$. This indicates that Fe more strongly inhibits the cracking of nitriles and cyclic amides to form HCN. Moreover, the generated HCN then reacts with Fe to form a complex accompanied by the H$_2$ generation (see eq 3). The H radicals attack quaternary nitrogen, aromatic amines, and other nitrogen-containing heterocycles to generate NH$_3$, which weakens the inhibitory effect of Fe on NH$_3$. Therefore, Fe has a stronger inhibitory effect on HCN than on NH$_3$, which further reduces the gap between HCN and NH$_3$ formation rates. During the high-
temperature polycondensation stage, the formation rate of HCN from the cracking of R and R* are only 3−4 orders of magnitude higher than that of NH3. The reason is that at the high-temperature polycondensation stage, Fe catalyzes the polycondensation and dehydrogenation of aromatic rings in macromolecules, which increases the precipitation of H2, promotes NH3 generation, significantly increases the generation rate of NH3 during the condensation stage, and further greatly narrows the gap between the generation rates of HCN and NH3.

5. CONCLUSIONS
This work makes a thorough analysis on the influence mechanism of Fe on the precipitation of NH3 and HCN by DFT, and the effect of Fe on the nitrogen distribution during coal pyrolysis is further studied by TG-MS. Combining theoretical calculation results and experimental analysis, the following conclusions can be obtained:

(1) Fe increases the Mulliken charge density on the NS surface, which makes the rate-determining step of NH3 formation by coal pyrolysis necessary to overcome a higher energy barrier and inhibit the NH3 formation.

(2) Fe significantly enhances the bonding energy between σ N5-C6 and π N5-C6 increases the activation energy required for N stripping from the pyridine ring (about 69.14 kJ/mol higher than that without Fe), and inhibits HCN formation.

(3) Fe changes the distribution of nitrogen-containing components. Fe combines with part of the generated NH3 into a nitrogen- and iron-containing complex, which inhibits the NH3 precipitation. Fe highly catalyzes the decomposition of HCN in volatiles, reducing the amount of HCN formation. The nitrogen fixation of Fe inhibits HNCO formation. Fe catalyzes the cleavage of long-ring or long-chain nitrogen-containing heterocycles and promotes the CH3CN generation.

(4) The kinetic analysis shows that the formation rate of HCN is higher than that of NH3, and the formation rate of NH3 and HCN from R pyrolysis are lower than those from R* pyrolysis, which indicates that Fe reduces the precipitation rates of NH3 and HCN.

(5) In the active pyrolysis stage (700−800 K), the formation rate of NH3 from R is 2 orders of magnitude lower than that from R*, and the formation rate of HCN from R is 6−7 orders of magnitude lower than that from R*. Kinetic results show that Fe has a stronger inhibitory effect on HCN than on NH3, which agrees very well with the TG-MS experimental results.

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Notes
The authors declare no competing financial interest.

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