Control of the emission of NOx during coal combustion by inhibiting the formation of NOx precursor in the pyrolysis process

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Abstract. NOx emitted from coal combustion cause serious pollution to the ecological environment. At present, controlling and reducing NOX emissions has become one of the most important technologies to control the pollutants in the atmosphere. Due to the formation of a large amount of NOX precursor HCN, NH₃, char-N during coal pyrolysis, and these nitrogen species with O₂ in the air cause the emissions of NOx during combustion. Therefore, it is of great significance to study the control of NOX precursors during coal pyrolysis. The addition of additives to coal has an important catalytic effect on the control of NOX precursors during coal pyrolysis. In this paper, the catalytic effect of additive Fe, Ca, Na on nitrogen transport during pyrolysis of raw coal or demineralized coal was discussed. It can be concluded that Fe, Ca, Na can catalyze the conversion of NH₃, HCN and char-N to N₂, thus reducing the NOX precursor in the pyrolysis of coal and reducing the emission of NOX in the subsequent combustion process. The result provides an important scientific basis for the control of NOX emission by reducing NOX precursor formed in pyrolysis during coal combustion.

1. Introduction

Coal consumption accounts for approximately 63% of the primary energy in China¹. Coal is integral to the Chinese economy as it provides reliable and affordable power. However, NOx (nitrogen oxide) released from coal combustion has caused great harm to human health and ecological environment. It is estimated that NOX emissions during coal combustion account for 67% of the total atmospheric NOX emissions. How to control and reduce the emission of NOX during coal combustion has become one of the most important technologies to control pollutants in the atmosphere.

Pyrolysis is the initial process of coal combustion, part of the nitrogen is released as volatile-N (the nitrogen in the volatile), such as tar-N (the nitrogen in the tar), HCN, NH₃ and N₂, the remainder being retained as char-N (the nitrogen in the devolatilized char) during coal pyrolysis. Char-N and tar-N, HCN, NH₃ are the precursors of NOX during coal combustion. The traditional methods for controlling NOX release from coal combustion are as follows: flue gas denitrification² and decoupling combustion³, and decoupling combustion denitrification takes full account of the pyrolysis process.
In recent years, it has been proposed to complete the coal pyrolysis and nitrogen reduction and coal combustion denitrification by two-step independent separation of coal low-temperature pyrolysis and high-temperature combustion, and finally realize the economical, clean and effective reduction of NOx release technology. In other words, reduce the precursor of NOx during coal pyrolysis, thus reducing the emission of NOx in the subsequent combustion process. Therefore, the migration of nitrogen during coal pyrolysis has a significant effect on the formation of NOx. The addition of additives to coal has an important catalytic effect on the control of NOx precursors during coal pyrolysis. Therefore, studying the catalytic effect of additives on the control of NOx precursors during coal pyrolysis and its influencing factors will help us find suitable pyrolysis conditions and additives for coal pyrolysis, and preparing coal-based clean fuel by coal pyrolysis to reduce NOx precursors. This will provide an important scientific basis for denitrification during coal combustion directly.

2. Nitrogen form in coal and its influencing factors

2.1. Content and form of nitrogen in coal

The nitrogen in the coal (coal-N) is derived from plants in the geological stage of coal formation and is then fixed in the coal during the peat formation stage. Coal-N is almost organic nitrogen and the nitrogen content in coal is in the range of 0.5-2.5mass%. The nitrogen in coal includes four types of nitrogen, namely pyrrolic (N-5), pyridinic (N-6), quaternary (N-Q) and e nitrogen oxide (N-X), and the corresponding electron binding energies to: 398.8(±0.4)ev, 400.2(±0.3)ev, 401.4(±0.3)ev and 402.9(±0.5)eV[4], besides, high binding energy nitro type complexes(-NO2) found above 405eV, or 406.2 (± 0.1) eV.

N-5 and N-6 refer to nitrogen on the edge of coal molecular unit structure, but the six-membered ring of N-6 is more stable than five-membered ring of N-5. The N-Q is located inside the coal molecule and is more stable than the N-5 and N-6, and the nitrogen atom in the pyridine is directly connected to the oxygen atom to form the nitrogen oxide[5].

2.2. Factors affecting the content and form of nitrogen in coal

The content of nitrogen in coal is related to the coal rank. Low-rank coal molecular structure has a low degree of aromatization, and the form of nitrogen in low-rank coal is mainly N-5, followed by N-6 and N-Q. The high-rank coal has a higher degree of aromatization, and the organic nitrogen is mainly N-Q. Researchers have found that the nitrogen content is not affected by coal rank, and the nitrogen content in different microscopic components is: vitrinite (1.5%-2.0%)＞exinite (1.0%-1.4%) ＞ semi-fusinite (0.7%-1.4%)＞ fusinite (0.4%-0.8%) [6].

The influence of magma intrusion on coal has been extensively studied, and it has been found that the content of organic nitrogen in coal is higher near magma intrusion. However, some studies have found that the coal invaded by magma has a certain reduction in nitrogen content. In recent research, it has been found that the nitrogen content in coal is indeed reduced due to magma intrusion, which is caused by the complete disappearance of N-5 in coal; at the same time, the "protonated" quaternary nitrogen converts N-Q to N-6 due to deprotonation; Magma intrusion leads to the conversion of unstable nitrogen forms in coal to more stable forms[7].

3. Distribution of gas-N, tar-N and char-N during coal pyrolysis

Coal-N transform into gas-N, tar-N and char-N during pyrolysis. About 65% of the coal-N remains in the coke, about 20% is released into the gas, and about 10% is transferred to the tar-N. Ga-N in the form of HCN, NH3, N2, HNCO, N2O, and the most abundant is HCN and NH3, which are the precursors of NOx formation. The tar-N in the form of nitrogen compounds with aromatic structures such as N-5, N-6 and so on, which is the main source of soot. The soot decomposes to form HCN at high temperature[8].

3.1. Gas-N
About 10% of the coal-N was released into the gas phase in the form of HCN, NH₃, N₂, HNCO, N₂O, among which HCN and NH₃ were dominated. HCN mainly comes from N-5 and N-6 at the edge of coal molecule, and NH₃ is mainly derived from N-Q in coal molecules. HCN is mainly formed by ring opening reaction of unstable nitrogen-containing structure and secondary reaction of tar nitrogen in coal. The formation of HCN is also related to free radicals, especially H radical. Generated HCN also reacts with H radical to form NH₃. In recognition of the release characteristics of volatile-N in the form of HCN and NH₃, there are basically two views: (a) Part of the coal-N with the volatile will form HCN and NH₃ simultaneously; (b) Volatile-N will form HCN first, then HCN form NH₃.

Compared with the HCN and NH₃, N₂ is clean, and there is little research on N₂ formation during pyrolysis. Isocyanic acid (HNCO) is also the intermediate product of coal pyrolysis. Nelson et al. first reported the formation of HNCO during coal pyrolysis. Pyridone is the only nitrogen functional group in coal which may form HNCO during pyrolysis, and the yield of HNCO decreases with the increase of temperature.

3.2. Tar-N
Volatile released from coal pyrolysis form tar at low temperatures. Solomon initially found that the structure of tar-N is similar to that of raw coal. Baxter thought that tar-N mainly exists in aromatic compounds such as N-5, N-6 and so on. In recent studies, Hou identified 57 kinds of nitrogen-containing compounds using GC-MS, in which basic nitrogen was 79.65% and non-basic nitrogen was 20.35%. Tar-N is also the precursor of NOₓ formation during coal pyrolysis. More attention is paid to the formation and conversion mechanism of tar nitrogen, which will be beneficial to reduce the formation of NOₓ.

3.3. Char-N
Char-N exists in the form of N-5, N-6, N-Q and N-X. The change of Char-N content is determined by the change of the structure of nitrogen compound and the content of catalytic component. The generated free radicals activate the open-loop transformation of N-5 and N-6 in coal to generate HCN. In addition, due to the polycondensation reaction, N-5 and N-6 at the edge of the coal structure enter the aromatic ring and transform into N-Q. The N-Q shows the nitrogen-containing site with the cleavage of the C-N bond in the aromatic ring, and combines with H to convert to NH₃.

At present, there are few studies on the distribution of Char-N, but the content and distribution characteristics of Char-N in coal pyrolysis are directly related to the emission of NOₓ pollutants during coal combustion, so it is especially important to further study it in depth.

4. Catalytic effect of additives on controlling of the NOₓ precursor during coal pyrolysis
The nitrogen transport during pyrolysis is affected by the inherent minerals in coal and additives. The catalytic action in coal pyrolysis not only changes the partition and transformation of nitrogen-containing products, but also changes the surface area and micropore structure of coal coke. Reaction of minerals in coal with nitrogen-containing heterocyclic aromatic rings to form MCₙNₓHᵧ (M represents mineral elements, such as Ca, Fe), which makes the structure of nitrogen-containing aromatic rings more unstable and produces N₂. Different additives have different catalytic effects on nitrogen transport, and it has different effects with the characteristics of coal and external conditions such as pyrolysis temperature and load.

4.1. Iron-based additive
Iron-based (Fe-based) additives play an important role in catalyzing nitrogen transport during coal pyrolysis. Wang et al. found that the total amount of gaseous products produced during the pyrolysis of Fe-loaded coal was larger than that of raw coal and demineralized coal. Fe catalyzed mainly in the later stage of condensation. Yan et al. found that adding Fe to bituminous coal promoted the formation of N₂. Fe inhibited the formation of HCN during pyrolysis and significantly decreased the char-N content when loading FeCl₃ on model coal.
Pyrolysis atmosphere has an effect on HCN release in Fe catalytic coal pyrolysis. Liu et al.\textsuperscript{[15]} loaded Fe(C\textsubscript{3}H\textsubscript{5})\textsubscript{2} in Shenmu coal and carried out pyrolysis experiments in Ar atmosphere. It was found that Fe reduced the release of HCN. Some researchers carried out pyrolysis experiments in N\textsubscript{2} atmosphere, and pointed out that Fe promoted the formation of HCN. Coal rank also has a certain influence on HCN release during coal pyrolysis. Three typical coals with different ranks were studied by demineralization and adding Fe, and found that Fe restrain HCN release from medium rank coals, but promote that from low rank coals.

Iron morphology varies with temperature during coal pyrolysis. There is a strong interaction between Fe and C-O functional groups on the surface of coal. The change of Fe chemical morphology with the increase of heat treatment temperature is as follows: Fe-O/C complexes, FeOOH, Fe\textsubscript{2}O\textsubscript{4}, α - Fe and Fe\textsubscript{3}C. Fe\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{3}O\textsubscript{4} are the main phases of Fe in coal coke prepared at low temperature, α - Fe and iron-carbon species (Fe, C) are the main forms of iron at high temperature\textsuperscript{[16]}.

Fe-based additives can catalyze the decomposition of quaternary amine salts at lower temperatures. Fe can also catalyze the removal of N-6. There are two mechanisms of Fe-based additives effect on nitrogen transport during coal pyrolysis: a. Iron can promote the secondary decomposition of volatile matter and catalyze the conversion of most volatile-N to N\textsubscript{2}; b. Iron catalyzes the conversion of char-N to N\textsubscript{2}. The reaction mechanism can be found in the reaction equations (1) and (2)\textsuperscript{[17]}.

\begin{equation}
\alpha\text{-Fe} + \text{char} - N \rightarrow \text{Fe.N(}or\text{Fe.C}_{x}\text{N)}
\end{equation}

Fe.N(\text{orFeC}_{x}\text{N}) \rightarrow \alpha\text{-Fe} + \text{N}_{2}
\tag{2}

\section{4.2. Calcium-based additive}

Calcium-based (Ca-based) additives also have an important effect on nitrogen transport during coal pyrolysis. Ca promotes the formation of N\textsubscript{2} and NH\textsubscript{3} while reducing the nitrogen content in coke and tar. Ca promotes the release of HCN in different coal ranks, and inhibites the precipitation of NH\textsubscript{3} with medium rank coals but promotes the lower rank coals. Wu et al.\textsuperscript{[18]} found that the content of char-N decreased significantly after loading Ca(OH)\textsubscript{2} in model coal.

Ca can increase the formation of H radicals and ultimately promote the conversion of char-N to volatile-N during coal pyrolysis. The loading Ca increases the probability of obtaining H radicals and reduces the free energy of tar cracking. The nitrogen-containing aromatic ring in the tar is subjected to ring opening hydrogenation to resolve into a small molecule nitrogen gas, and NH\textsubscript{3} is increased due to the secondary reaction of HCN. CaO has a chemical adsorption effect on the acid center on the surface of pulverized coal through its alkaline characteristics, which promotes the breakage of small molecules in the pulverized coal. With the increase of temperature, Ca on the surface of the semi-coke catalyst to form CaO, or combine with the oxygen-containing functional to form R-O-Ca-O-R microstructure to increase the surface active site, which promote the conversion of tar-N\textsuperscript{[19]}.

Nitrogen release during high temperature pyrolysis of catalytic role of calcium in N\textsubscript{2} formation has been studied with a fixed bed quartz reactor. It was found that low rank coals and demineralized coal increases yields of tar-N, HCN and char-N, but decreases NH\textsubscript{3} and N\textsubscript{2}. It is likely that the highly dispersed CaO catalyzes efficiently conversion reactions of char-N to N\textsubscript{2} in the process of carbon crystallization. The reaction pathway is represented by the equations (3), (4) and (5)\textsuperscript{[20]}.

\begin{equation}
\text{CaO} + \text{char} - N \rightarrow \text{CaC}_{x}\text{N}_{y} + \text{CO}
\end{equation}

\begin{equation}
\text{CaC}_{x}\text{N}_{y} \rightarrow \text{CaG} + \text{N}_{2}
\end{equation}

\begin{equation}
\text{CaC}_{x}\text{N}_{y} + \text{H#} \rightarrow \text{CaC}_{y} + \text{NH}_{3}
\end{equation}

Lower emission of NO\textsubscript{x} precursors was observed with mixed-Fe/Ca additives than with either Fe or Ca individually. This is because the generation of Ca\textsubscript{2}Fe\textsubscript{2}O\textsubscript{3} enhanced the tranformation of intermediates (Fe\textsubscript{1}N\textsubscript{x} and Ca\textsubscript{x}C\textsubscript{y}N\textsubscript{y}) to N\textsubscript{2}\textsuperscript{[21]}. Nitrogen conversion route affected by mixed-Fe/Ca additives during pyrolysis is illustrated in Figure 1.
4.3. Sodium-based additive

The Na in raw coal distributes uniformly, and it combines tightly with hydroxyl, carboxyl groups and other groups in coal. However, Na loaded on coal is generally distributed unevenly on the surface of coal. The presence of Na can improve the reactivity of coke and has a significant effect on the functional groups of coke, which can reduce the regularity of microcrystalline structure of coke during pyrolysis, hinder the graphitization of coke, and reduce the content of H radical, thus affects the conversion of coal-N to HCN.

Zhao et al\cite{1} found that Na catalyzes the conversion of char-N to volatile-N at high temperature. It has been reported that, Na promoted the conversion of coal-N to NH\textsubscript{3} at low temperature, but inhibited at high temperature. Meanwhile, for any given pyrolysis temperature, the production of HCN will be suppressed by Na. When the temperature is higher, the increase of Na content in coal causes the reduction of char-N and promotes N-Q formation. When the amount of Na-loaded on coal is higher, more Na is easy to block the pores of coal and agglomeration, which is unfavorable to the volatilization of Na and the secondary decomposition of tar to form NH\textsubscript{3}. Therefore, only a suitable loading can promote the conversion of coal-N to NH\textsubscript{3}.

5. Conclusion

Demineralized coal is loaded with Fe-based, Ca-based and Na-based additives, which promote conversion reactions of char-N to N\textsubscript{2}. For the Fe-based additives, on the one hand, Fe promotes the secondary decomposition reaction of volatile matter, which make most of the volatile-N convert to N\textsubscript{2}; on the other hand, char-N to N\textsubscript{2} through solid-solid interactions. Highly dispersed CaO promotes the crystallization of carbon, and CaO effectively catalyzes the conversion of Char-N to N\textsubscript{2}. Na promotes nitrogen release from coal char and produces a large amount of N\textsubscript{2}.

Although a great deal of studies have been done on the catalytic effect of minerals and additives on the NO\textsubscript{X} precursors during coal pyrolysis, the mechanism of additives is still unclear. Most of them are confined to the analysis and study of gas-N in volatile-N during coal pyrolysis, but lack of research on char-N. It will be very important to study nitrogen transport and transformation in coal pyrolysis process from both volatile-N and Char-N.

The goal of nitrogen reduction in the coal pyrolysis stage is that the nitrogen in the coal is released into the volatile matter as much as possible in the gas-N, especially N\textsubscript{2}, thereby significantly reducing the char-N content, and finally reducing the NO\textsubscript{X} emission during combustion. This paper studies the catalytic effect of metal additives on NO\textsubscript{X} precursor during coal pyrolysis, which provides an important scientific basis for reducing NO\textsubscript{X} precursors, and coal combustion directly to reduce NO\textsubscript{X} emissions.

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