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Effects of calcium on the evolution of nitrogen during pyrolysis of a typical low rank coal

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Abstract This study aims to investigate the effects of calcium on the migration of nitrogen in coal (coal-N) to N-containing gas species, particularly, NH_3 and HCN (volatile-N) in volatiles, as well as the chemical transformation of the N in char during coal pyrolysis under different temperatures. The pyrolysis experiments of Shengli brown coal and its derived coal samples loaded with different contents of calcium were conducted under 600–800 °C in a novel fluidized bed reactor. The experimental results showed that during coal pyrolysis, the generation of NH_3 is mainly derived from secondary reactions among volatiles, tar and char with the catalytic effect of mineral matter, especially calcium in coal. Increasing pyrolysis temperature from 600 to 800 °C could enhance the release of N in coal to volatiles. Meanwhile, the increased pyrolysis temperature could also inhibit the generation of NH_3 while facilitating the formation of HCN. The release of HCN is more sensitive to pyrolysis temperatures. Specifically, under higher pyrolysis temperatures, more N-containing structures in coal would become thermally unstable and crack into HCN; On the other hand, higher pyrolysis temperature could also enhance the decomposition of N in coal to N-containing species in tar or N_2, thus reducing the release of HCN and NH_3. Nitrogen in tar could either undergo secondary decomposition reactions, generating NH_3, HCN, N_2 and other N-containing species in gas phase, or experience condensation polymerization by forming macromolecular structure and be retained in char at high pyrolysis temperatures. Calcium could significantly restrain the release of N from coal, thus reducing the yields of NH_3 and HCN. During coal pyrolysis, calcium catalytically enhances the fracture and combination of chemical bonds, generating abundant free radicals. These free radicals could continuously attack N-containing structures and consequently release the N-containing gaseous products, such as NH_3, HCN, N_2 etc., resulting in the decrease of N in char. Calcium also plays important roles in nitrogen transformation in char during coal pyrolysis by catalytically intensifying the transformation of N in char from pyridinic nitrogen (N-6) and pyrrolic nitrogen (N-5) to quaternary type nitrogen (N-Q) during coal pyrolysis.

Keywords Brown coal · Pyrolysis · Nitrogen · Calcium · Transformation

1 Introduction

The emission of nitrogen-containing poisonous gas (mainly NO_x and HCN) is environmentally concerned as it could result in acid rain, photochemical smog, greenhouse effect, and the ozone layer depletion (Chen et al. 2009). However, coal combustion is considered as the major source of NO_x emission. Specifically, when coal is injected into a combustor, it would first undergo pyrolysis and part of the nitrogen in coal (coal-N) could be released as volatile-N, including the nitrogen contained in tar (tar-N), HCN and

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NH_3, while the other coal-N is retained in char (char-N) (Nelson et al. 1992; Lázaro et al. 1996). Subsequently, the volatile-N and char-N would respectively react with oxygen and further contribute to the emission of NO_x and HCN. Therefore, the distribution of coal-N in volatile-N and char-N during coal pyrolysis is fundamentally important in understanding the emission mechanism of nitrogen during coal combustion. Accordingly, many efforts have been made to clarify the evolutionary behaviour of nitrogen transformation during coal pyrolysis, including the effect of pyrolysis temperatures (Yan et al. 2005), coal properties, and different forms of nitrogen in coal (Nelson et al. 1992; Pels et al. 1995; Kambara et al. 1993). Especially, the influence of inorganic species in high-rank coal on the migration and transformation of N during pyrolysis has been extensively investigated (Tsubouchi and Ohtsuka 2002; Wu et al. 2001; Ohtsuka et al. 1997; Zhang et al. 2004; Friebel and Köpsel 1999). It was concluded that inherent minerals, especially alkali and alkaline earth metal species (AAEMs), along with transition metal species, could promote the release of NH_3 and N_2 while inhibiting the formation of HCN by altering the reaction paths during coal pyrolysis. Besides, it is also reported that the effect of inherent minerals on nitrogen transformation could also be significantly affected by coal rank and pyrolysis conditions. With the increasing consumption of high-rank coal, brown coal has been considered as one of the most important solid fuels in the long term due to its highly amorphous carbon structure and vast reserve, while it often features abundant inorganic species, especially AAEMs. However, whether those conclusions drawn above could be extrapolated to the pyrolysis of brown coal is largely unknown. More importantly, the effect of calcium which is one of the most abundant inorganic species in coal, especially in brown coal, on the transformation mechanism of nitrogen has not been systematically investigated (Tsubouchi and Ohtsuka 2002; Wu et al. 2001). The main objective of this study is thus to elaborate the influence of calcium with different contents on the migration and transformation of N during pyrolysis of brown coal. Specifically, Shengli brown coal and coal samples loaded with calcium were subjected to pyrolysis under temperatures ranging from 600 to 800 °C The release of N from coal-N to gas-N (NH_3, HCN) and the chemical transformation of the N remained in char were tentatively investigated. This study is expected to deliver a deeper insight into the roles of inherent inorganic species in nitrogen transformation during practical coal utilization.

2 Experimental

2.1 Samples preparation

The as-received Shengli brown coal was dried at 70 °C in an oven for 48 h, ground and then sieved to the size fraction of 60–96 μm as the raw sample. To prepare coal samples with different contents of calcium, calcium hydroxide was loaded into the raw coal with the loading percentages (defined as the mass percentage of calcium in coal samples after loading) of 1.5%, 3.0% and 6.0%, respectively. Specifically, the desired amount of Shengli brown coal was immersed in the pre-prepared $Ca(OH)_2$ aqueous solution and stirred for 14 h at room temperature and then dried at 70 °C for 48 h. Accordingly, the coal samples loaded with calcium were then termed as 1.5% Ca + coal, 3% Ca + coal and 6% Ca + coal, correspondingly. Therefore, any difference in the migration and transformation of N would be largely attributed to the variation in Ca contents. The proximate and ultimate analysises, in the Shengli brown coal, are shown in Table 1.

2.2 Coal pyrolysis experiments

In this experiment, a newly-designed fluidized bed quartz reactor was used, as shown in Fig. 1. The weighed (~ 1.2 g) coal sample and 50 g quartz sand were preloaded evenly on the bottom quartz frit in the reactor. 5.7 L/min of high purity argon gas (the purity > 99.999%) was passed through the bottom of the reactor to fluidize the sand and coal retained on the bottom quartz frit, while the upper quartz frit could prevent the fluidized coal or char from being carried out of the reactor. The fluidized-bed reactor was heated by an external electrical furnace with a heating rate of 25 °C/min to the desired temperatures (600 °C, 700 °C and 800 °C) and maintained for 160 min. Temperatures inside the reactor were monitored by a thermocouple. The absorption of NH_3 and HCN during pyrolysis was carried out in two separated experiments. The target product NH_4^+ was collected by 0.02 mol/L

Table 1 Proximate and ultimate analysis in the Shengli brown coal

Coal	Proximate analysis (wt%)				Ultimate analysis (w_{daf}%)				
	M_{ad}	A_d	V_d	FC_d	C	H	O^a	N	S
Value	6.44	8.54	45.93	54.07	64.72	4.98	28.62	1.02	0.66

[a] By difference; *db* dry base, *daf* dry ash free base

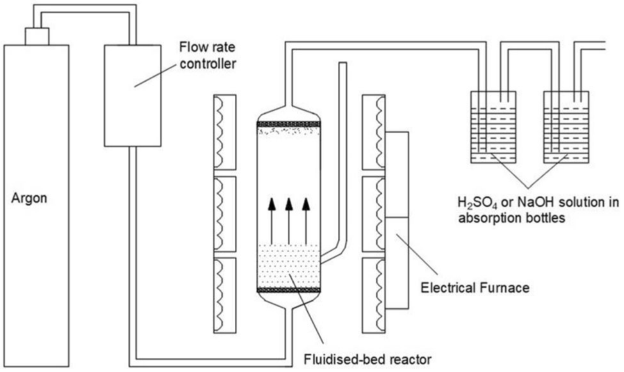

Fig. 1 Schematic diagram of coal pyrolysis system

H_2SO_4 solution in one experiment while in another experiment, CN^- was absorbed and collected by 0.1 mol/L NaOH solution in four gas washing bottles. The NH_3 or HCN was collected during the heating-up period and holding period, respectively. It should be noted that complete collection was achieved for all the experiments in this study without CN^- and NH_4^+ being observed in the last gas washing bottle.

2.3 Sample analysis

The NH_4^+ in diluted H_2SO_4 solution was analyzed by Nessler's Reagents spectrophotometer with a detection range of 0.025–2.000 μg/mL, while CN^- in 0.1 mol/L NaOH solution was analyzed by isonicotinic acid-pyrazolone spectrophotometry with a detection range of 0.004–0.250 μg/mL. The standard solution of NH_4^+ was self-prepared while that of CN^- was purchased from the National Research Center for Certified Reference Material (NRCCRMS).

The content of nitrogen in char was determined by Elementar Vario MICRO cube elemental analyzer, while the occurrence of N in coal or char was analyzed by a photoelectron spectrometer (XPS, Thermo Fisher Scientific 250 XI) equipped with AlK-α light with energy of 40 eV and step length of 50 meV. The internal standard was calibrated with C1s (287.6 eV).

The yields of N-containing products during coal pyrolysis are calculated on the basis of N in gas, char and coal, as follows:

$$\begin{aligned}&\text{The yield of N in NH}_3\text{ or HCN }(\%)\\&\quad=[\text{The amount of N in NH}_3\text{ or HCN(mg)}]/\\&\qquad[\text{The amount of N in coal (mg)}]\times 100\%\end{aligned}\tag{1}$$

$$\begin{aligned}&\text{The yields of N in char }(\%)\\&\quad=[\text{The amount of N in char (mg)}]/\\&\qquad[\text{The amount of N in coal (mg)}]\times 100\%\end{aligned}\tag{2}$$

3 Results and discussion

3.1 Effect of calcium on the yields of NH_3 and HCN during coal pyrolysis at different temperatures

Figures 2 and 3 show the yields of NH_3 and HCN from pyrolysis of raw coal and coal samples loaded with calcium in the heating and holding period. Figure 2a–c shows that during the pyrolysis of raw coal and Ca-loaded coal samples, the total yield of NH_3 decreased with the increase of the pyrolysis temperature. The yield of NH_3 released during pyrolysis of raw coal or Ca-loaded coal increased with increasing final temperature in the heating period; however,

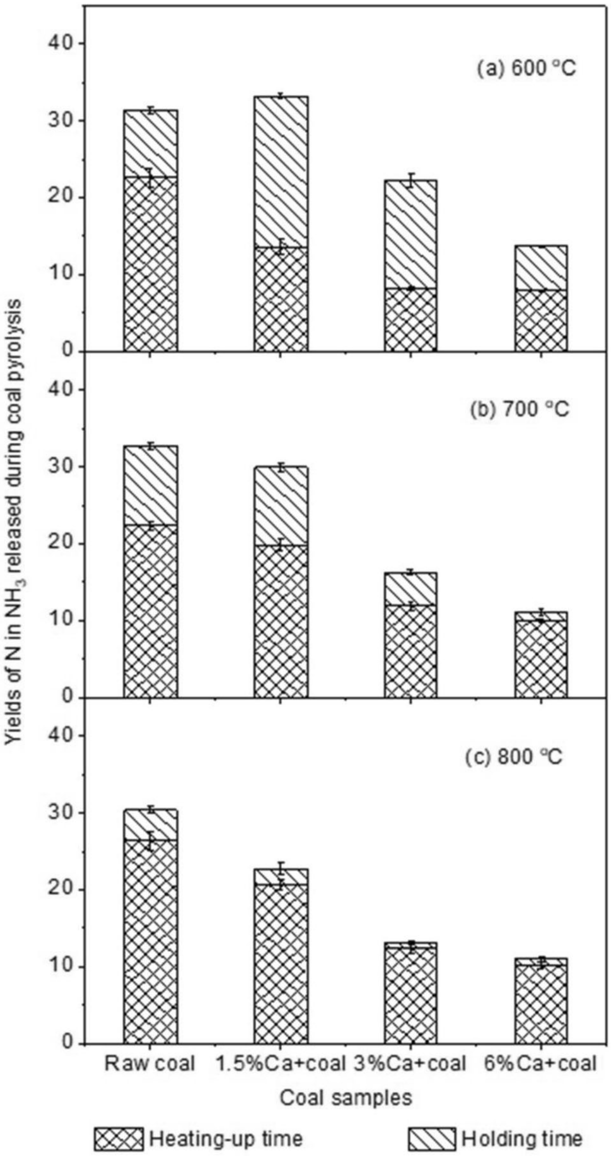

Fig. 2 The yields of NH_3 during the pyrolysis of raw coal and coal samples loaded with different contents of calcium at the heating-up time and holding time at different temperatures

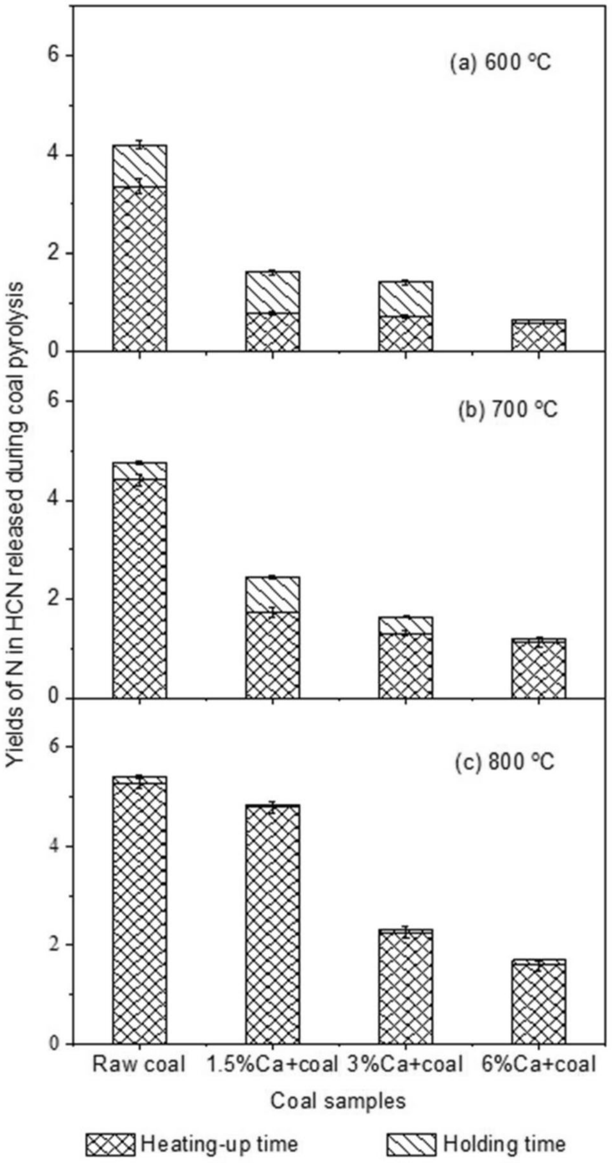

Fig. 3 The yields of HCN during the pyrolysis of raw coal and coal samples loaded with different contents of calcium at the heating-up time and holding time at different temperatures

it decreased at the higher final temperature during the holding period. During coal pyrolysis, the generation of NH_3 is mainly derived from secondary reactions among volatiles, tar and char with the catalytic effect of inherent mineral in coal. During the heating period with gradually increasing temperatures, the volatile is gradually released and then the reactions between volatiles and char are prolonged, thus enhancing the release of NH_3 at the heating period of pyrolysis. However, at a higher temperature (800 °C), the interactions between NH_3 and minerals in char was enhanced (Li and Tan 2000), leading to the decrease in the yield of NH_3.

More interestingly, under the same pyrolysis temperature, calcium addition could decrease the yields of NH_3 in both heating and holding periods, except for the pyrolysis of 1.5% Ca + coal at 600 °C, where the yield of NH_3 was significantly increased at holding time. These results suggest that the addition of 1.5% calcium facilitates the NH_3 release at lower pyrolysis temperatures, while the further addition of calcium or higher temperatures would inhibit the release of NH_3. This might be caused by the different effects exerted by the added calcium under different temperatures. At lower temperature, calcium could enhance the decomposition of N-containing species in brown coal into NH_3. However, at a higher temperature, the interaction between the internal minerals and the loaded calcium was enhanced and deactivate the catalytic effect of the added Ca, consequently reducing NH_3 release (Tsubouchi and Ohtsuka 2002).

Figure 3 shows that the yield of HCN is significantly increased with increasing temperature at the heating period while it is decreased at holding period during coal pyrolysis. Compared with that of NH_3, the release of HCN is more sensitive to temperatures. Reasonably, with increasing pyrolysis temperature, more N-containing structures become thermally unstable and cracked into HCN. For example, at a higher temperature, some inorganic species, such as alkali species which might be associated with N-containing structures in coal, are released, thus further contributing to the HCN release.

At the same temperature, more calcium in coal significantly reduces the release of HCN, especially during the heating period, which might be due to the catalytic effect of the added calcium on the hydrogenation of N-sites and/or the in situ catalytic hydrogenation of HCN produced during pyrolysis (Li and Tan 2000).

3.2 Effect of calcium on the distribution of N in pyrolysis products

Figures 4 and 5 show the yields of char and the distribution of N during pyrolysis of raw coal and the Ca-loaded coal samples under different temperatures, respectively. It should be noted that the volatile-N could be calculated by the difference in Fig. 5. In other words, volatile-N includes tar-N and the N contained in gases, such as N_2, NH_3 and HCN. Four important observations can be made from Figs. 4 and 5. First, as shown in Fig. 4, increasing calcium content in coal could gradually decrease char yields. Calcium could increase coal porosity and surface area (Mims and Pabst 1983) with the separation of Ca from –$(COO)_2Ca$, thus enlarging the contact area of char and volatile, and consequently enhancing volatile-char interactions. In addition, calcium could catalytically facilitate the decomposition and polycondensation of coal/char

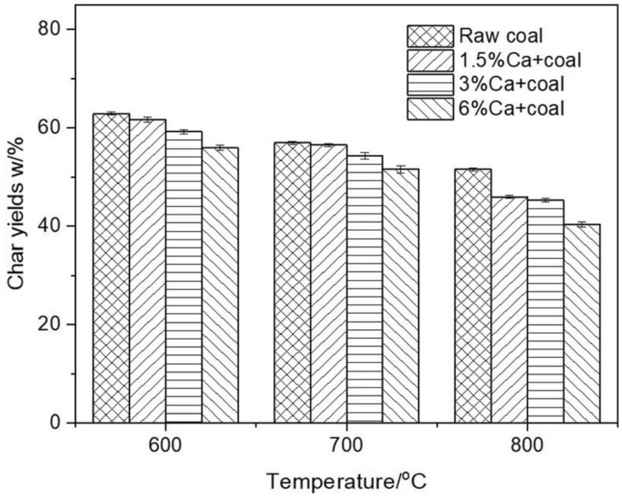

Fig. 4 The char yields during pyrolysis of raw coal and Ca-loaded coal samples at different temperatures

macromolecular structure (Franklin et al. 1981), leading to the further release of small molecules gas and the decrease of char yield.

As shown in Fig. 5, with the temperature rising from 600 to 800 °C, the contents of N in the chars produced from raw coal and Ca-loaded coal samples decreased, indicating that higher temperature could enhance the release of N from coal to volatile. Physically, the variation in char-N content is governed by the evolution of N-containing structures in coal during pyrolysis. With the increase in pyrolysis temperature, more N-containing structures in coal become unstable and would be finally cracked into small molecular gases or tar with heterocyclic structures, thus leading to the decrease in char-N content. In addition, higher temperatures could enhance the secondary decomposition of char, which further increases the conversion of char-N to volatile-N, accompanied by the decrease in char yields.

For the same coal samples (e.g. 1.5% Ca + coal) with increasing pyrolysis temperatures, the decrements in the yields of char-N are not consistent with the increments in the amount of nitrogen contributed by NH_3 and HCN. This might be caused by the fact that higher temperature could enhance the decomposition of coal-N into tar-N or N_2 (Ohtsuka et al. 1997), thus affecting the release of HCN and NH_3. The release of NH_3 and HCN might also come from the decomposition of tar-N. For example, tar-N could undergo secondary decomposition reactions, which could generate NH_3, HCN, N_2 and other N in gas phase (Johnsson 1994), with the catalytic effect of calcium in coal (Tsubouchi and Ohtsuka 2008). On the other hand, tar-N could also experience condensation polymerization by forming macromolecular structure and returned to the char-N at high temperatures.

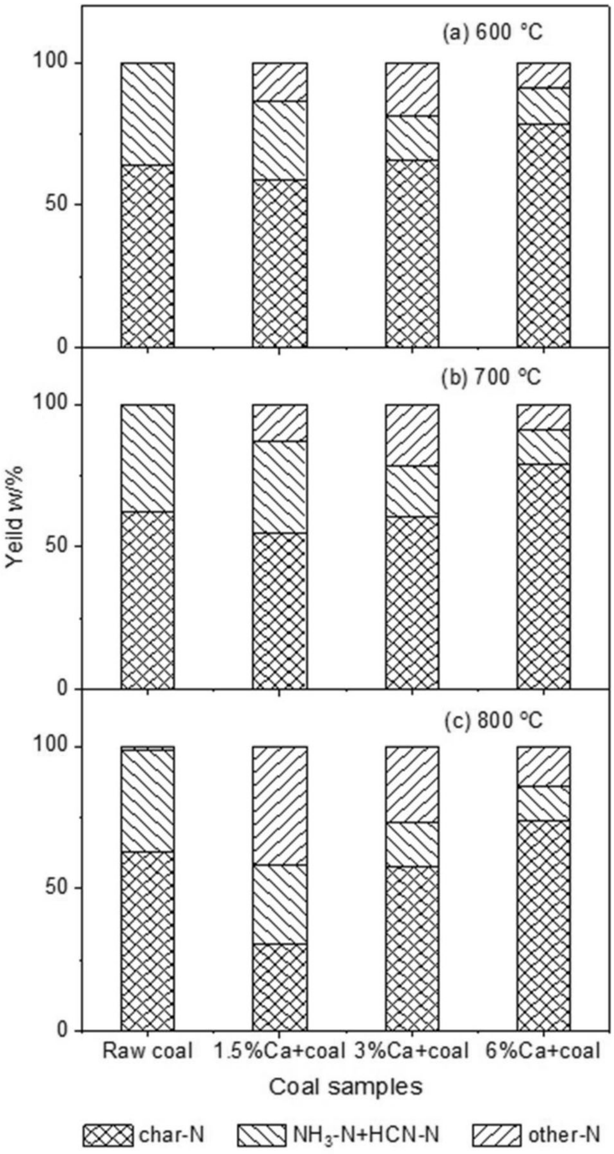

Fig. 5 The distribution of N in char and volatiles during pyrolysis of coal and Ca-loaded coal samples at different temperatures

At the same temperature, the addition of 1.5% calcium significantly increased the yield of volatile-N, especially at 800 °C. However, further increasing the calcium content to 3% or 6% in coal led to the decrease of volatile-N. These results suggest that different calcium contents in coal exert various effects on N distribution during coal pyrolysis. Specifically, coal samples loaded with 1.5% Ca enhanced the conversion from coal-N to volatile-N, while higher calcium contents, such as 3% or 6% in coal would inhibit the release of N during coal pyrolysis. During pyrolysis, calcium could catalytically enhance the fracture and combination of chemical bonds, generating abundant free radicals (Li et al. 2000). These free radicals could continuously attack N-containing structures and consequently release the N-containing gaseous products, such as NH_3, HCN, N_2 etc., leading to the decrease in char-N content. However, the excessive presence of Ca in coal increased the char-N yield, which is probably because the excessive amounts of Ca could increase the density of the coal/char matrix (Sathe et al. 2003). Thus, the release of volatiles from the particles would be more difficult, resulting in more N retained in char.

3.3 Effect of calcium on the transformation of N in char during pyrolysis

Figure 6 shows XPS spectra and the fitting results of raw coal and chars produced at 800 °C with the distributions of different forms of nitrogen being presented in Fig. 7. Clearly, three main N-containing structures, namely, pyridinic nitrogen (N-6) at 398.7 eV, pyrrolic nitrogen (N-5) at 400.3 eV and quaternary type nitrogen (N-Q) at 401.4 eV were observed in raw coal and its derived char (Stanczyk 2004; Kelemen et al. 1998). Particularly, N-5 (60%) was the dominant occurrence mode of N for raw Shengli brown coal, followed by N-Q (25%) and N-6 (15%).

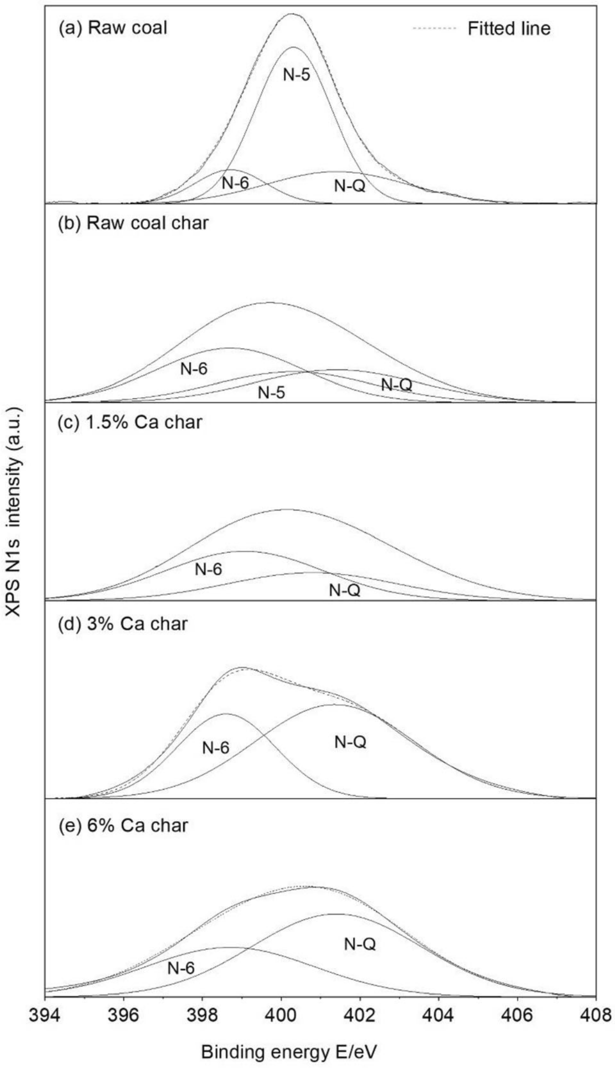

Fig. 6 XPS (N 1s) spectra of Shengli lignite and its pyrolysis chars from 800 °C

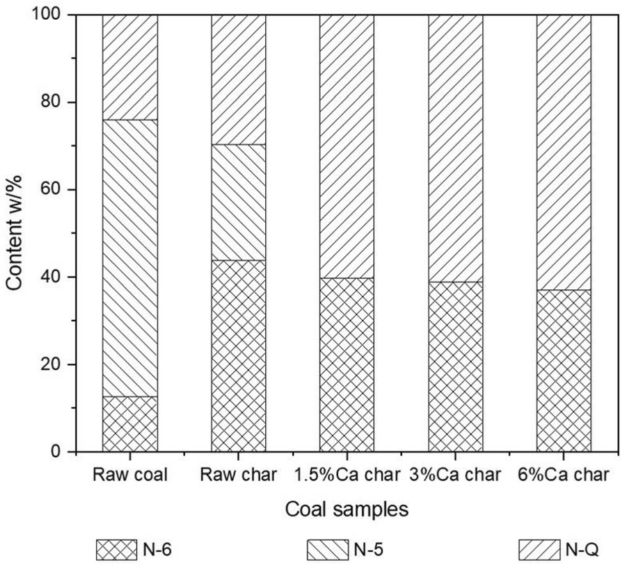

Fig. 7 The distributions of N in chars after pyrolysis of coal and Ca-loaded coal samples at 800 °C

Figure 7 demonstrates that the content of N-5 in char produced from raw coal pyrolysis at 800 °C significantly decreased, while that of other N-containing structures, especially N-6 substantially increased. Theoretically, the bond energies of N-5 and C-N were lower (Zhang et al. 2013), compared with that of N-6 and N-Q, indicating that N-5 would become unstable during pyrolysis and cracked into the gas phase and form the thermally stable N-6 and/or N-Q. Meanwhile, pyridine (though a little) could also be converted into N-6. Figure 7 also implies that calcium could significantly enhance N conversion from N-5 and N-6 to N-Q in char as calcium could catalyze the decomposition of both pyrrolic and pyridinic nitrogen in coal (Wu et al. 2001). During pyrolysis, N-Q was relatively more stable, and the polymerization and carbonization reaction might also stabilize the nitrogenous system (Li and Tan 2000).

It should also be noted that only a single form of calcium (calcium hydroxide) was loaded into the raw coal samples for the purpose of this study. While considering the abundant inorganic species in brown coal, the effect of other forms of calcium, such as calcium chloride and phosphates as well as the interactions between different forms of inorganic species on the release and evolutionary transformation of nitrogen during brown coal pyrolysis should also be further investigated in the future work.

4 Conclusions

This study investigated the chemical transformation behavior of N in coal, especially the effects of calcium on the migration of N from coal samples to gases (NH_3 and HCN) and char-N during pyrolysis. Based on the experimental results, it can be concluded that during coal pyrolysis, the release of NH_3 is mainly derived from secondary reactions among volatiles, tar and char with the catalytic effect of inherent mineral, especially calcium in coal. Increasing the pyrolysis temperature from 600 to 800 °C significantly enhances the conversion of coal-N to volatile-N. The increase of pyrolysis temperatures also inhibits the generation of NH_3 while facilitates the formation of HCN. The release of HCN during coal pyrolysis is very sensitive to the temperature. For example, increasing pyrolysis temperature would lead to the cracking of the N-containing structures in coal into gaseous species. Higher pyrolysis temperature also promotes the decomposition of coal-N into tar-N or N_2, thus reducing the release of HCN and NH_3. Interestingly, tar-N could either undergo secondary decomposition reactions with the release of NH_3, HCN, N_2 and/or other gaseous N, or experience condensation polymerization by forming macromolecular structure in char, thus maintaining in solid phase at high pyrolysis temperature. Calcium plays significant roles in both nitrogen release and transformation in solid phase during brown coal pyrolysis. First, calcium could substantially restrain the conversion of coal-N to volatile-N, thereby reducing the release of NH_3 and HCN. During brown coal pyrolysis, calcium could also catalytically enhance the fracture and combination of chemical bonds, generating abundant free radicals, which are expected to continuously attack N-containing structures and consequently release the N-containing gaseous products, leading to the decrease of nitrogen content in char. Second, calcium also catalyzes the transformation of N in char from pyridinic nitrogen (N-6) and pyrrolic nitrogen (N-5) to quaternary type nitrogen (N-Q) during coal pyrolysis.

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