Effect of Alkali Metal Ions on the Formation Mechanism of HCN During Pyridine Pyrolysis

Ji Liu

North China Electric Power University

Wei Zhao

North China Electric Power University

Xin-rui Fan

North China Electric Power University

Ming-xin Xu

North China Electric Power University

Shu Zheng

North China Electric Power University

Qiang Lu (✉ qianglu@mail.ustc.edu.cn)

National Engineering Laboratory for Biomass Power Generation Equipment, North China Electric Power University, Beijing 102206, China <https://orcid.org/0000-0002-4340-1803>

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Abstract

The present work aims at the effects of alkali metal ions (Na^+ , K^+) on the NO_x precursor formation during coal pyrolysis by employing the N-containing pyridine as the model compound. Density functional theory (DFT) calculations were used to elucidate the pyridine pyrolysis mechanism and pathways for the HCN formation. The calculation results indicate that Na^+ and K^+ have distinct influences on different pyrolysis reactions. The two alkali metal ions can facilitate the initial hydrogen transfer from C_1 to N and C_2 , while it is the opposite situation for other hydrogen migration reactions. Both Na^+ and K^+ significantly reduce the activation energies for the C-C bond breakage and the formation of the triple bond, whereas the activation energies are increased for isomerization reactions. The two alkali metal ions modulate the rate-determining step of the pyrolysis process and promote the formation of HCN from pyridine by decreasing the activation energies of the rate-determining steps in different pathways.

1. Introduction

Nitrogen oxide (NO_x) emissions are predominantly ascribed to the combustion of fossil fuels especially coal, and have caused severe adverse effects on the environment and human health (Kampa et al. 2008; Wu et al. 2010). Apart from the acid rain, NO_x also contributes a lot to the greenhouse effect which is 260 times as great as CO_2 (Tsiliyannis et al. 2016; Chu et al. 2020). During the initial pyrolysis stage of coal combustion, organic N-containing compounds are firstly converted into small-molecule compounds (e.g., NH_3 and HCN), which can react with oxygen to form NO_x (Koger et al. 2005; Zhang et al. 2011; Ye et al. 2019). Therefore, understanding the formation mechanism of NH_3 and HCN (NO_x precursors) from organic N-containing compounds is critical to control NO_x emissions, which has attracted widespread attention in recent decades.

Both experimental and computational approaches have been widely applied to explore the pyrolysis mechanisms of various N-containing compounds in coal, e.g., pyridine and its derivatives (Hämäläinen et al. 1994; Molina et al. 2000; Adamczyk et al. 2014; Ikeda et al. 1995; Mackie et al. 1990; Hong et al. 2013; Ninomiya et al. 2000; Gu et al. 2013). HCN and cyanoacetylene have been detected as major products in the pyrolysis of pyridine and 2-methylpyridine, based on which Ikeda et al. (1995) developed a kinetic model to simulate pyrolysis reactions. Mackie et al. (1990) reported similar findings for pyridine pyrolysis in an argon atmosphere. They proposed that all C-H bonds in the pyridine ring were feasible to be ruptured, especially the one at the *ortho*-position of the nitrogen atom which was relatively weaker than the others. Intermediates and products from pyridine pyrolysis were detected by using tunable synchrotron vacuum ultraviolet photoionization and molecular-beam mass spectrometry technique in the work of Hong et al. (2013) Following the homolytic breakage of the C-H bond, *o*-, *p*-, and *m*-pyridyls were generated and then decomposed by cleaving the pyridine ring. The *m*-pyridyl was deemed as the major source for the HCN formation. Besides experimental studies, computational methods have also been applied to investigate the pyrolysis mechanism of pyridine. The semi-empirical PM3 calculations indicated the C-H bond of pyridine was broken to generate radicals, and then decomposition fragments

were successively generated by rupturing the weakest bond of the radicals (Ninomiya et al. 2000). Gu et al. (2013) carried out the decomposition mechanism study of pyridine by the B3LYP functional and 6-31G(d,p) basis set. The results indicated that the breakage of the C-H bond in pyridine preferentially produced the o-pyridyl radical. Besides, the ring-opening via C-N bond cleavage in o-pyridyl radical was more favorable than that of the C-C bond, as the former had a lower activation barrier. Differently, the concerted hydrogen transfer was confirmed more feasible for the breakage of C-H bond than direct homolysis, according to our density functional theory (DFT) calculations.

During the real coal pyrolysis/combustion process, the pyrolysis process of pyridine and other N-containing compounds can be affected by the other components in coal, such as metal ions. In addition, the metal salts can be used as process accelerators of coal gasification, as the salts ions can turn into various active species by reacting with the carbonaceous material. Owing to the above facts, the effects of alkali metal ions in coal pyrolysis have been paid much attention. Na and K are the major ion-exchangeable alkalis in low-rank coals, existing as carboxylates ($-\text{COO}_m\text{R}_n$, $\text{R} = \text{Na/K}$) or as soluble salts (R_mCl_n , $\text{R} = \text{Na/K}$) (Liu et al. 2000). Na and K are easily volatilized during pyrolysis, which affects the evolution channels and the product distribution of coal (Durie et al. 2013). Ohtsuka et al. (1997) found that the total conversion of coal-N to NO_x precursors (HCN , NH_3) and N_2 strongly depended on the alkali metal ions at a high temperature of 1000 °C. Franklin et al. (1983) investigated the roles of metal ions by pyrolyzing raw coal in the presence of calcium, sodium, and potassium in a helium atmosphere at 1400K. They found that sodium and potassium ions had greater effects than calcium ion. This conclusion was supported by Wood et al. (1984) who found that pyrolysis reactions using alkali metal salts as catalysts often produced significant catalytic results.

Currently, the HCN formation mechanism from the pyrolysis of pure pyridine-N in the non-catalytic condition has been comprehensively investigated, whereas few studies, especially computational investigations, have reported the effects of alkali metal ions on the pyridine pyrolysis mechanism. In this study, DFT calculation was employed by focusing on the catalytic effects of typical alkali metal ions K^+ and Na^+ on the HCN formation from pyridine pyrolysis.

2. Calculation Details

All calculations were completed using Gaussian 16 (Frisch et al. 2016). Based on the electron density of the system, many studies have used DFT calculations to shed light on the pyrolysis chemistry of N-containing compounds (e.g., pyrrole, indole, and pyridine) (Liu et al. 2018a, 2018b, 2020). All stable geometries of the reactants, intermediates, transition states, and products were obtained using the B3LYP/6-31G (d, p) method, which has been confirmed to be accurate to optimize organic species (Liu et al. 2018a, 2018b, 2020). Besides, according to Glukhovtsev et al. (1997), B3LYP calculations on iron-containing species gave reliable results, which were comparable with experimental data.

All optimized geometry configurations were further examined by frequency analysis. The reactants, intermediates, and products were verified as the local minima, whereas all transition states were

confirmed to be first-order saddle points. Corresponding minima and first-order saddle points were verified to be on the same potential energy surface by following intrinsic reaction coordinate (IRC) calculations. Enthalpies at 298.15 K and 1 atm were used for the energetics discussion (Liu et al. 2018a). The activation energy was defined as the enthalpy difference between the reactants and the concerted transition states (Glukhovtsev et al. 1997).

3. Results And Discussion

In our previous investigation, DFT calculations were conducted to investigate the possible HCN formation pathways from pyridine pyrolysis under non-catalytic conditions. Pyridine tends to decompose through initial hydrogen transfer processes, as shown in Figure S1. According to our preliminary work, the pyridine pyrolysis to form HCN includes five pathways, i.e., path-a, path-b, path-c, path-d, and path-e (Figure S2). Based on DFT calculation results, the effects of Na^+ and K^+ on the initial hydrogen transfer and the formation of HCN are discussed.

3.1 Effects of Na^+ or K^+ on the initial hydrogen transfer reactions

Table 1 summarizes the activation energies of the initial hydrogen transfer reactions under the non-catalytic and Na^+/K^+ -catalyzed conditions. The two alkali metal ions have different influences on these five sites of the hydrogen transfer. The departure of H on C_1 (Reactions a and b) is promoted by Na^+ and K^+ . As for Reactions a, Na^+ has a greater decreasing effect on the activation energy than K^+ , whereas it is opposite for Reaction b. Notably, the activation energy decrease by 69.4 and 71.9 kJ/mol in the presence of Na^+ and K^+ for the hydrogen transfer from C_1 to C_2 (Reaction b). The differences of activation energy for Reaction a (C_1 to N) are less than 10 kJ/mol for the non-catalytic and ion-catalyzed conditions. Whereas, other hydrogen transfer reactions are hindered in the presence of alkali metal ions, and the inhibition is relatively manifest in the presence of Na^+ . Based on the above results, it can be inferred that the alkali metal ions affect the decomposition of pyridine and the formation of HCN by influencing the initial hydrogen transfer processes, and Na^+ has a greater influence than K^+ . Among all the five hydrogen transfer reactions, Reaction b is the most feasible in the presence of alkali metal ions, whereas it is Reaction a that dominates without catalysis. The detailed effects of alkali metal ions on HCN formation pathways will be discussed below.

Table 1 Comparison of the activation energies of the initial hydrogen transfer in the absence and presence of Na⁺ or K⁺

Hydrogen transfer sites		(a)	(b)	(c)	(d)	(e)
		C ₁ to N	C ₁ to C ₂	C ₂ to C ₁	C ₂ to C ₃	C ₃ to C ₂

Activation	Non-catalytic	357.7	413.9	389.6	406.6	389.4
energies	Na ⁺ -catalyzed	349.6	344.5	411.0	423.0	423.4
(kJ/mol)	K ⁺ -catalyzed	354.4	342.0	404.7	419.5	418.0

3.2 Effects of Na⁺ or K⁺ on the HCN formation pathways

The presence of metal ions will not change the possible pathways to form HCN from pyridine, but change the geometries of transition states and intermediates. The detailed pathways are compared below, and the letters “n” and “k” are used to represent the presence of Na⁺ and K⁺, respectively.

3.2.1 HCN formation from pathway-a

Energy profiles of the HCN formation with/without catalysis via path-a are depicted in Fig. 1. As discussed above, the decomposition of pyridine starts from the hydrogen transfer from C₁ to N, disturbing the stability of the N-heterocycle. The transition states a-1t, a-n-1t, and a-k-1t are involved in this step for the non-catalytic, Na⁺- and K⁺-catalyzed conditions, with the activation energies of 357.7, 349.6, and 354.4 kJ/mol. Afterward, the six-membered intermediate a-1m isomerizes into the five-membered ring a-2m through the C₁-N bond cleavage and the C₁-C₆ bond generation simultaneously. The presence of Na⁺ and K⁺ increases the activation energy from 462.2 kJ/mol to 468.1 and 470.2 kJ/mol, respectively. Thus, Na⁺ and K⁺ inhibit the isomerization reaction of the pyridine ring, and the impact of K⁺ is greater than Na⁺.

Subsequently, the five-membered ring of intermediate a-2m is cleaved via a concerted ring-opening reaction, where the C = N double bond turns into a triple bond. This step requires 511.3 kJ/mol of activation energy without catalysis. As for Na⁺- and K⁺-catalyzed pyridine pyrolysis, the ring-opening needs to overcome the activation energy of 460.4 and 467.0 kJ/mol, respectively. It indicates that Na⁺

and K^+ can significantly reduce the activation energy (~ 50 kJ/mol) of the concerted ring-opening reaction of pyridine derivatives. Finally, the C_4 - C_5 bond of intermediate a-3m cleaves via the hydrogen transfer from C_4 to C_5 , producing a-4m (vinylacetylene) and HCN. The final step requires to overcome an activation energy of 561.2 kJ/mol under the non-catalytic condition. The addition of Na^+ and K^+ lowers the activation energy by 84.7 and 36.4 kJ/mol, respectively, showing that Na^+ and K^+ promote the breakage of the C-C bond to form HCN. Moreover, Na^+ has a greater impact than K^+ in this step. Notably, the final step is the rate-determining step regardless of the presence of alkali metal ions in path-a, and the overall activation energies are 561.2, 476.5, and 524.8 kJ/mol for the non-catalytic, Na^+ - and K^+ -catalyzed conditions, respectively.

In summary, alkali metal ions (Na^+ and K^+) can significantly promote the concerted ring-opening and final hydrogen transfer in path-a. What the two reactions have in common is both of them involve the C-C bond rupture. On the contrary, the isomerization reaction and the initial hydrogen transfer of path-a are less affected by the two alkali metal ions. Na^+ and K^+ can lower the overall activation energy to promote the HCN generation via path-a, with Na^+ having a greater catalytic effect than K^+ .

3.2.2 HCN formation from pathway-b

The effect of alkali metal ions on the pyrolysis of pyridine in path-b is shown in Fig. 2. The initial hydrogen transfer from the C_1 position to the C_2 position is special, in comparison with those in other pathways. The N-heterocycle is cleaved by the C_1 - C_2 bond cleavage, accompanied by the hydrogen transfer. As stated above, this reaction is facilitated in the presence of alkali metal ions. The activation energies are 413.9, 344.5, and 342.0 kJ/mol for the non-catalytic, Na^+ and K^+ -catalyzed conditions. Then, intermediate b-1m undergoes isomerization by forming the C_1 - C_5 bond and breaking the C_5 -N bond at the same time. The activation energy is 371.5 kJ/mol under the non-catalytic condition. During catalytic pyridine pyrolysis, the activation energies of the transition states in the presence of Na^+ and K^+ are 395.0 kJ/mol and 389.9 kJ/mol, which are 23.5 kJ/mol and 5.1 kJ/mol higher than that without alkali metal ions, respectively. This phenomenon shows that Na^+ and K^+ inhibit the isomerization reaction of the pyridine ring, and Na^+ has a slightly stronger effect than K^+ . Finally, the newly formed C_1 - C_5 bond cleaves through a hydrogen transfer reaction to produce b-3m (vinylacetylene) and HCN. Without catalysis, the activation energy is 561.2 kJ/mol, and it is the rate-determining step of path-c. In the presence of Na^+ and K^+ , the activation energy decreases by 84.7 and 89.4 kJ/mol, respectively. Even so, this reaction is still the rate-determining step under the Na^+ - and K^+ -catalyzed conditions.

To sum up, the two alkali metal ions promote the formation of HCN by significantly reducing the overall activation energy in path-b. The overall catalytic ability of the two alkali metal ions is close, with K^+ having a slight advantage over Na^+ . As expected, the two alkali metal ions have manifest promotion to the breakage of C-C bonds (step 1 and step 3).

3.2.3 HCN formation from pathway-c

Figure 3 shows the energy profiles of path-c under the non-catalytic and alkali metal ions-catalyzed conditions. The hydrogen transfer from C_2 to C_1 initiates the decomposition of pyridine in path-c. Under the non-catalytic condition, transition state c-1t is involved with an activation energy of 389.6 kJ/mol. Under the catalysis of Na^+ and K^+ , transition states c-n-1t and c-k-1t are involved, with the activation energy increasing by 21.4 and 15.1 kJ/mol, respectively. Hence, both Na^+ and K^+ can hinder internal hydrogen transfer (C_2 to C_1), and the effect of Na^+ is slightly greater than that of K^+ . Following the initial hydrogen transfer, the H at C_1 then migrates to the N atom (485.1 kJ/mol) under the non-catalytic condition. Similarly, the activation energies of this step are also increased under the alkali metal ions, which are 535.2 and 527.6 kJ/mol for Na^+ and K^+ , respectively.

Different from path-a, the intermediate c-2m undergoes the ring-opening reaction to break the C_1 -N bond, without involving a five-membered intermediate. The activation energy slightly decreases from 359.0 kJ/mol to 355.6 (Na^+) and 354.2 kJ/mol (K^+). Subsequently, the N-H bond rotates into a proper position for the final hydrogen transfer from the N atom to the C_4 position. Finally, the concerted cleavage of the C_4 - C_5 bond leads to the production of HCN and b-5m (vinylacetylene). The presence of Na^+ and K^+ greatly decreased the activation energy of the final hydrogen transfer (687.4 kJ/mol vs 503.0 (Na^+) and 516.6 (K^+) kJ/mol). In this step, Na^+ has a greater promotion effect than K^+ .

According to the above results, the rupture of C-C bonds in the ring-opening and final hydrogen transfer reactions are facilitated by the alkali metal ions, which is similar to path-a. Differently, they have little effects on other reactions that do not involve the rupture of C-C bonds. In addition, the two alkali metal ions also alter the rate-determining step of path-c. The final step determines the reaction rate without catalysis, whereas the second step of hydrogen transfer (C_1 to N) is the rate-determining step during the Na^+/K^+ -catalyzed pyridine pyrolysis. In total, Na^+ and K^+ significantly promote the concerted decomposition during pyridine pyrolysis to form HCN, and Na^+ shows a greater catalytic effect than K^+ .

3.2.4 HCN formation from pathway-d

Figure 4 gives the catalytic effects of Na^+ and K^+ on path-d. As mentioned above, the initial hydrogen transfer from C_3 to C_2 is hindered in the absence of the alkali metal ions. The activation energy increases from 406.6 kJ/mol to 423.0 (Na^+) and 419.5 (K^+) kJ/mol. Afterward, the C_1 -N bond breaks along with the hydrogen transfer from C_5 to the N atom. It's hardly surprising that the activation energy is greatly reduced by the catalysis of Na^+/K^+ (660.5 kJ/mol vs 433.3 (Na^+) and 431.6 (K^+) kJ/mol). The H atom bound to the N atom then migrates to the C_4 position to form the $C \equiv N$ triple bond. It is notable that the activation energy is also reduced greatly with the catalysis of the two alkali metal ions. This reaction does not involve the breakage of a C-C bond but a transformation from the double bond to the triple bond. The non-catalytic activation energy is 587.1 kJ/mol. When Na^+ is included, the activation energy

(454.6 kJ/mol) is lowered by 132.5 kJ/mol, while the activation energy (461.8 kJ/mol) with K^+ is 125.3 kJ/mol lower. Similarly, HCN and d-4m (vinylacetylene) are also formed by a final breakage of the C_4-C_5 bond via hydrogen transfer, and the activation energy is 620.9 kJ/mol. The activation energies with Na^+ catalysis (540.4 kJ/mol) and K^+ catalysis (550.6 kJ/mol) are 80.5 and 70.3 kJ/mol lower than that without catalysis. Thus, Na^+ and K^+ significantly promote the final C-C bond cleavage to form HCN, and the promotion effect of Na^+ is stronger than K^+ .

In the presence of alkali metal ions, not only the scission of the C-C bond but also the formation of the triple bond from the double bond is facilitated by the catalysis of Na^+ and K^+ . Additionally, the final step reaction determines the reaction rate of path-d, which is different from the non-catalytic condition where the second step of hydrogen transfer is the rate-determining step. All in all, both Na^+ and K^+ alter the rate-determining step of path-d, reduce the activation energy, and promote the formation of HCN, with Na^+ having a greater influence than K^+ .

3.2.5 HCN formation from pathway-e

Figure 5 illustrates the energy profiles of path-e under the non-catalytic, Na^+ - and K^+ -catalyzed conditions. First, the H atom at the C_3 position of pyridine transfers to the C_2 position to form e-1m via an internal hydrogen transfer reaction. The transition state is e-1t in the absence of alkali metal ions, which has an activation energy of 389.4 kJ/mol. Both Na^+ and K^+ inhibit the internal hydrogen transfer reaction. The activation energy with Na^+ catalysis is 423.4 kJ/mol, which is 34.0 kJ/mol higher than that without an alkali metal ion. K^+ has a slightly weaker influence than Na^+ by increasing the activation to 418.0 kJ/mol. Then, the intermediate e-1m undergoes a concerted ring-opening reaction to break the C_2-C_3 bond via the transition state e-2t (481.5 kJ/mol). As for the Na^+/K^+ -catalyzed pyrolysis of pyridine, the activation energy is lowered to 399.6 kJ/mol and 402.5 kJ/mol, respectively. Different from the other four pathways, the breakage of the C_5-N bond results in the formation of the $C \equiv N$ triple bond, producing HCN and e-3m. The final step determines the reaction rate of path-e without catalysis, and the overall activation energy is 625.3 kJ/mol. The presence of Na^+ and K^+ significantly decreases the activation free energy of this reaction by 163.7 and 157.9 kJ/mol, respectively. Even so, the final C-N bond scission is still the rate-determining step under the Na^+ - and K^+ -catalyzed conditions, with the overall activation energy of 461.6 and 467.4 kJ/mol, respectively.

The above calculation results indicate that alkali metal ions significantly promote the C-C bond scission and the formation of the $C \equiv N$ triple bond of path-e. Na^+ and K^+ lower the overall activation energies for pyridine pyrolysis, further promoting the formation of HCN. Overall, Na^+ has a slightly greater catalytic effect than K^+ .

4. Conclusion

The present work has explored the role of Na^+ and K^+ in the pyrolysis of pyridine to produce HCN using DFT calculations. Based on the computational results, the effects of the two alkali metal ions are concluded as follows.

Na^+ and K^+ play a dual role in the initial hydrogen transfer reactions. The migration from C_1 to N or C_2 is facilitated by reducing the activation energy. Particularly for Reaction b (C_1 to C_2), the activation energy decreases by 69.4 and 71.9 kJ/mol under the catalysis of Na^+ and K^+ , respectively. Oppositely, the activation energies of other initial hydrogen transfer (C_2 to C_1 , C_2 to C_3 , C_3 to C_2) are increased by 13.1 to 54.0 kJ/mol. In all cases, Na^+ has greater effects than K^+ except the hydrogen transfer from C_1 to C_2 .

As for the elementary reactions in the HCN formation pathways from pyridine pyrolysis, Na^+ and K^+ significantly decrease the activation energy of the C-C bond breakage and the formation of the triple bond. Differently, other reactions are slightly influenced by the two alkali metal ions, and the isomerization reactions are even hindered by them.

In addition, the presence of Na^+ and K^+ significantly lower the overall activation energies and even alters the rate-determining steps for path-c and path-d. Hence, the formation of HCN can be promoted by the presence of Na^+ and K^+ . Therefore, the inclusion of Na^+ and K^+ in coal should be considered for source-control NO_x abatement techniques.

Declarations

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Figures

Figure 1

Energy profiles of non-catalytic and Na⁺/K⁺-catalyzed pyridine pyrolysis to form HCN via path-a. Unit: kJ/mol.

Figure 2

Energy profiles of non-catalytic and Na⁺/K⁺-catalyzed pyridine pyrolysis to form HCN via path-b. Unit: kJ/mol.

Figure 3

Energy profiles of non-catalytic and Na⁺/K⁺-catalyzed pyridine pyrolysis to form HCN via path-c. Unit: kJ/mol.

Figure 4

Energy profiles of non-catalytic and Na⁺/K⁺-catalyzed pyridine pyrolysis to form HCN via path-d. Unit: kJ/mol.

Figure 5

Energy profiles of non-catalytic and Na⁺/K⁺-catalyzed pyridine pyrolysis to form HCN via path-e. Unit: kJ/mol.

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