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Published in:
Journal of the Energy Institute

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
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Download date: 19. Apr. 2020
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PII: S1743-9671(17)30764-X
DOI: 10.1016/j.joei.2018.03.012
Reference: JOEI 436

To appear in: Journal of the Energy Institute

Received Date: 6 October 2017
Revised Date: 18 March 2018
Accepted Date: 19 March 2018


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Mechanism Study on the Effect of Alkali Metal Ions on the Formation of HCN as NOx Precursor during coal pyrolysis

Ji Liu\textsuperscript{a}, Xiaolei Zhang\textsuperscript{b,*}, Qiang lu\textsuperscript{a,**}, Alexander Shaw\textsuperscript{b}, Bin Hu\textsuperscript{a}, Xiaoyan Jiang\textsuperscript{a}, Changqing Dong\textsuperscript{a}

\textsuperscript{a} National Engineering Laboratory for Biomass Power Generation Equipment, North China Electric Power University, 102206, China;
\textsuperscript{b} School of Mechanical and Aerospace Engineering, Queen’s University of Belfast, BT9 5AH, UK

* Corresponding author. E-mail: xiaolei.zhang@qub.ac.uk (X. Zhang).

** Corresponding author. E-mail: qlu@ncepu.edu.cn (Q. Lu.)

Abstract

Coal, as a typical fossil fuel, is a current major contributor to the global emission of nitrogen oxides (NO\textsubscript{x}). The NO\textsubscript{x} formation process during coal utilisation can be described as the thermal decomposition of N-containing model compounds into NO\textsubscript{x} precursors followed by NO\textsubscript{x} formation. The existence of alkali metal ions, Na\textsuperscript{+} and K\textsuperscript{+}, during the coal utilisation process has a significant influence on the formation of NO\textsubscript{x} species. However, the information about this influence is currently lacking within the available literature. Within this research, the effect of Na\textsuperscript{+} and K\textsuperscript{+} on the formation mechanism of NO\textsubscript{x} during pyrrole pyrolysis were investigated using density functional theory (DFT). A hydrogen migration occurs from the meta-position of pyrrole-N is transferred to the ortho-position, and then pyrrole-N disconnected from the ortho-position C, which makes the ring opened. Lastly, in a concerted mechanism, a long carbon bond breaking between the migrating hydrogen and the carbon, nitrogen atoms. It was found that Na\textsuperscript{+} and K\textsuperscript{+} have a catalytic effect on the internal hydrogen transfer and ring-opening of pyrrole but have an inhibitory effect on internal hydrogen isomerization and concerted decomposition reaction. It was also found that those alkali metal ions (Na\textsuperscript{+} and K\textsuperscript{+}) have strong interactions with pyrrole and its derived compounds (HCN and propyne molecules), those interactions are much larger than the existing attractive interactions among HCN, propyne molecules and their complexes. Additionally, it was found that both Na\textsuperscript{+} and K\textsuperscript{+} inhibit the pyrrole formation of HCN from pyrrole, with Na\textsuperscript{+} has a higher inhibition effect than that of K\textsuperscript{+}. Furthermore, the mechanisms discussed in this research may well play a role in the thermal decomposition of other coal compounds such as indole and carbazole.
Keywords: coal; NOx; pyrrole; mechanism; pollution

1. Introduction

NOx species are precursor compounds for the formation of surface ozone which has been shown to cause adverse health effects when inhaled. [1] It was shown that the contribution of NOx to greenhouse gases is 260 times greater than that of CO2 for a time horizons of 20 years [2,3]. Nitrogen oxides (NO, NO2) emissions are mainly produced from combustion of fossil fuel, especially, from coal. Currently, coal is still the main energy source in rapid developing and large population countries. For example, the consumption of coal in India has increased by 50% over Year 2005-2014, which is consistent with changes in Chhattisgarh, an area rich in coal and with numerous thermal power plants [4]. In China, coal-fired power plant emissions are the major source of anthropogenic NOx emissions [5].

The primary NOx pollutant precursors formed from coal are HCN and NH3 [6,7], so the NOx formation process during coal utilisation can, by and large, be described by the thermal decomposition of N-containing model compounds to NH3 and HCN. Functional forms of nitrogen in coals have been determined by X-ray photoelectron spectroscopy [8]. Within all of the N-containing compounds identified in coal, it was found that pyrolic-type species were the predominant nitrogen source (50-60% coal nitrogen) [8] and this concentration varies slightly between different ranks of coal [9,10]. Thus, the thermal decomposition of pyrrolic groups plays an important role in NOx formation. Pyrrole and its derivatives have been extensively studied and commonly selected as N-containing model compounds in coal [11–13] and therefore it was also selected as the model compound for this research.

Several studies on the mechanisms for the pyrolysis of pyrrole and pyrrolic-type compounds have been carried out [14–18]. Earlier works proposed three possible pathways for HCN formation from pyrrole by concerted reactions. As shown in Fig.1, the isomerization of pyrrole to a cyclic carbene, an allenic imine type intermediate is achieved through a ring opening reaction, producing HCN in a low energy concerted reaction [15–17]. The crucial initial step of the model was postulated to be the reversible tautomerization of pyrrolidine, giving 2H-pyrrole, which is then expected to undergo ring scission, yielding three pathways (path1, path2, and path3 in Fig. 1). In path1, the species of the study were computed using the Complete Active Space SCF (CASSCF) method and the correlation consistent cc-pVDZ basis set. The rate-determining step (r.d.s.), through transition state (TSP1), has an overall energy barrier of 316.31 kJ/mol [15]. Path2 [14], using the same method as path1, but with a different basis set, which with two sets of polarisation functions (VTZ2P), found that the r.d.s. is through TSP2, overcoming an energy barrier of 346 kJ/mol (exact digits follow the original paper). Path3 [17] fully optimised by the Lee Yang & Parr correlation functional (B3LYP) and the 6-31G(d,p)
basis set, underwent a high rate-determining step (TSP3), with an overall energy barrier of 497.06 kJ/mol. It can be seen through a comparison of the energy barriers that path1 is the most feasible.

Fig.1 The formation of HCN from pyrrole without an alkali metal ions. The numerical values are energies in kJ/mol relative to that of pyrrole.

Additionally, low-rank coals contain significant contents of ion-exchangeable alkalies, such as sodium and potassium. Lignite contains sodium in two forms; as a carboxylate (-COONa), forming a part of the coal organic matter, or as a soluble salt (NaCl), that, when dissolved in the coal-bed moisture, can account for more than 70% of the total sodium in coal [19]. Na is easily volatilised under pyrolysis conditions and, as such, is able to impact upon the reactions of larger aromatic ring systems [20]. Previous experiments have shown that the effect of alkali metal ions in coal pyrolysis process is significant [20–23]. Wood et al. [22] showed that the ions (Na⁺, K⁺, Ca²⁺, Mg²⁺) catalyse gasification of low-rank coals. Franklin et al. [23] studied the effects of ions on the rapid pyrolysis of a low-rank coal, finding sodium and potassium ions had a larger effect on decomposition of carboxyl groups than calcium ions. Moreover, Ohtsuka. et al. [21] highlighted the effect of alkali and alkaline earth metal cations on nitrogen release during coal pyrolysis. However, the effect of alkali metal ions on the pyrolysis mechanism and influence of coal forming NOₓ pollutant precursors have not been considered so far. This work aims to investigate the effects of the alkali metal ions K⁺ and Na⁺ on the formation mechanism of the NOₓ pollutant precursor HCN from pyrrole and analyse the influence of alkali metal ions on HCN forming pathways. We first investigate the optimal pathway from pyrrole to HCN without the influence of alkali metal ions, by comparison of the energy barriers that have been previously proposed by other researchers (path1 is the most feasible, Fig. 1). Following this, we highlight the discrepancies in values between the methods used in the present work and those of earlier researchers. Finally, the effects of Na⁺ and K⁺ on the formation of HCN during pyrrole pyrolysis are discussed.
2. Methodology

2.1 Calculation details

Within this work, all calculations were carried out using Gaussian 09 program [24]. The equilibrium geometries of the reactants, intermediates, transition states, and products were optimised by the density functional theory (DFT) computational method, which derives properties of a system based on the electron density. The Becke’s three-parameter hybrid functional combined with the Lee, Yang, and Parr correlation functional (B3LYP) [25], run with the 6-31G(d, p) basis set [26], is a good choice of a model chemistry for most systems. DFT calculations have proved to be an efficient theoretical way to reveal the pyrolysis mechanism of pyrrole model compounds at the molecular level [14,15]. Moreover, the B3LYP method correctly reproduces the experimental dissociation energy of ions, and 6-31 G* basis set was used for most types of atoms [27].

In this work, structural optimisation calculations of all reactants, intermediates, transition states, and products were further evaluated by frequency analysis, adopting the same level of method and basis set. Intrinsic reaction coordinate (IRC) calculations were performed to ensure the correctness of each transition state. Enthalpies were used for the discussion on energetics, under the standard condition of 298.15 K and 1 atm.

2.2 Modelling validation

The work herein focuses on the role of metal ions (K⁺ and Na⁺) in the formation of HCN from pyrrole. Often difficulties arise in the modelling of metallic species, which may require treatment of nondynamical correlation; however, previous work by Glukhovtsev et al. [28] showed that the B3LYP functional was able to produce reliable energies and geometries of iron containing complexes, when compared with experimental data. More recently Zhang and Liu [29] studied the effects of alkali metals during biomass pyrolysis at the B3LYP/6-31G (d, p) level.

To investigate the applicability of using the aforementioned functional for our work, we calculated the reaction energies of path1 in Fig. 1 at the B3LYP/6-31G(d,p) level and made the comparison to the values obtained by Bacskaay et al. [15] as shown in Fig. 2.

Across step I (ΔH=305.75 kJ/mol), the pyrrole undergoes a hydrogen migration reaction via transition state (a-1t) to form a-1m, with an overall barrier of 305.75 kJ/mol. The intermediate, a-1m is converted in step II (ΔH=25.48 kJ/mol), via what we have termed a synergy open ring transition state (a-1-2t), with an overall energy barrier of 291.92 kJ/mol, to yield an imine with an allenic group (a-2m). Step III (ΔH=110.69 kJ/mol), involves an isomerization reaction via transition state (a-3t) to form the cis isomer a-3m, with an overall energy barrier of 282.98 kJ/mol. Step IV (ΔH=170.55 kJ/mol) proceeds via a concerted decomposition transition state (a-1-2t), to form the a-4m(cluster), with an overall energy barrier of 337.88 kJ/mol.
Our results showed slight deviations from the previously reported values, with the largest difference being observed for the step IV. Here, the barrier height is risen to 337.88 kJ/mol from 316 kJ/mol, an increase of 21.2 kJ/mol. The changes in energy can be accounted for the differing choice of calculation methods. As the routes from the present work and Bacskay et al.’s work still follow a similar pattern of barrier heights, the calculation differences on energy changes are not considered significant enough as to impact the findings of the present study. These results suggest that the B3LYP functional is an appropriate selection for assessing the effect of alkali metal ions upon the formation of HCN from pyrrole.

Fig. 2 The optimal energy pathway for the decomposition of pyrrole to HCN. The relative energies for the present work and that of Bacskay et al. are shown in blue dash line and red dash line respectively. Energies are given in kJ/mol and are relative to that of pyrrole.

3. Results and discussion

3.1. The effect of Na\(^{+}\) on the decomposition of pyrrole to HCN

The energy pathway for the decomposition of pyrrole to HCN with Na\(^{+}\) is shown in Fig. 3. Moreover, reactants, intermediates, transition states and products showing the influence of Na\(^{+}\) during pyrrole decomposition in Fig. 4. Table 1 gives the energy barriers of the four elementary reaction steps for two scenarios: with and without the Na\(^{+}\) present.
When the Na\(^+\) is present, the hydrogen migration transition state (a-n-1t), across step I is reduced in energy to 220.18 kJ/mol, and also the a-1m intermediate is stabilised by 109.38 kJ/mol highlighting that the Na\(^+\) catalyses the hydrogen migration reaction. The relative energy of transition state a-n-2t is also reduced when the Na\(^+\) is present, dropping by 28.26 kJ/mol. However, the intermediate product (a-n-2m) is considerably higher in energy compared to a-2m meaning that step II becomes endothermic. For this step and the previous one, Na\(^+\) has a catalytic effect to pyrrole pyrolysis by lowering the activation energies.

The isomerisation reaction in step III is hindered by the presence of Na\(^+\), increasing the a-n-3t transition state energy to 334.54 kJ/mol, 51.56 kJ/mol higher than a-3t. The intermediate product a-n-3m is also raised in energy relative to a-3m, with an energy of 180.45 kJ/mol. The energy barrier for step IV is raised by 50.29 kJ/mol when Na\(^+\) interacts with the transition state a-n-4t. The high energy for this final elementary reaction increases the overall energy barrier for the Na\(^+\) pyrrole decomposition to 388.17 kJ/mol. The predicted a-n-4m(cluster) products have a higher relative energy than a-4m(cluster), resulting in the Na\(^+\) influenced reaction being more endothermic. This higher enthalpy change, coupled with the greater reaction energy barrier means that Na\(^+\) has an inhibitory effect upon the formation of HCN from pyrrole.

Table 1. The effect of Na\(^+\), \(E_a\) and reaction types for four steps.

<table>
<thead>
<tr>
<th>Steps</th>
<th>Species</th>
<th>Alkali Metal Ions</th>
<th>(E_a) (^{a})</th>
<th>Reaction description</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>pyrrole → a-1t pyrrole → a-n-1t</td>
<td>none</td>
<td>Na(^+) 305.75 220.18</td>
<td>Hydrogen from the meta-position of pyrrole-N transferred to the ortho-position</td>
</tr>
<tr>
<td></td>
<td>a-1m → a-2t a-n-1m → a-n-2t</td>
<td>Na(^+)</td>
<td>25.48 106.7</td>
<td>The pyrrole-N is disconnected from the ortho-position C, which makes the ring opened</td>
</tr>
<tr>
<td>II</td>
<td>a-2m → a-3t a-n-2m → a-n-3t</td>
<td>none</td>
<td>Na(^+) 110.69 102.93</td>
<td>Hydrogen on the pyrrole-N isomerize to a cis isomer</td>
</tr>
<tr>
<td>III</td>
<td>a-4t → a-3m a-n-4t → a-n-3m</td>
<td>none</td>
<td>Na(^+) 170.55 141.01</td>
<td>A long C-C breaking bond between the migrating hydrogen and the carbon, nitrogen atoms</td>
</tr>
</tbody>
</table>

\(^{a}\) The units for relative energies are kJ/mol.

A-n-4m(cluster) includes a-n-4m, HCN and Na\(^+\). Structural optimization and frequency analysis being calculated together lead to the corresponding reaction energy barrier of 240.13 kJ/mol. However, when a-4m, HCN and Na\(^+\) are calculated separately, the sum of energy is 350.21 kJ/mol, which is much higher (\(\delta_n=110.14\) kJ/mol) than a-n-
4m(cluster). It is clearly that Na\(^+\) has a strong interaction with HCN and a-n-4m molecules, much larger than the ubiquitous short-range attractive interaction between molecules \([30]\) (\(\Delta = 7.14\) kJ/mol, Fig. 3), forming complexes.

Fig. 3 The optimal energy pathway decomposition of pyrrole to HCN with presence of Na\(^+\). The numerical values are energies in kJ/mol relative to that of pyrrole.
Fig. 4 The Na+ interactions and binding sites in pyrrole and its derivatives. The purple spheres represent Na⁺; the blue spheres represent nitrogen atoms; the gray spheres represent carbon atoms; and the white spheres represent hydrogen atoms. All distances are given in ångströms (Å).

3.2. The effect of K⁺ on the decomposition of pyrrole to HCN

Fig. 5 outlines the relative energies of reactants and intermediates for the decomposition of pyrrole to HCN, with the presence of a K⁺ ion. Moreover reactants, intermediates, transition states and products showing the influence of K⁺ during pyrrole decomposition in Fig. 6. Generally, Table 2 shows the difference in activation energies for each step of the reaction when a K⁺ is added and when no ionic species are present, as well as a description for each reaction step.

When K⁺ is present, the activation energy for the hydrogen migration (Step I) is reduced significantly to 239.32 kJ/mol. This is to a lesser extant than the Na⁺ ion and can be explained through their differing interactions with the lone pair found on the a-n-1m intermediate.
In step II the intermediate (a-k-1m) is converted to a-k-2m via the transition state a-k-2t, with an overall energy barrier of 264.58 kJ/mol. The energy of this intermediate is only 0.82 kJ/mol higher than when the sodium ion is present and 27.34 kJ/mol lower than when no metallic species are present. Step III involves the conversion of the intermediate a-k-2m to a-k-3m in a cis-trans isomerization reaction. The transition state (a-k-3t) has a relative energy of 325.83 kJ/mol. The interaction with K⁺, causes the a-3t and a-3m energies to be increased, up 42.85 kJ/mol and 65.78 kJ/mol respectively, hindering the isomerization process. In step IV, the intermediate a-n-3m undergoes a concerted decomposition, via transition state (a-k-4t) (380.48 kJ/mol), to give the a-k-4m(cluster). The presence of the K⁺ ion increases the transition state (a-2t) energy barrier 42.6 kJ/mol relative to the transition state a-4t.

Table 2. The effect of K⁺, Eᵦ and reaction types for four steps

<table>
<thead>
<tr>
<th>Steps</th>
<th>Species</th>
<th>Alkali Metal Ions</th>
<th>Eᵦ (kJ/mol)</th>
<th>Reaction Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>pyrrole → a-1t</td>
<td>None</td>
<td>305.75</td>
<td>Hydrogen from the meta-position of pyrrole-N transferred to the ortho-position</td>
</tr>
<tr>
<td></td>
<td>pyrrole → a-k-1t</td>
<td>K⁺</td>
<td>239.32</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>a-1m → a-2t</td>
<td>None</td>
<td>25.48</td>
<td>The pyrrole-N is disconnected from the ortho-position C, which makes the ring opened</td>
</tr>
<tr>
<td></td>
<td>a-k-1m → a-k-2t</td>
<td>K⁺</td>
<td>82.77</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>a-2m → a-3t</td>
<td>None</td>
<td>110.69</td>
<td>Hydrogen on the pyrrole-N isomerize to a cis isomer</td>
</tr>
<tr>
<td></td>
<td>a-k-2m → a-k-3t</td>
<td>K⁺</td>
<td>104.44</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>a-4t → a-3m</td>
<td>None</td>
<td>170.55</td>
<td>A long C-C breaking bond between the migrating hydrogen and the carbon, nitrogen atoms</td>
</tr>
<tr>
<td></td>
<td>a-k-4t → a-k-3m</td>
<td>K⁺</td>
<td>147.45</td>
<td></td>
</tr>
</tbody>
</table>

* The units for relative energies are kJ/mol.

The overall enthalpy change for this four-step mechanism is 236.17 kJ/mol. When a-4m, HCN and K⁺ are calculated separately, the sum of energy is 307.32 kJ/mol, 71.15 kJ/mol greater than a-k-4m(cluster). It is clearly that K⁺ has a strong interaction with HCH and a-k-4m molecules, forming complexes. However, the same step of reaction with Na⁺, δn=110.14 kJ/mol, which is 38.99 kJ/mol higher than the reaction with K⁺, which means Na⁺ is having a stronger interaction between molecules, HCN and a-4m, than K⁺. In summary, the K⁺ have a catalytic effect on the internal hydrogen transfer and ring-opening of pyrrole and have an inhibitory effect on internal hydrogen isomerization and concerted decomposition.
Fig. 5 The optimal energy pathway decomposition of pyrrole to HCN with presence of K+. The numerical values are energies in kJ/mol relative to that of pyrrole.
Fig. 6 The K+ interactions and binding sites in pyrrole and its derivatives. The purple spheres represent K\textsuperscript{+}; the blue spheres represent nitrogen atoms; the gray spheres represent carbon atoms; and the white spheres represent hydrogen atoms. All distances are given in ångströms (Å).

3.3 The different effects of Na\textsuperscript{+} and K\textsuperscript{+} on pyrrole pyrolysis

Fig. 7 gives the relative energies, reaction types, and alkali metal ions for reactant, intermediates, products, and transition states about the optimal energy pathway of pyrrole to HCN in our research. In Fig. 7, the energies of all structures are given in kJ/mol relative to that of reactants: pyrrole, pyrrole and Na+, pyrrole and K\textsuperscript{+} for the three scenarios respectively.

Comparison of the influence of Na\textsuperscript{+} and K\textsuperscript{+} shows that both species have a similar effect on pyrrole decomposition. However, there are some differences as shown in Fig. 7. The energy barriers for step I with Na\textsuperscript{+} and K\textsuperscript{+} are 239.32kJ/mol and 220.18kJ/mol respectively, equivalent to energy barrier reductions of 85.57kJ/mol and 66.43kJ/mol, meaning that both ionic species promote the hydrogen migrating reaction in the pyrrole ring. This is due to the interaction of metal ions (Na\textsuperscript{+}, K\textsuperscript{+}) with the π surface, which
increases the stability of pyrrole [31]. It can be concluded that Na\textsuperscript{+} is better than K\textsuperscript{+} to promote the hydrogen migration reaction on the pyrrole ring. Moreover, the presence of Na\textsuperscript{+} or K\textsuperscript{+}, make the synergy open ring transition state (a-2t) energy barrier reduce by 28.26 kJ/mol and 27.34 kJ/mol respectively. This because the organic can interact with relatively strong Lewis acids (Na\textsuperscript{+}, K\textsuperscript{+}) [32], and it is also good for forming carbon bond [33] and contributes to the open-loop reaction [34] at steps of migrating hydrogen and synergy open ring.

However, the addition Na\textsuperscript{+} or K\textsuperscript{+} to the isomerization reaction raises the energy barrier by 51.56 kJ/mol and 42.85 kJ/mol, respectively, hindering the intermediate isomerization in the reaction. Further, the addition of Na\textsuperscript{+} or K\textsuperscript{+} to concerted decomposition raises the energy barrier by 50.29 kJ/mol and 42.6 kJ/mol respectively. Finally, the concerted decomposition reaction, in which a-4t interconverts to form the a-4m(cluster), has a higher energy barrier when either Na\textsuperscript{+} or K\textsuperscript{+} are added.

Ohtsuka et al [21] studied the effect of alkali metals on nitrogen release during coal pyrolysis. In the presence of Na\textsuperscript{+} and K\textsuperscript{+} releasing species, the rate of HCN formation decreased within the temperature range of 450-600 °C. Conversely, the rate of HCN release was increased at higher temperatures which is in agreement with our findings that the overall reaction enthalpy for HCN formation is higher than the scenario when alkali ions are present. Ohtsuka et al suggest that the change in the rate of HCN formation may be explained by secondary reactions with alkali compounds, leading to the formation of KCN and NaCN; however, neither of these species were observed during their x-ray diffraction measurements. Furthermore, the total concentration of HCN formed was reported to be unaffected by addition of the alkali metals, further suggesting that the mechanism for HCN formation is inhibited under the influence of Na\textsuperscript{+} and K\textsuperscript{+}. The reason possibly is that metal ions can form a metal-carbon bond, which counterworks this reaction [35].
Fig. 7 The different effects of alkali metal ions (Na\(^+\) and K\(^+\)) on pyrrole pyrolysis. The numerical values are energies in kJ/mol.

In a summery, both of Na\(^+\) and K\(^+\) have a catalytic effect on the internal hydrogen transfer and ring-opening of pyrrole and have an inhibitory effect on internal hydrogen isomerization and concerted decomposition. Moreover, Na\(^+\) not only has a better catalytic effect on the hydrogen migration and synergy open-ring of pyrrole than K\(^+\) but also better inhibits the formation of HCN role than K\(^+\) and none ion cases in the concerted decomposition reaction.

4. Conclusions

In this work, the effects of Na\(^+\) and K\(^+\) on the thermal decomposition of pyrrole to produce HCN and propyne have been investigated using DFT computational method. It was found that the alkali metal ions Na\(^+\) and K\(^+\) have strong interactions with pyrrole and its derived compounds and their existence has a significant influence on the HCN formation process:

1. Both Na\(^+\) and K\(^+\) have a catalytic effect on the internal hydrogen transfer reaction and ring-opening of pyrrole. However, Na\(^+\) and K\(^+\) have an inhibitory effect on
internal hydrogen isomerization reaction and concerted decomposition reaction in
the process of pyrrole pyrolysis,

2. Na\(^+\) and K\(^+\) not only influence the pyrrole pyrolysis progress but also have a
strong interaction with the final products. The presence of the ionic species
inhibits the attractive forces that lead to the formation of the a-4m cluster,
increasing the endothermicity of the overall reaction by 23.22 and 27.18 kJ/mol
for K\(^+\) and Na\(^+\) respectively.

3. We conclude that the addition of Na\(^+\) or K\(^+\) promotes the initial decomposition
steps and inhibits the further HCN formation steps from pyrrole during the
pyrolysis process. Moreover, Na\(^+\) has a greater effect than K\(^+\), owing to the larger
changes on activation energy barrier and energy level of final products.

Acknowledgments

The authors thank the National Natural Science Foundation of China (51576064),
Beijing Nova Program (Z17110000117064), Beijing Natural Science Foundation
(3172030), Engineering and Physical Sciences Research Council (EP/R010986/1),
Fundamental Research Funds for the Central Universities (2016XS60) and
Foundation of Stake Key Laboratory of Coal Combustion (FSKLCCA1706) for
financial support.

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1. The existence of alkali metal ions, Na$^+$ and K$^+$, has a significant influence on the formation of NOx species during the coal decomposition process.

2. The effect of Na$^+$ and K$^+$ on the formation mechanism of NOx during pyrrole pyrolysis were firstly investigated using density functional theory (DFT).

3. Those alkali metal ions (Na$^+$ and K$^+$) have strong interactions with pyrrole and its derived compounds.

4. Both Na$^+$ and K$^+$ catalyze the initial pyrrole decomposition and inhibit the final step of HCN formation from pyrrole, with Na$^+$, has a higher inhibition effect than that of K$^+$. 