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Proceedings of the Combustion Institute 000 (2022) 1–9
Proceedings of the Combustion Institute
www.elsevier.com/locate/proci

A reactive molecular dynamics study of NO removal by nitrogen-containing species in coal pyrolysis gas

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Received 29 December 2021; accepted 15 July 2022
Available online xxx

Abstract

Coal splitting and staging is a promising technology to reduce nitrogen oxides (NOx) emissions from coal combustion through transforming nitrogenous pollutants into environmentally friendly gasses such as nitrogen (N_2). During this process, the nitrogenous species in pyrolysis gas play a dominant role in NOx reduction. In this research, a series of reactive force field (ReaxFF) molecular dynamics (MD) simulations are conducted to investigate the fundamental reaction mechanisms of NO removal by nitrogen-containing species (HCN and NH_3) in coal pyrolysis gas under various temperatures. The effects of temperature on the process and mechanisms of NO consumption and N_2 formation are illustrated during NO reduction with HCN and NH_3, respectively. Additionally, we compare the performance of NO reduction by HCN and NH_3 and propose control strategies for the pyrolysis and reburn processes. The study provides new insights into the mechanisms of the NO reduction with nitrogen-containing species in coal pyrolysis gas, which may help optimize the operating parameters of the splitting and staging processes to decrease NOx emissions during coal combustion.

Keywords: NO reduction; Coal pyrolysis gas; Molecular dynamics; Reactive force field

1. Introduction

Nitrogen oxides (NOx) from coal combustion cause serious environmental problems such as photochemical smog and acid rain [1]. To protect the environment from pollution, a variety of technologies for reducing NOx emissions from coal combustion have been developed. Fuel staging or reburning is a well-know technology for NOx reduction, where the NOx emissions are reduced to N_2 by the injection of reburn fuels into the flue gas downstream of the combustion zone [2].

Many fuels have been investigated as reburn fuels during coal combustion such as natural gas [3], oil [4], coal [5] and coal pyrolysis gas [6,7]. Among them, coal pyrolysis gas, also called fuel splitting and staging, has better performance in NOx reduction than other fuels [6,7]. In this process, coal is separated into char and pyrolysis gas through

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https://doi.org/10.1016/j.proci.2022.07.154

pyrolysis process first. The char burns in the main zone to release heat and generate NOx. Pyrolysis gas is injected downstream of the main zone to create a fuel rich reburning zone, where NOx is transformed into N_2. After the reburning zone, additional air is provide to ensure complete combustion of remaining fuel fragments. Previous studies [3–5] have identified that the nitrogenous species in pyrolysis gas are important for NOx reduction performance in the coal splitting and staging process. Therefore, it is of great interest to study the mechanisms of NO reduction by nitrogenous species in pyrolysis gas, as this may help optimize the operating conditions that would decrease NOx emissions during coal combustion.

Based on previous works, there are two types of nitrogenous species in coal pyrolysis gas, which are hydrogen cyanide (HCN) and ammonia (NH_3) [8,9]. NO is chosen as the target molecule in this study, as it accounts for about 95% of NOx emissions [10,11]. Regarding NO removal by NH_3, its mechanisms have been studied for a long time in the selective non-catalytic reduction (SNCR), where NH_3 is used to decrease NOx emissions in flue gas under fuel lean conditions [12,13]. Results indicated that reactions of NO and NH_2 radicals arising from NH_3 are the principal pathway for NO abatement. However, as temperature increases, the active OH, O and H radicals rise, leading to the oxidation of NH_3 molecules, and producing NO eventually. Consequently, there is an optimal temperature where the amount of NO reaches the lowest point. However, the NO reduction process in the reburning zone is under fuel rich conditions, which may affect the performance of NH_3 in the process of reducing NO. Moreover, there is a lack of understanding of the underlying mechanisms of NO reduction with HCN till now. Accordingly, it is of necessity and importance to explore the fundamental mechanisms of NO reduction by HCN and NH_3, respectively.

To obtain a deeper understanding of how NO molecules are converted to N_2 by HCN and NH_3, the reaction pathways of HCN and NH_3, especially on the NO consumption and N_2 formation, during the reduction process are investigated. Nonetheless, it is costly and difficult to examine intermediates by experimental studies due to the limitations of current measurement methods. Computational approaches can be developed to overcome these problems. Quantum mechanics (QM) methods are able to study chemical reactions but the computational costs are extremely high to simulate large systems [14]. Molecular dynamics (MD) methods can simulate atomistic dynamics with reasonable computational costs, however they are conventionally formulated for the physical process rather than the chemical kinetics [15]. To resolve these issues of QM and MD methods, an attractive alternative method called the reactive force field (ReaxFF) molecular dynamics (MD) is developed combining features of QM and MD, which can simulate complex chemical reactions at affordable computational costs [16–18].

In this study, ReaxFF MD simulations are carried out to study fundamental mechanisms of NO removal by HCN and NH_3 under different temperatures. Time evolutions of main reactants (NO, HCN and NH_3) and products (N_2) are studied first. Then, the mechanisms of NO removal by HCN and NH_3 are explored at different temperatures, and the temperature influence on NO reduction performance is explained at atomic level. Finally, we compare the NO control performance between HCN and NH_3, and propose preferred operating conditions to improve NOx reduction efficiency.

2. Methods

2.1. Reactive force field (ReaxFF) molecular dynamics (MD) simulation

ReaxFF employs a bond-order formalism in conjunction with polarisable charge descriptions to describe both reactive and non-reactive interactions between atoms, which allows ReaxFF to accurately model both covalent and electrostatic interactions for a diverse range of materials [19]. The function of potential energy can be calculated as [20]:

$$E_{system} = E_{bond}+E_{over}+E_{under}+E_{lp}+E_{val}+E_{tor} +E_{vdWaals}+E_{Coulomb} \quad (E1)$$

where E_{system}, E_{bond}, E_{over}, E_{under}, E_{lp}, E_{val}, E_{tor}, $E_{vdWaals}$, and $E_{Coulomb}$ represent total energy, bond energy, overcoordination, energy penalty, undercoordination stability, lone pair energy, valence angle energy, torsion angle energy, van der Waals energy, and Coulomb energy, respectively [20].

2.2. Simulation details

All the simulations are performed with the REAXC package in LAMMPS software (Large-scale Atomic/Molecular Massively Parallel Simulator) [21,22] with C/H/O/N force field parameters [23,24]. Two three-dimensional and cubic systems with different sizes are established at the same density of 0.15 g/cm^3, and the configurations are $120NO/120HCN/90O_2$ and $120NO/120NH_3/30O_2$ to study the reactions of NO removal by HCN and NH_3, respectively. The periodic boundary conditions are chosen in all three directions. The equivalence ratios of reactants are calculated considering the reduction equation as follows:

$$4NO + 4NH_3+O_2 \rightarrow 4N_2+6H_2O \quad (E2)$$

$$4NO + 4HCN + 3O_2 \rightarrow 4N_2 +2H_2O + 4CO_2 \quad (E3)$$

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The canonical ensemble (NVT) [25] is selected for ReaxFF MD simulations with the Nosé-Hoover thermostat employing a damping constant of 100fs. The time step employed in this study is 0.1fs, which has been proven to be sufficiently small. At the beginning, every system undergoes energy minimization and equilibration for 20 ps at 40 K to optimize the initial geometric configuration that would otherwise cause simulation collapses. Then, the systems are heated to final temperatures ranging from 2400 to 3400 K with an increment of 200 K and then kept constant at final temperatures. The total simulation time is 1000 ps for all the simulations. The temperature employed in this study is higher than those in experiments. The adoption of a higher temperature is a common practice in MD to ensure manageable computation costs, as mentioned in [23,24].

Three replica simulations are conducted for every case with a unique starting configuration, and thus 36 simulations have been carried out and analysed in the current study. The bond order cutoff is 0.3 to recognize intermediates formed during ReaxFF MD simulations. The reactions are analysed using Chemical Trajectory Analyzer (ChemTrayzer) scripts [26]. The net flux (NF) indicates how often the reaction was observed during the simulation time, which is calculated by the number of times the direct reaction occurred minus the number of times the reverse reaction happened [27].

3. Results

3.1. Comparison of NO reduction by HCN and NH_3

As shown in Fig. 1a and b, the consumption rates of HCN and NH_3 increase remarkably with temperature rising and NH_3 molecules are consumed faster than HCN at all temperatures. As to NO molecules, higher temperature shows better NO reduction performance by NH_3. However, the final values of NO almost remain the same in HCN environment at 2400K-3000 K, and the final amount of NO removal by HCN decreases as temperature increases when temperature is higher than 3000 K. Besides, according to Fig. 1e and f, the production of N_2 increases as temperature rises in both cases and the production of N_2 is more by NH_3 rather than HCN. The above results indicate NH_3 presents better NO reduction performance than HCN. To acquire a better understanding of NO removal by HCN and NH_3, reaction pathways are scrutinized in Sections 3.2 and 3.3, respectively.

3.2. Mechanisms of NO removal by HCN

Fig. 2 reveals the mechanisms of NO reduction by HCN at 2400K-3400 K. Overall, high temperatures promote new pathways of N_2 formation such as the conversion from N, HN_2 and CN_2O_2 to N_2 at 2600K-3400 K and NH to N_2 at 3400 K. During the process of NO reduction with HCN, there are three different contributions of HCN to NO removal.

The first pathway is that HCN molecules are oxidized to NO through the channel HCN → CN → CNO_2 → NO, causing negative influence on NO reduction. The second way is N_2 formation by pathways HCN → CHNO → CNO → $C_2N_2O_2$ → N_2 and HCN → CHNO → CNO → $C_2N_2O_2$ → CN_2O → N_2. Among them, the important intermediate $C_2N_2O_2$ is generated by the reaction:

$$CNO + CNO \rightarrow C_2N_2O_2 \quad (R1)$$

The CNO intermediates are from the oxidation of HCN. Therefore, though N_2 is formed in this process, there is no contribution to NO removal. In the third pathway, HCN molecules undergo oxidation and decomposition forming radicals N, NH and CNO, which will further react with NO via R2 to R7 generating N_2 finally.

$$CNO + NO \rightarrow CN_2O_2 \quad (R2)$$

$$CNO + NO \rightarrow CO{+}N_2O \quad (R3)$$

$$NH + NO \rightarrow HN_2O \quad (R4)$$

$$NH + NO \rightarrow N_2H + O \quad (R5)$$

$$NH + NO \rightarrow N_2{+}H + O \quad (R6)$$

$$N + NO \rightarrow N_2{+}O \quad (R7)$$

In addition to R6 and R7, the main reactions of N_2 formation from N_2O, HN_2O, CN_2O, $C_2N_2O_2$, CN_2O_2 and HN_2 during NO removal with HCN are as follows:

$$N_2O \rightarrow N_2{+}O \quad (R8)$$

$$NO{+}N_2O \rightarrow N_2{+}NO_2 \quad (R9)$$

$$HN_2O \rightarrow N_2{+}HO \quad (R10)$$

$$CN_2O \rightarrow N_2{+}CO \quad (R11)$$

$$C_2N_2O_2 \rightarrow N_2{+}CO + CO \quad (R12)$$

$$CN_2O_2 \rightarrow N_2{+}CO + O \quad (R13)$$

$$N_2H + CO_2 \rightarrow N_2{+}CHO_2 \quad (R14)$$

$$N_2H \rightarrow N_2{+}H \quad (R15)$$

To further identify how temperature affects the amount of NO consumption and N_2 formation, the NFs of main elementary reactions linked with N_2 and NO are investigated in Tables 1 and 2.

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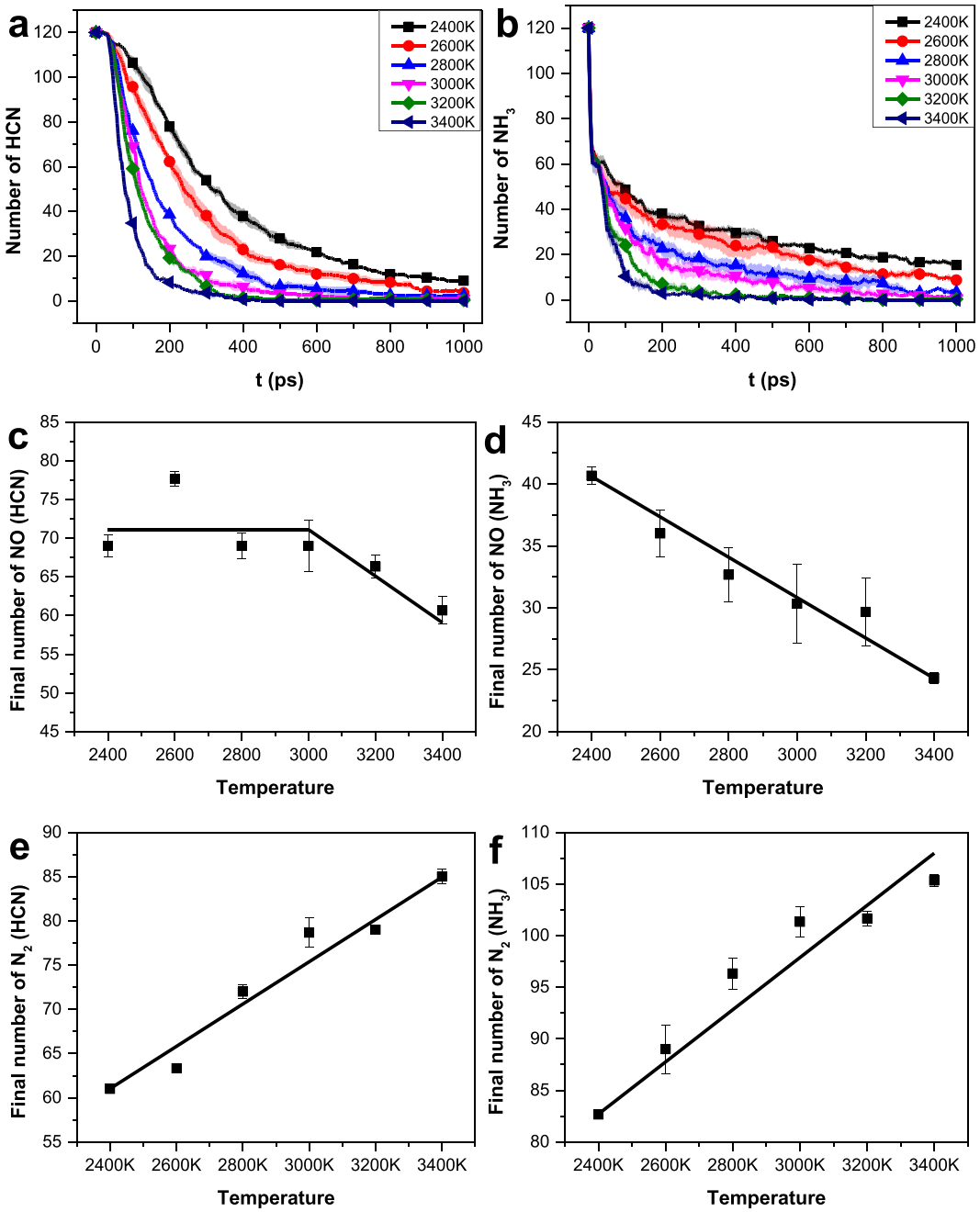

Fig. 1. Time evolution of reducing agents and final number of main products ($t = 1000$ ps) during NO removal process. (a) HCN; (b) NH_3; (c) NO in HCN environment; (d) NO in NH_3 environment; (e) N_2 in HCN environment; (f) N_2 in NH_3 environment.

According to Table 1, it can be noticed that the total NF of NO reduction almost remains the same at 2400K-3000 K, and increases when the temperature is higher than 3000 K. That agrees with the changes of NO numbers at different temperatures as shown in Fig. 1c. Besides, the formation and reduction of NO take place simultaneously during NO removal with HCN. On the whole, the NF of NO reduction presents an upward trend with increasing temperature through the promotion of reactions between NO and NH as well as N (R4-R7). There is no significant enhancement of the

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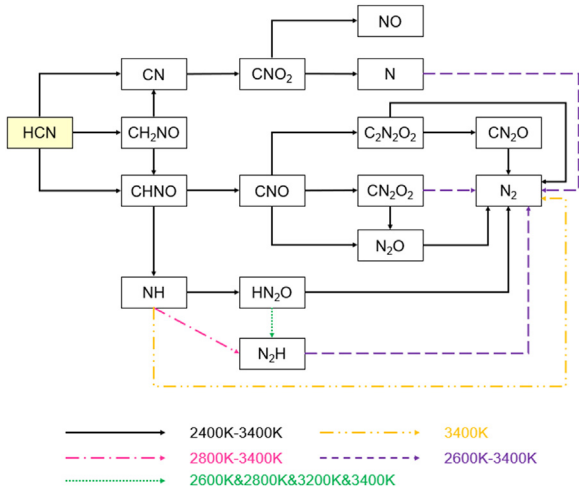

Fig. 2. Transfer pathways of NO reduction with HCN. HCN in the yellow box is the starting species.

Table 1
Net flux (NF) of main elementary pathways for NO consumption and formation during NO removal with HCN at 2400 K to 3400 K.

Pathways	2400K	2600K	2800K	3000K	3200K	3400K
$CNO \rightarrow CN_2O_2$	46	54	34	46	48	43
$CNO \rightarrow N_2O$	15	19	25	18	20	18
$NH \rightarrow HN_2O$	11	13	15	17	12	21
$N \rightarrow N_2$	0	5	8	6	9	12
$NH \rightarrow N_2H$	0	0	11	11	6	7
$NH \rightarrow N_2$	0	0	0	0	0	12
NO consumption	72	91	93	98	95	113
$CNO_2 \rightarrow NO$	37	51	57	60	43	55
Total consumption	35	40	36	38	52	58

Table 2
Net flux (NF) of main elementary pathways for N_2 formation during NO removal with HCN at 2400 K to 3400 K.

Pathways	2400K	2600K	2800K	3000K	3200K	3400K
$N_2O \rightarrow N_2$	39	40	36	54	50	44
$HN_2O \rightarrow N_2$	13	15	14	19	9	6
$CN_2O \rightarrow N_2$	17	14	19	19	21	15
$C_2N_2O_2 \rightarrow N_2$	11	12	10	19	11	14
$CN_2O_2 \rightarrow N_2$	0	11	13	17	30	30
$N \rightarrow N_2$	0	5	8	6	9	12
$N_2H \rightarrow N_2$	0	6	15	8	11	13
$NH \rightarrow N_2$	0	0	0	0	0	12
Total	80	103	115	142	141	146

reactions of NO and CNO. Regrading the NO generation, it is from the decomposition of CNO_2 via R16.

$$CNO_2 \rightarrow NO + CO \quad \text{(R16)}$$

The NF of R16 shows the parabolic trend and peaks at 3000 K, which is the main reason why the number of NO almost remains the same at 2400K-3000 K.

Table 2 displays the NF of main elementary pathways for N_2 formation under NO reduction with HCN conditions. The total NF of N_2 formation increases remarkably with temperature rising, accounting well for the upward trend of N_2 amount at 2400–3400 K. Specifically, the increase of N_2 production is mainly owing to the strengthening of pathways $CN_2O_2 \rightarrow N_2$ (R13), $N \rightarrow N_2$ (R7), $N_2H \rightarrow N_2$ (R14&R15) and $NH \rightarrow N_2$ (R6).

To sum up, when the temperature increases, the NO consumption and N_2 generation rise through the enhancement of the following reaction pathways: a. $HCN \rightarrow CN \rightarrow CNO_2 \rightarrow N \rightarrow N_2$

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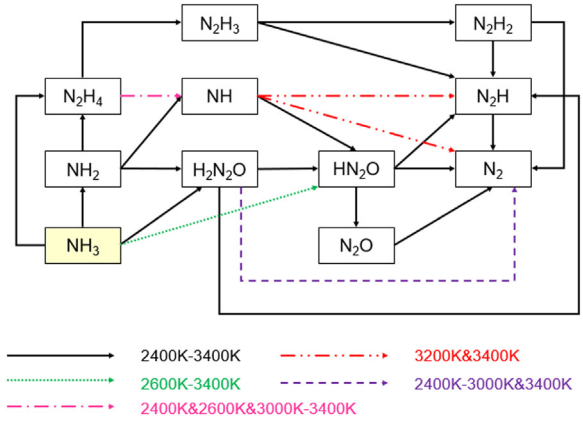

Fig. 3. Transfer pathways of NO reduction with NH_3. NH_3 in the yellow box is the starting species.

b. HCN → CNHO → NH → N_2 c. HCN → CNHO → NH → HN_2O → N_2H → N_2 d. HCN → CNHO → NH → N_2H → N_2 e. HCN → CNHO → CNO → CN_2O_2 → N_2

3.3. Mechanisms of NO removal by NH_3

As observed in Fig. 3, the main intermediates for NO abatement are NH_3, NH_2 and NH by reactions R17-R34. And R17 only occurs at 2600K-3400 K.

$$NH_3+NO \rightarrow HN_2O+H_2 \quad (R17)$$

$$NH_3+NO \rightarrow H_2N_2O+H \quad (R18)$$

$$NH_3+NO+HO \rightarrow H_2N_2O+H_2O \quad (R19)$$

$$NH_2+NO \rightarrow H_2N_2O \quad (R20)$$

$$NH+NO \rightarrow HN_2+O \quad (R21)$$

$$NH+NO \rightarrow N_2+H+O \quad (R22)$$

$$NH+NO \rightarrow HN_2O \quad (R23)$$

$$N_2H+NO \rightarrow N_2+HNO \quad (R24)$$

The N_2 molecules are generated by reactions as follows:

$$HN_2O \rightarrow N_2+HO \quad (R25)$$

$$HN_2O \rightarrow N_2+H+O \quad (R26)$$

$$N_2H \rightarrow N_2+H \quad (R27)$$

$$N_2H+HO \rightarrow N_2+H_2O \quad (R28)$$

$$N_2H+NO \rightarrow N_2+HNO \quad (R29)$$

$$N_2H_2 \rightarrow N_2+H_2 \quad (R30)$$

$$N_2O \rightarrow N_2+O \quad (R31)$$

$$H_2N_2O \rightarrow N_2+H_2O \quad (R32)$$

$$H_2N_2O \rightarrow N_2+H+HO \quad (R33)$$

$$NH+NO \rightarrow N_2+H+O \quad (R34)$$

Among them, the channel NH → N_2 occurs at 3200K-3400 K and H_2N_2O → N_2 happens when temperatures are 2400K-3000 K and 3400 K. Besides, the pathways of N_2 formation via NH_3 → NH_2 → H_2N_2O → N_2 and NH_3 → NH_2 → H_2N_2O → N_2H → N_2 are also confirmed by previous studies [12,13].

Moreover, there are also channels of N_2 generation from ammonia molecules without NO reduction. Firstly, intermediate N_2H_4 is formed by R35-R36, which will be converted to N_2 through channels N_2H_4 → N_2H_3 → N_2H → N_2 and N_2H_4 → N_2H_3 → N_2H_2 → N_2.

$$NH_2+NH_2 \rightarrow N_2H_4 \quad (R35)$$

$$NH_3+NH_3 \rightarrow N_2H_4+H+H \quad (R36)$$

$$NH_3+NH_3+O_2 \rightarrow N_2H_4+HO_2+H \quad (R37)$$

To further clarify the temperature influence on the final amount of NO and N_2, we explore the contributions of pathways linked with NO abatement and N_2 formation under various temperatures as shown in Tables 3 and 4. The total NF of N_2 formation and NO consumption increases with temperature rising, which is in consistence with the yields of NO and N_2 at 2400K-3400 K.

As indicated in Table 3, the conversion from NH → HN_2O via R23 has an overwhelmingly dominant contribution to the increase of NO consumption with rising temperature. And the channel NH_2 → H_2N_2O via R20 plays a vital role in NO reduction especially when the temperature is in the range of 2400K-3000 K. In addition, high temperatures have a negative impact on the reaction between NH_2 and NO. The pathways NH → N_2H

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Table 3
Net flux (NF) of main elementary pathways for NO consumption during NO removal with NH_3 at 2400 K to 3400 K.

Pathways	2400K	2600K	2800K	3000K	3200K	3400K
$NH \rightarrow HN_2O$	12	16	31	34	35	47
$NH_3 \rightarrow H_2N_2O$	18	16	16	18	26	21
$NH_2 \rightarrow H_2N_2O$	71	69	65	60	27	34
$NH_3 \rightarrow HN_2O$	0	4	5	7	3	7
$NH \rightarrow HN_2$	0	0	0	0	16	15
$NH \rightarrow N_2$	0	0	0	0	7	13
Total	101	105	117	119	114	137

Table 4
Net flux (NF) of main elementary pathways for N_2 formation during NO removal with NH_3 at 2400 K to 3400 K.

Pathways	2400K	2600K	2800K	3000K	3200K	3400K
$HN_2O \rightarrow N_2$	41	46	53	53	57	49
$N_2H \rightarrow N_2$	50	60	58	58	72	78
$N_2H_2 \rightarrow N_2$	13	11	20	18	24	17
$N_2O \rightarrow N_2$	11	15	9	15	13	20
$H_2N_2O \rightarrow N_2$	13	3	8	18	0	7
$NH \rightarrow N_2$	0	0	0	0	7	13
Total	128	135	148	162	173	184

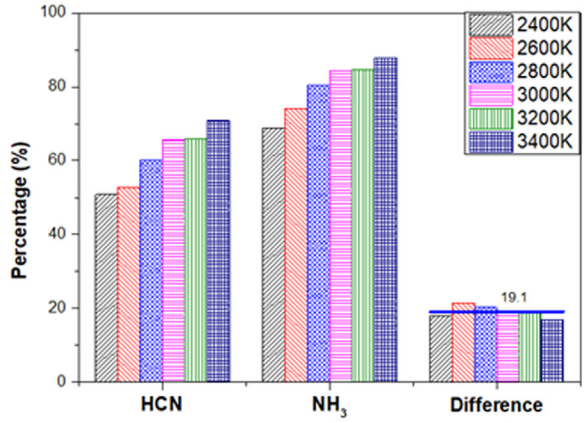

Fig. 4. Reduction efficiency of nitrogen-containing reactants.

through R21 and $HN \rightarrow N_2$ through R22 are enhanced at 3200K-3400 K.

As to N_2 formation, the pathways $HN_2O \rightarrow N_2$ via R25-R26 and $N_2H \rightarrow N_2$ via R27-R29 are promoted when the temperature ranges from 2400 K to 3400 K. There is a slight increase for channel $N_2H_2 \rightarrow N_2$ through R30 at 2400K-3400 K. As to the channel $N_2O \rightarrow N_2$ by R31, its contribution of N_2 formation almost remains the same from 2400 K to 3200 K, and increases when the temperature is 3400 K. The channel $NH \rightarrow N_2$ via R34 is strengthened at 3200K-3400 K.

Based on the above analysis, it can be concluded that high temperature promotes N_2 formation and NO consumption and NO reduction with NH_3 by pathways: f. $NH_3 \rightarrow NH \rightarrow HN_2O \rightarrow N_2$ g. $NH_3 \rightarrow NH \rightarrow N_2H \rightarrow N_2$ h. $NH_3 \rightarrow NH \rightarrow N_2$

4. Discussion

In this research, we use ReaxFF MD simulations to investigate fundamental reaction mechanisms of NO removal with HCN and NH_3 under different temperatures, which play a dominant role in NOx reduction during fuel staging with coal pyrolysis gas. To provide guidance on the reduction of NOx emissions, it is important to compare performance of NO reduction by HCN and NH_3 in the context of the existing literature.

Regarding the NOx control performance, the number of NO molecules is adopted to indicate the removal efficiency in previous studies [12,13,28,29]. On the other hand, in addition to NO, the remaining nitrogen-containing species in the system will be oxidized to NOx in the subsequent burnout

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zone, causing pollution to the environment. Therefore, in this study, the number of N_2 produced is used as an indicator to reflect the reduction efficiency of nitrogen-containing reactants as shown in Fig. 4. It is clear that the NOx control performance is promoted by rising temperature in both cases, and NH_3 shows about 19.1% higher capability than HCN for the NO reduction from 2400 K to 3400 K. Moreover, the optimal temperature is not observed in our simulations during NO removal by NH_3, which is inconsistence with the phenomena in SNCR process using ammonia [12,13,28,29]. That is because the SNCR process is operated under excess oxygen conditions, and high temperature promotes the oxidation of NH_3 forming NO, resulting in the lowered performance of NO reduction. However, NO molecules are consumed under fuel rich conditions in the reburning zone, and the oxidation of nitrogenous intermediates is supressed at high temperatures. Thus, the behaviours of NO reduction with NH_3 are not inhibited with temperatures rising.

Base on the above analysis, the increase of the reaction temperature is an effective method to improve the NOx reduction performance of coal pyrolysis gas. In addition, promotion of the conversion from HCN to NH_3 during reduction process also benefits the decrease of NOx pollutants, which can be achieved by increasing temperature, pressure and moisture during coal pyrolysis [8,9]. To obtain better control strategies for staging combustion with pyrolysis gas, extended simulations with different reducing agents and oxygen contents are required.

5. Conclusions

ReaxFF simulations are performed to explore the mechanisms of NO removal by HCN and NH_3 with temperature ranging from 2400 K to 3400 K, respectively. Based on the analysis of simulation results, the following conclusions can be drawn:

(1) There are three different contributions of HCN during NO removal. The first pathway is that HCN molecules are oxidized to NO through $HCN \rightarrow CN \rightarrow CNO_2 \rightarrow NO$. The second way is N_2 formation by pathways $HCN \rightarrow CHNO \rightarrow CNO \rightarrow C_2N_2O_2 \rightarrow N_2$ and $HCN \rightarrow CHNO \rightarrow CNO \rightarrow C_2N_2O_2 \rightarrow CN_2O \rightarrow N_2$, where there is no contribution to NO consumption and production. In the final way, the NO molecules react with intermediates (CNO, N and NH) from HCN generating N_2 eventually.

(2) As to NH_3 molecules, part of them directly generates N_2 without coupling with NO via $NH_3/NH_2 \rightarrow N_2H_4 \rightarrow N_2H_3 \rightarrow N_2H \rightarrow N_2$ and $NH_3/NH_2 \rightarrow N_2H_4 \rightarrow N_2H_3 \rightarrow N_2H_2 \rightarrow N_2$. In addition, N_2 formation can also come from the reactions between NO and nitrogen-containing particles (like NH_3, NH_2 and NH).

(3) NH_3 is about 19.1% more capable of NO reduction than HCN at 2400K-3400 K. The NO reduction performance is promoted by rising temperature under both HCN and NH_3 conditions via pathways:
   a $HCN \rightarrow CN \rightarrow CNO_2 \rightarrow N \rightarrow N_2$
   b $HCN \rightarrow CNHO \rightarrow NH \rightarrow N_2$
   c $HCN \rightarrow CNHO \rightarrow NH \rightarrow HN_2O \rightarrow N_2H \rightarrow N_2$
   d $HCN \rightarrow CNHO \rightarrow NH \rightarrow N_2H \rightarrow N_2$
   e $HCN \rightarrow CNHO \rightarrow CNO \rightarrow CN_2O_2 \rightarrow N_2$
   f $NH_3 \rightarrow NH \rightarrow HN_2O \rightarrow N_2$
   g $NH_3 \rightarrow NH \rightarrow N_2H \rightarrow N_2$
   h $NH_3 \rightarrow NH \rightarrow N_2$

This research provides new insight into the mechanisms of NO reduction with nitrogen-containing species (HCN and NH_3) in coal pyrolysis gas, which may lead to guidance on the optimization of run conditions that would increase the NOx control performance.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Support from the UK Engineering and Physical Sciences Research Council under the project "UK Consortium on Mesoscale Engineering Sciences (UKCOMES)" (Grant No. EP/R029598/1) is gratefully acknowledged. This work made use of computational support by CoSeC, the Computational Science centre for Research Communities, through UKCOMES.

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Please cite this article as: Z. Bai, X.Z. Jiang and K.H. Luo, A reactive molecular dynamics study of NO removal by nitrogen-containing species in coal pyrolysis gas, Proceedings of the Combustion Institute, https://doi.org/10.1016/j.proci.2022.07.154

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