

Effects of nitrogen-free species on NO removal performance by coal pyrolysis gas via reactive molecular dynamics simulations

Zhongze Bai^a, Xi Zhuo Jiang^{b,*}, Kai H. Luo^{a,**}

^a Department of Mechanical Engineering, University College London, Torrington Place, London, WC1E 7JE, UK

^b School of Mechanical Engineering and Automation, Northeastern University, Shenyang, Liaoning, 110819, PR China

ARTICLE INFO

Handling Editor: Paul Williams

Keywords:

NO reduction
Coal pyrolysis gas
Reactive force field molecular dynamics
Nitrogen-free additives

ABSTRACT

Coal splitting and reburning is a promising technology to control NO emissions during coal combustion. During this process, coal pyrolysis gas is used as reburn fuel to convert NO to N₂. Nitrogen-containing compounds (HCN and NH₃) play dominant roles in the NO reduction performance. In this study, we investigated the influence of nitrogen-free species (CH₄, CO and H₂) in coal pyrolysis gas on the NO reduction by HCN and NH₃ via reactive force field (ReaxFF) molecular dynamics (MD) simulations. The nitrogen distribution in products is determined and monitored during the process of NO removal by HCN and NH₃ under different additives. In addition, mechanisms of NO reduction by HCN and NH₃ are revealed, accounting for the changes of nitrogen distribution in the products at the atomic level. The present research provides new insights into the influence of CH₄, CO and H₂ on the NO reduction by HCN and NH₃, which may be helpful to reduce the NOx emissions during coal combustion by optimising the nitrogen-free components of coal pyrolysis gas.

1. Introduction

NOx emissions from coal combustion cause severe air pollution problems such as photochemical smog and acid rain [1]. To solve this problem, a variety of technologies have been developed to reduce NOx emissions from coal. Among them, coal splitting and reburning is a promising technology to control NO emissions with excellent NO reduction performance as well as relative low operating cost [2].

The combustion process of coal is divided into three zones. Coal undergoes pyrolysis forming pyrolysis gas and solid char first. Heat is released when char is oxidized in the main zone and NOx is formed. In the reburn zone, pyrolysis gas is injected to convert NOx from the main zone to clean N₂ under fuel-rich conditions. In the burnout zone, excess air is provided to oxidize remaining species and ensure complete combustion. Usually, the reburn fuel (coal pyrolysis gas) plays a vital role in the NOx reduction behaviours of this technology.

Previous studies have reported the feasibility of using nitrogen-containing species (HCN and NH₃) to reduce NOx in coal pyrolysis gas [2,3]. The presence of nitrogen-free compounds (CH₄, CO and H₂) also influences NOx performance by nitrogen-containing species in pyrolysis gas. NO is the main component of NOx emissions, accounting for about

95% of the total [4,5]. To explore the influence of CH₄, CO and H₂ on NO removal by HCN and NH₃ will be helpful to understand the NOx control mechanism and lay theoretical foundations for NOx control strategies.

Greul and co-workers carried out experiments and pointed out that the nitrogen-free species showed negative influence on the NO reduction process by coal pyrolysis gas [3]. For NO abatement by NH₃, its processes have long been researched in selective non-catalytic reduction (SNCR), in which NH₃ is employed to reduce NOx emissions in flue gas under fuel lean circumstances [6–8]. The results showed that NH₂ radicals derived from NH₃ are the key intermediate for NO abatement. Also, a few studies have investigated the NO reduction by NH₃ in the SNCR process with CO and CH₄ [9,10]. However, those studies focus on the effects of additives on the optimum temperature of NO abatement process in a fuel-lean condition which differs from the optimum air/fuel ratio when NO is removed by coal pyrolysis gas. The NO removal by HCN with additives is rarely considered in previous studies. To better understand the effects of nitrogen-free compounds on NO reduction by HCN and NH₃, the investigation of reaction pathways is of great importance.

Due to the limitations of current measurement techniques, it is hard or extremely expensive for traditional experimental studies to

* Corresponding author.

** Corresponding author.

E-mail addresses: jiangxz@mail.neu.edu.cn (X.Z. Jiang), k.luo@ucl.ac.uk (K.H. Luo).

<https://doi.org/10.1016/j.joei.2023.101172>

Received 6 August 2022; Received in revised form 1 January 2023; Accepted 3 January 2023

Available online 4 January 2023

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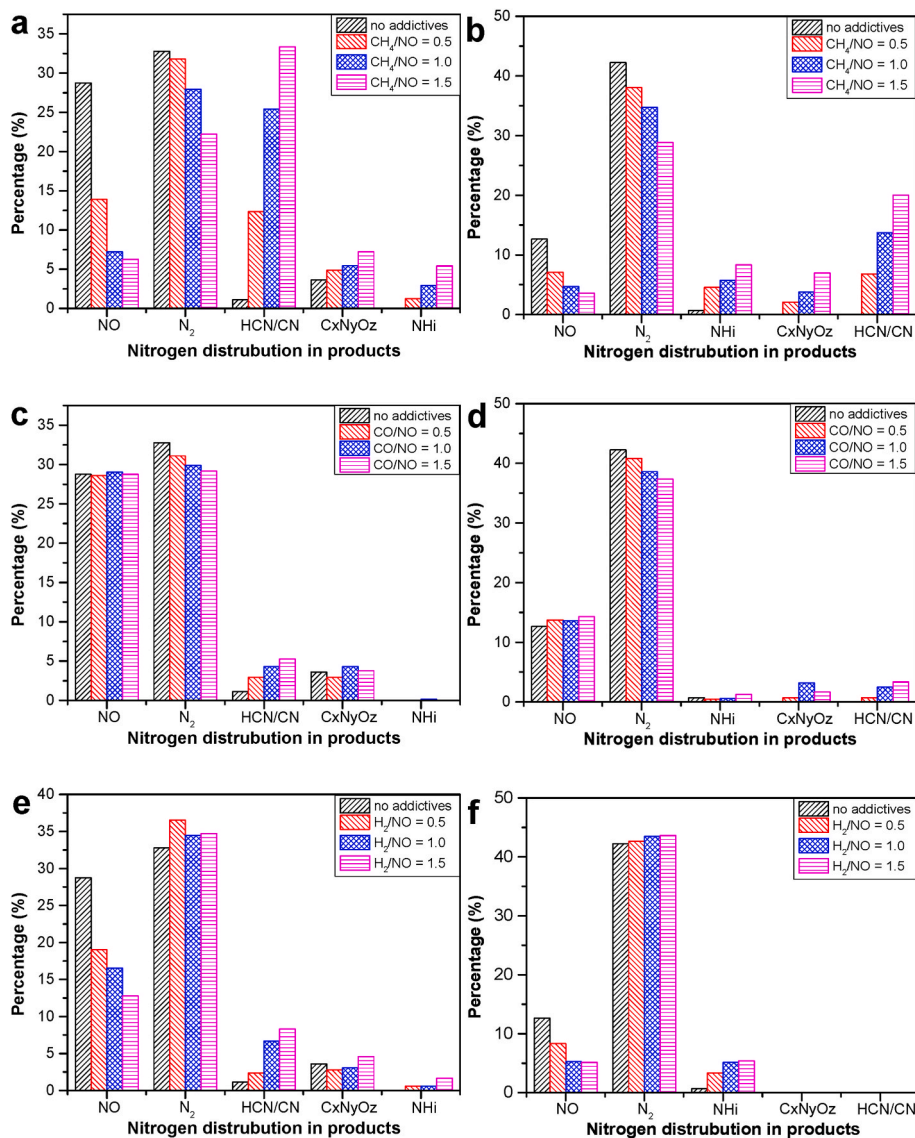


Fig. 1. Nitrogen distribution in products during NO reduction process. (a) HCN with CH₄ addition. (b) NH₃ with CH₄ addition. (c) HCN with CO addition. (d) NH₃ with CO addition. (e) HCN with H₂ addition. (f) NH₃ with H₂ addition. C_xN_yO_z present species containing C, N and O elements. NH_i is an umbrella term of NH₃, NH₂ and NH.

dynamically track all the intermediates to provide both spatially and temporally resolved information. By contrast, reactive force field (ReaxFF) molecular dynamics (MD) has the potential to solve such a problem, which can simulate chemical processes with affordable computational costs and high accuracy [11–13].

ReaxFF employs a bond-order formalism in conjunction with polarisable charge descriptions to describe both reactive and non-reactive interactions between atoms. ReaxFF allows accurate modelling of both covalent and electrostatic interactions for a diverse range of materials [14]. The function of potential energy can be calculated as [15]:

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lp}} + E_{\text{val}} + E_{\text{tor}} + E_{\text{vdW}} + E_{\text{Coulomb}} \quad (1)$$

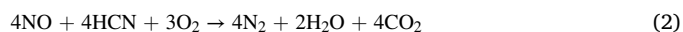
where E_{system} , E_{bond} , E_{over} , E_{under} , E_{lp} , E_{val} , E_{tor} , E_{vdW} , and E_{Coulomb} represent total energy, bond energy, overcoordination energy penalty, undercoordination stability, lone pair energy, valence angle energy, torsion angle energy, van der Waals energy, and Coulomb energy, respectively [15].

In the present study, ReaxFF MD simulations are performed to investigate the effects of CH₄, CO and H₂ addition on NO reduction performance by HCN and NH₃. The nitrogen distribution of products is

studied firstly under varying numbers of CH₄, CO and H₂. Then, the mechanisms of NO removal by HCN and NH₃ with different additives are explored. The present simulation results and previous experimental results are discussed, and proposed strategies regarding adjustment of nitrogen-free components in pyrolysis gas to improve NO_x reduction efficiency are provided.

2. Methods

The equivalence ratios of reactants are calculated considering the reduction reactions as follows:



To study the NO reduction by HCN or by NH₃, MD simulations are performed, each simulation box contains 120 NO and 120 HCN or NH₃. To study effects of nitrogen-free species on NO reduction by HCN and NH₃, CH₄, CO and H₂ molecules are added to the simulation system with molar ratios of CH₄/NO, CO/NO and H₂/NO being 0.5, 1.0 and 1.5. The

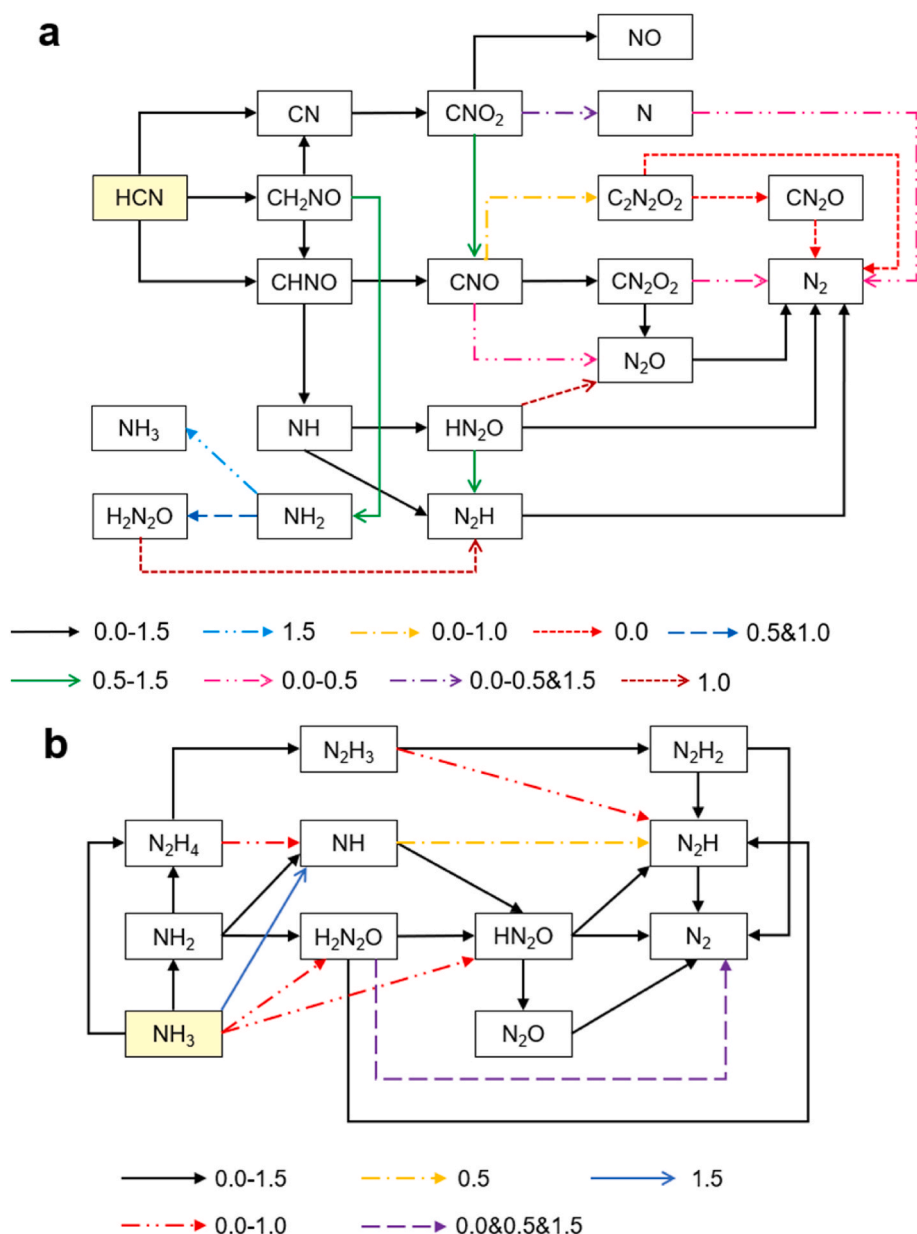


Fig. 2. Reaction pathways of NO reduction by (a) HCN and (b) NH₃ with CH₄ addition. The numbers in the figure are the molar ratios of CH₄ to NO. HCN and NH₃ in the yellow box are the starting molecules. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

density of all the simulated system is maintained at 0.15 g/cm³ by changing the length of simulation box.

All the simulations were performed with the REAXC package in LAMMPS software (Large-scale Atomic/Molecular Massively Parallel Simulator) [16,17] with C/H/O/N force field parameters [18,19]. Three replicates were set up for every case with different initial configurations. The canonical ensemble (NVT) [20] was selected for ReaxFF MD simulations with a damping constant of 100 fs. Before “production simulation”, every system underwent energy minimization and equilibration for 20 ps at 40 K to optimize the initial geometric configuration. Afterwards, the systems were heated to 3000 K and then the temperature was kept constant. The time step and total simulation time were 0.1 fs and 1000 ps for all simulations, respectively. The data of NO removal by HCN and NH₃ without additives are shared with our previous work [21].

The reaction pathways are analysed using Chemical Trajectory Analyzer (ChemTrayzer) scripts with the bond order cutoff of 0.3 [22]. A net flux (NF) indicates how often the reaction was observed during the simulation time, which is calculated by the occurrence difference

between the forward reaction and the reverse reaction [23].

3. Results

3.1. Nitrogen distribution in products during NO removal by HCN and NH₃ under different additives

Fig. 1 shows nitrogen distribution in the NO removal process by HCN and NH₃ with different additives. Overall, the nitrogen-free additives significantly influence the yields of main nitrogen-containing products (NO, N₂, HCN/CN, C_xN_yO_z and NHi).

Specifically, as observed in Fig. 1a and b, CH₄ benefits NO reduction in both HCN and NH₃ cases. On the other hand, the conversion from NO to N₂ formation is inhibited in the NO reduction by HCN and NH₃ with CH₄ addition. The proportion of HCN/CN, NHi and C_xN_yO_z is promoted by CH₄ molecules in both HCN and NH₃ cases.

Fig. 1c and d illustrate the influence of CO on nitrogen distribution when NO is removed by HCN and NH₃. The influence of CO addition on

Table 1Net flux (NF) of main pathways for NO consumption and N₂ formation in the NO removal process by HCN and NH₃ with varying CH₄/NO molar ratios.

NO reduction with HCN	0	0.5	1	1.5	NO reduction with NH ₃	0	0.5	1	1.5
CNO → CN ₂ O ₂	46	9	14	14	NH → HN ₂ O	34	27	18	15
CNO → N ₂ O	18	11	0	0	NH → N ₂ H	0	10	0	0
NH ₂ → H ₂ N ₂ O	0	10	19	0	NH ₃ → HN ₂ O	7	9	6	0
NH → HN ₂ O	17	17	9	22	NH ₃ → H ₂ N ₂ O	18	12	10	0
NH → N ₂ H	11	9	9	8	NH ₂ → H ₂ N ₂ O	60	36	30	59
N → N ₂	6	5	0	0	NO consumption	119	94	64	74
NO consumption	98	61	51	44	HN ₂ O → N ₂	53	45	37	31
CNO ₂ → NO	60	28	22	7	N ₂ H → N ₂	58	67	64	59
Net NO consumption	38	33	29	37	N ₂ H ₂ → N ₂	18	22	15	19
N ₂ O → N ₂	54	33	16	12	N ₂ O → N ₂	15	14	14	5
HN ₂ O → N ₂	19	24	15	17	H ₂ N ₂ O → N ₂	18	3	0	6
N ₂ H → N ₂	8	11	23	17	N ₂ formation	162	151	130	120
CN ₂ O → N ₂	19	0	0	0					
C ₂ N ₂ O ₂ → N ₂	19	0	0	0					
CN ₂ O ₂ → N ₂	17	6	0	0					
N → N ₂	6	5	0	0					
N ₂ formation	88	79	54	46					

the number of NO in the HCN cases is insignificant, but CO slightly promotes the number of NO in the NH₃ cases. The yields of N₂ decrease with CO addition in both HCN and NH₃ cases. When NO is removed by HCN, the percentage of HCN/CN increases slightly with CO addition. The numbers of C_xN_yO_z and NH_i almost remain the same in Fig. 1c. For NO removal with NH₃, CO addition promotes the formation of C_xN_yO_z and HCN/CN, but has insignificant influence on the NH_i production.

Regarding the effects of H₂ addition on NO reduction process as shown in Fig. 1e and f, H₂ molecules promote the NO consumption significantly and N₂ formation slightly in both HCN and NH₃ cases. In NO removal by HCN cases, the H₂ addition also increases the percentages of HCN/CN and NH_i, but the C_xN_yO_z content remains the same with H₂/NO ratios changing from 0 to 1.5. The NH_i content shows an upward trend with H₂ addition during NO reduction with NH₃.

To sum up, the above results demonstrate the addition of nitrogen-free species could modify the nitrogen distribution in products during the NO removal process by HCN and NH₃. To further explore mechanisms, the reaction pathways are scrutinized.

3.2. Effects of CH₄ addition on mechanisms of NO reduction by HCN and NH₃

Fig. 2a shows reaction pathways of NO reduction by HCN with the addition of CH₄. N, CNO, NH and NH₂ are key intermediates initiating the oxidation and decomposition of HCN, which can react with NO molecules forming N₂ eventually. The pathway from N to N₂ occurs in molar ratios of CH₄/NO being 0 and 0.5. CNO participates in reactions with NO generating CN₂O₂ and N₂O, and generates N₂ eventually. The pathway CNO → CN₂O₂ is found in all cases, but CNO → N₂O only happens when the CH₄/NO molar ratios are 0 and 0.5. The N₂ formation from CNO occurs when molar ratio CH₄/NO is 0. CH₄ shows insignificant changes for N₂ formation from reactions where NH reacts with NO generating HN₂O and N₂H. CH₄ promotes the generation of NH₂ intermediates, and the consumption of NO molecules by NH₂ is observed in cases where CH₄/NO molar ratios are 0.5 and 1.0.

According to Fig. 2b, in NO reduction with NH₃ cases, NO molecules are consumed by reactions with NH₃, NH₂ and NH species generating intermediates, such as H₂N₂O, HN₂O and N₂H, which will convert to N₂ finally. CH₄ has no influence on NO consumption via NH₂ → H₂N₂O and NH → HN₂O. The pathways NH₃ → H₂N₂O and NH₃ → HN₂O are not observed when molar ratio CH₄/NO is 1.5. The conversion from NH to N₂H occurs when the molar ratio of CH₄/NO is 0.5. Regarding N₂ formation, N₂H₂, N₂H, HN₂O are main precursors in all cases, but the conversion from H₂N₂O to N₂ is not observed in the case where the molar ratio CH₄/NO is 0.5. The reaction pathways suggest that N₂H₂ and part of N₂H can be generated directly from NH_i (NH₃, NH₂ and NH)

species without NO removal.

To further identify how CH₄ affects the NO reduction performance with HCN and NH₃, the NF of main pathways is explored as shown in Table 1. In the NO removal with HCN cases, CH₄ inhibits the N₂ formation from reactions CNO + NO or CNO via pathways CNO → CN₂O₂/N₂O → N₂ and CNO → C₂N₂O₂/CN₂O → N₂. The NFs of NH → HN₂O/N₂H → N₂ almost remain the same under varying CH₄ to NO molar ratios. Also, the NFs of CN → CNO₂ → NO and CN → CNO₂ → N → N₂ decrease with CH₄ addition. Overall, CH₄ suppresses the conversion of HCN to both NO and N₂. Due to the inhibition influence of CH₄ on the oxidation process of HCN forming NO, the net NF of NO consumption almost remains the same in all cases. In addition, as the number of CH₄ addition increases, the NO abatement by NH and NH₃ is weakened in NO reduction with NH₃ cases. The NF of NH₂ → H₂N₂O reaches the lowest point when molar ratio CH₄/NO is 1. Regarding N₂ formation, the contribution of HN₂O, N₂O and H₂N₂O decreases with CH₄ addition, by contrast, the NFs of N₂H → N₂ and N₂H₂ → N₂ fluctuate with molar ratio CH₄/NO rising. To sum up, the behaviours for NH₃ and HCN to convert NO to N₂ are inhibited by CH₄ molecules addition. Such trends account for the changes of N₂ yield in Fig. 1a and b. The chemical effects of CH₄ on nitrogen-containing species are investigated subsequently to elucidate the N content on other products like NO, HCN/CN, C_xH_yO_z and NH_i under varying CH₄/NO molar ratios.

When NO is removed by HCN, the addition of CH₄ promotes the consumption of NO by generating HNO via R1 and R2.



CH₄ promotes the generation of NH_i by the pathway CH₂NO → NH₂, and HNO benefits the NH formation.

CH₃ radicals can react with CNO and form C₂H₃NO (R3), which will be converted to HCN/CN by pathways C₂H₃NO → CH₂N/CH₃N → HCN/CN. The addition of CH₄ reduces the numbers of OH, O and O₂ species by the generation of CO, inhibiting the consumption of HCN and CN by pathways CN → CNO₂, HCN → CHNO and HCN → CH₂NO. Therefore, the quantities of HCN and CN at the end of reactions are promoted by CH₄ molecules. In addition, CH₄ promotes the reactions between hydrocarbons (C_xH_y) and nitrogen-containing species like NO, HNO, HCN/CN, increasing the C_xN_yO_z content on products.



In the NO removal with NH₃ cases, CH₅N is formed in CH₄ addition cases via R4, which can be converted to HCN and CN eventually. And the

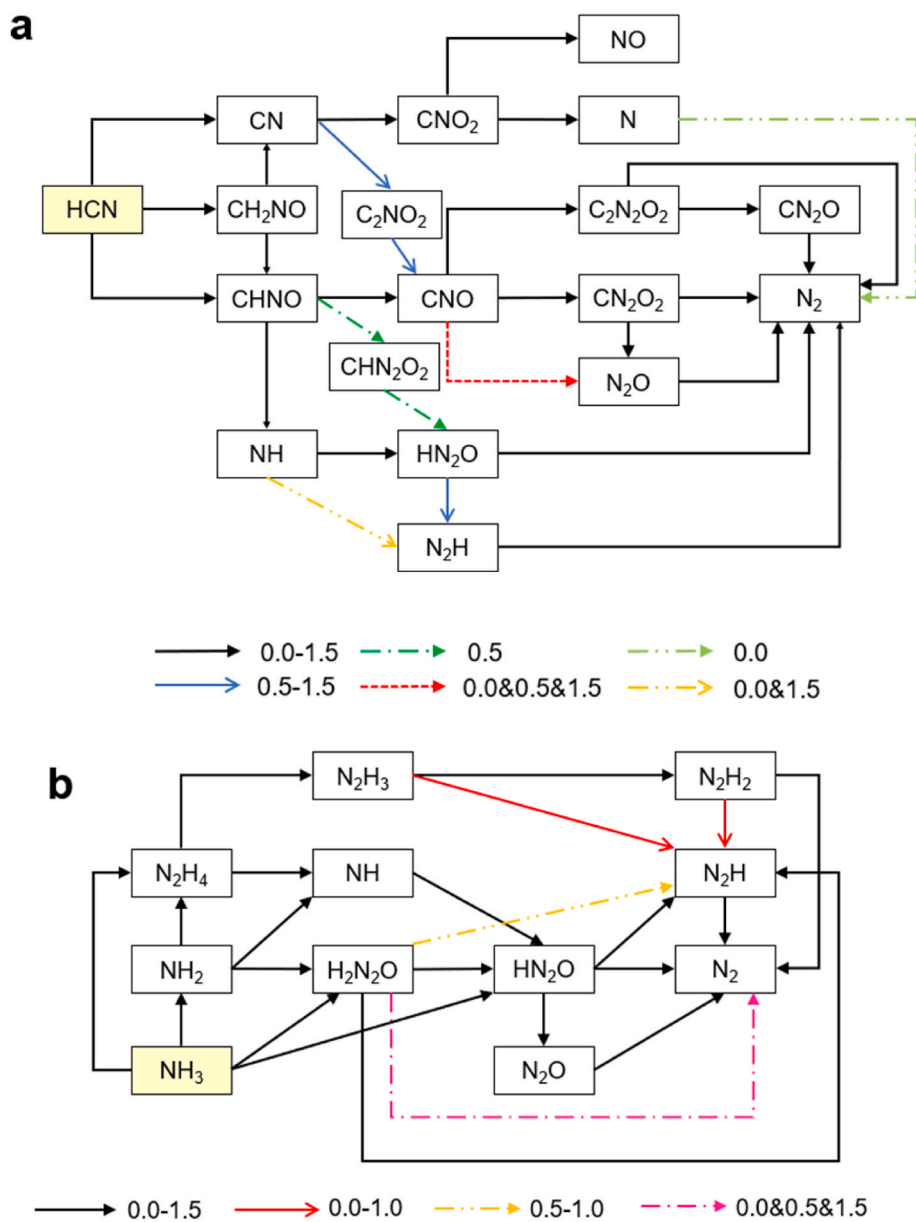


Fig. 3. Reaction pathways of NO reduction by (a) HCN and (b) NH₃ with CO addition. The numbers in legends are the molar ratios of CO to NO. Boxes in the yellow indicate species at the start of reactions. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 2

Net flux (NF) of main pathways for NO consumption and N₂ formation in the NO removal by HCN and NH₃ with varying molar ratios of CO to NO.

NO reduction with HCN	0	0.5	1	1.5	NO reduction with NH ₃	0	0.5	1	1.5
CNO → CN ₂ O ₂	46	36	43	37	NH → HN ₂ O	34	29	22	23
CNO → N ₂ O	18	13	0	14	NH ₃ → HN ₂ O	7	6	5	3
CHNO → CHN ₂ O ₂	0	11	0	0	NH ₃ → H ₂ N ₂ O	18	11	18	14
N → N ₂	6	0	0	0	NH ₂ → H ₂ N ₂ O	60	71	29	39
NH → HN ₂ O	17	23	27	18	NO consumption	119	116	74	79
NH → N ₂ H	11	0	0	7	HN ₂ O → N ₂	53	49	34	28
NO consumption	98	83	70	76	N ₂ H → N ₂	58	60	48	45
CNO ₂ → NO	60	51	39	32	N ₂ H ₂ → N ₂	18	17	18	16
Net NO consumption	38	32	31	44	N ₂ O → N ₂	15	11	19	18
N ₂ O → N ₂	54	39	30	24	H ₂ N ₂ O → N ₂	18	7	0	8
CN ₂ O → N ₂	19	19	18	16	N ₂ generation	162	144	119	115
C ₂ N ₂ O ₂ → N ₂	19	13	13	16					
CN ₂ O ₂ → N ₂	17	15	15	14					
N → N ₂	6	0	0	0					
HN ₂ O → N ₂	19	14	16	15					
N ₂ H → N ₂	8	11	17	19					
N ₂ formation	142	111	109	104					

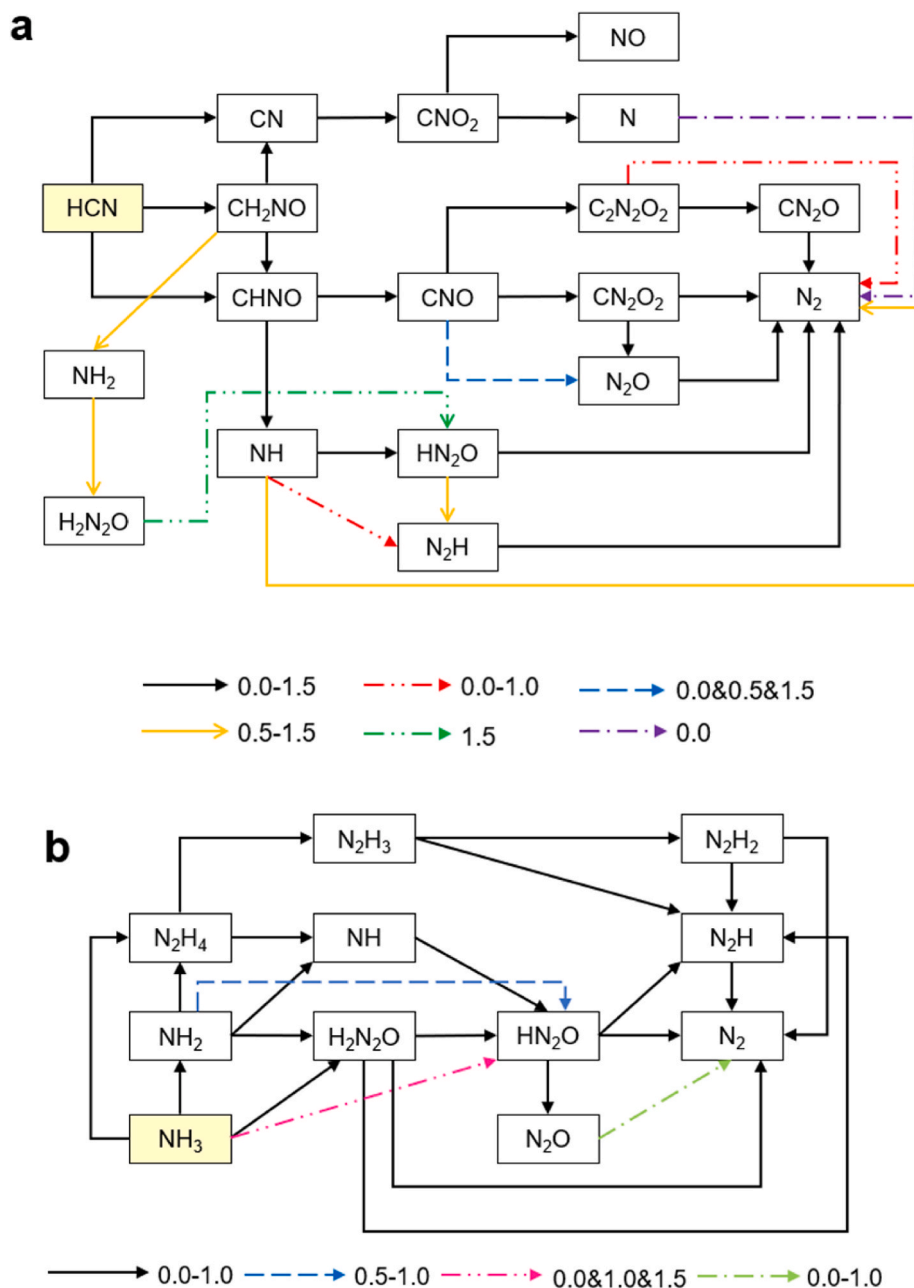


Fig. 4. Reaction pathways of NO reduction by (a) HCN and (b) NH_3 with H_2 addition. The numbers in legends are the molar ratios of H_2 to NO. Boxes in yellow indicate species at the start of the reactions. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

enhancement of HNO generation causes the increase of NO consumption. HNO also inhibits the consumption of NH_i radicals, leading to the decrease of NO reduction performance. The reactions of hydrocarbons (C_xH_y) and nitrogen-containing species increase the number of $\text{C}_x\text{N}_y\text{O}_z$ in products.

3.3. Effects of CO addition on mechanisms of NO reduction by HCN and NH_3

In Fig. 3, the CO molecules modify the reaction pathways in NO reduction by both HCN and NH_3 . The pathways $\text{CN} \rightarrow \text{C}_2\text{NO}_2 \rightarrow \text{CNO}$ and $\text{HN}_2\text{O} \rightarrow \text{N}_2\text{H}$ are found in NO reduction by HCN with CO addition cases. The conversion from CNO to N_2O occurs in molar ratio $\text{CO}/\text{NO} = 0, 0.5$ and 1.5 cases. $\text{CHNO} \rightarrow \text{CHN}_2\text{O}_2$ happens when molar ratio CO/NO is 0.5 . The NO consumption by $\text{NH} \rightarrow \text{N}_2\text{H}$ occurs in molar ratio $\text{CO}/\text{NO} = 0$ and 1.5 . The N_2 formation from reactions between N and NO is

not found in CO addition cases. Regarding the influence of CO on NO reduction process by NH_3 , CO inhibits the pathways $\text{N}_2\text{H}_3 \rightarrow \text{N}_2\text{H}$ and $\text{N}_2\text{H}_2 \rightarrow \text{N}_2\text{H}$, which occur when molar ratio CO/NO is less than 1.5 . The conversion from $\text{H}_2\text{N}_2\text{O}$ to N_2H happens in molar ratio $\text{CO}/\text{NO} = 0.5$ – 1.0 . The N_2 generation from $\text{H}_2\text{N}_2\text{O}$ is not detected in the molar ratio $\text{CO}/\text{NO} = 1.0$ case.

The influence of CO on the numbers of NO and N_2 at the end of reactions is further illustrated in terms of NFs reactions related to the formation of NO and N_2 .

In NO removal with HCN cases, CO molecules react with oxygen-containing species (such as O_2 , O and OH) and generate CO_2 . CO_2 promotes the conversion from CN to CNO via pathway $\text{CN} \rightarrow \text{C}_2\text{NO}_2 \rightarrow \text{CNO}$ as shown in R5 and R6.



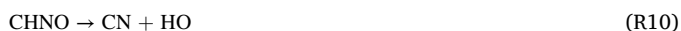
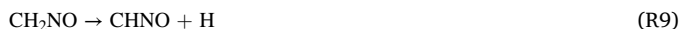
Table 3Net flux (NF) of main pathways for NO consumption and N₂ formation during NO removal with HCN and NH₃ with varying molar ratios of H₂ to NO.

NO reduction by HCN	0	0.5	1	1.5	NO reduction by NH ₃	0	0.5	1	1.5
CNO → CN ₂ O ₂	46	51	31	19	NH → HN ₂ O	34	22	23	25
CNO → N ₂ O	18	11	0	7	NH ₂ → HN ₂ O	0	11	8	2
NH → HN ₂ O	17	26	25	27	NH ₂ → H ₂ N ₂ O	60	64	54	48
NH → N ₂	0	5	7	7	NH ₃ → HN ₂ O	7	0	12	6
NH → N ₂ H	11	7	6	0	NH ₃ → H ₂ N ₂ O	18	26	18	58
NH ₂ → H ₂ N ₂ O	0	13	7	21	NO consumption	119	123	115	139
N → N ₂	6	0	0	0	HN ₂ O → N ₂	53	58	47	53
NO consumption	98	113	76	81	N ₂ H → N ₂	58	74	50	59
CNO ₂ → NO	60	29	14	2	N ₂ H ₂ → N ₂	18	22	25	31
Net NO consumption	38	84	62	79	N ₂ O → N ₂	15	16	16	0
HN ₂ O → N ₂	19	32	25	36	H ₂ N ₂ O → N ₂	18	3	8	7
NH → N ₂	0	5	7	7	N ₂ formation	162	173	146	150
CN ₂ O → N ₂	19	23	15	9					
C ₂ N ₂ O ₂ → N ₂	19	11	11	0					
CN ₂ O ₂ → N ₂	17	13	4	4					
N ₂ O → N ₂	54	39	32	34					
N → N ₂	6	0	0	0					
N ₂ H → N ₂	8	21	26	33					
N ₂ formation	142	144	120	123					



The decrease of O₂ inhibits in the conversion of CN to CNO₂. Thus the NFs of CNO₂ → NO and CNO₂ → N → N₂ reduce with the molar ratios of CO/NO as shown in Table 2. The reactions between CNO and NO are inhibited by CO addition, but CO has insignificant influence on NO consumption by NH radical. Overall, the NF of net NO consumption almost remains the same in all cases, which explains the trend of NO in Fig. 1c. Regarding N₂ formation, the NFs of C₂N₂O₂ → N₂ and CN₂O → N₂ decrease slightly with CO addition. CO inhibits N₂ formation via the pathway CNO → CN₂O₂/N₂O → N₂. CO enhances the conversion from N₂H to N₂, but mitigates the conversion of HN₂O to N₂ slightly. The consumption of oxygen-containing species by CO suppresses the conversion from HCN/CN to intermediates, such as CNO₂, CH₂NO and CHNO. The effects of CO on C_xN_yO_z and NHi formation and consumption are insignificant, and the C_xN_yO_z and NHi contents almost remain the same in all cases.

When NO is removed by NH₃ molecules, CO will react with NH₂ and form CH₂NO, which will finally be converted to CNO and CN (R7-R11). As a result, the contents of C_xN_yO_z and HCN/CN increase.



The ability of C_xN_yO_z to convert NO to N₂ is significantly lower than NHi radicals, causing the decrease of NO reduction performance in CO addition cases. That accounts for the NFs of NO consumption and N₂ formation reduces in CO addition cases as shown in Table 2. Specifically, CO has insignificant influence on NO consumption by NH₃ via pathways NH₃ → HN₂O and NH₃ → H₂N₂O. The conversion from NH to HN₂O is inhibited with molar ratio CO/NO. The NF of NH₂ → N₂ first increases with the CO addition and then decreases, and the peak NF occurs at molar ratio CO/NO of 0.5. As for N₂ formation, the conversion from HN₂O, N₂H and H₂N₂O to N₂ is inhibited as the number of CO addition increases. CO has insignificant influence on the NFs of pathways N₂H₂ → N₂ and N₂O → N₂.

3.4. Effects of H₂ addition on mechanisms of NO reduction by HCN and NH₃

Fig. 4 illustrates reaction pathways of NO reduction by HCN and NH₃ with H₂ addition. The addition of H₂ promotes the conversion from NH₂

to H₂N₂O, NH to N₂ and HN₂O to N₂H. N → N₂ and H₂N₂O → HN₂O are detected in molar ratio H₂/NO of 0 and 1.5 cases, respectively. The pathways NH to N₂H and C₂N₂O₂ to N₂ occur when H₂/NO molar ratios change from 0 to 1.0. In the NO reduction by NH₃ cases, the conversion from NH₂ to HN₂O is observed in molar ratio H₂/NO = 0.5–1.0. NH₃ → HN₂O is not found when the molar ratio of H₂/NO is 0.5. N₂ generation from N₂O takes place with H₂/NO molar ratio ranging from 0.0 to 1.0.

To further account for changes of nitrogen distribution in products with H₂ addition during NO abatement process, we investigated the NFs of main pathways related to NO reduction and N₂ formation as shown in Table 3. In NO removal with HCN cases, the H₂ addition reduces the NFs of CNO → CN₂O₂/N₂O and N → N₂, but slightly promotes the NO consumption by NH radical and the formation of HN₂O, N₂ and N₂H. The pathway CH₂NO → NH₂ → H₂N₂O is enhanced by H₂ molecules in the NO removal process. As for the NO formation, the addition of H₂ significantly inhibits the channel CN → CNO₂ → NO. In addition, the contribution of CNO intermediate to N₂ formation via CNO → C₂N₂O₂/CN₂O/CN₂O₂/N₂O → N₂ decreases with H₂ addition during NO abatement process. The NFs of N₂ generation from the NH radical via NH → N₂, NH → HN₂O/N₂H → N₂ increase in H₂ addition cases. When NO is reduced by NH₃, the NFs of NO consumption increase considerably with the number of H₂ added, but the contributions of NH and NH₂ on NO abatement are diminished in H₂ addition cases. Moreover, H₂ has insignificant influence on N₂ generation from HN₂O and N₂H, but promotes the conversion from N₂H₂ to N₂. The NF of H₂N₂O → N₂ decreases in H₂ addition cases. Regarding the pathway N₂O → N₂, the NF almost remains the same in molar ratio H₂/NO = 0.0–1.0, but decreases to 0 in the molar ratio H₂/NO of 1.5 case. The total NF changes of NO consumption and N₂ formation in both HCN and NH₃ cases are inconsistent with that of NO and N₂ content on products in Fig. 1e and f. To explain this phenomenon, the chemical effects of H₂ linked with NO and N₂ are investigated subsequently.

The addition of H₂ molecules increases H radical, which enhances the conversion from NO to HNO via R12. That is the main reason for the decrease of NO content in products in both NO reduction with HCN and NH₃ cases.



H₂ molecules also benefit the formation of HN₂O₂, which will be converted to N₂ eventually (R13-R15). Such pathways reveal the mechanisms for the enhancement of H₂ on N₂ formation in the NO reduction process.



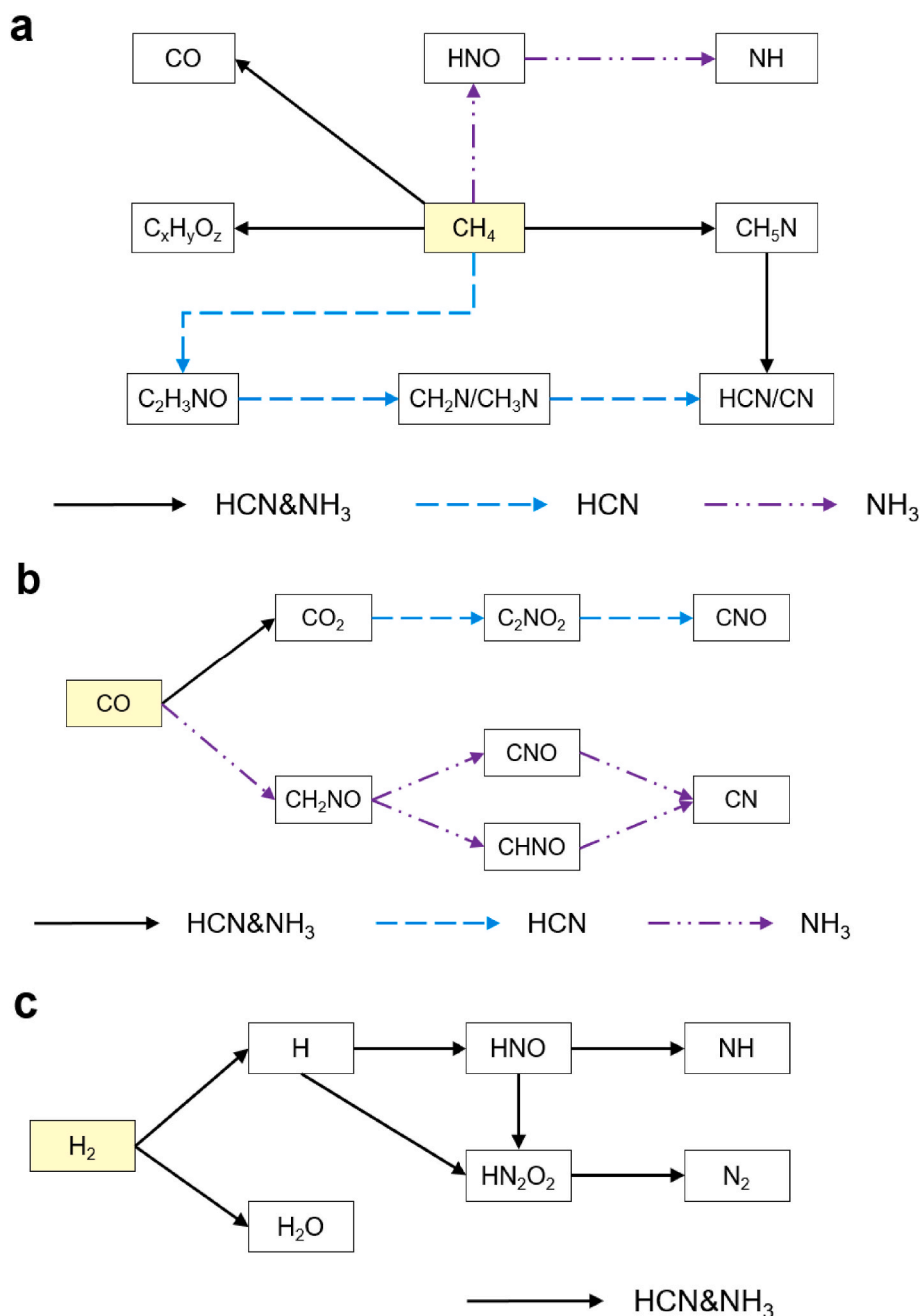
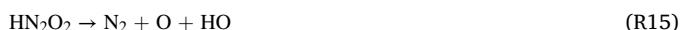


Fig. 5. Diagram of (a) CH₄, (b) CO, (c) H₂ affecting NO reduction by HCN and NH₃ processes.



Compared with NO, HNO is less reactive with nitrogen-containing intermediates and reduced numbers of N₂ and NH_i are formed. H₂ decreases the number of active species, such as OH, O and O₂, by the generation of H₂O, which inhibits the conversion of HCN/CN to CNO₂, CHNO and CH₂NO. The increase of HNO with H₂ addition also benefits the formation of NH in NO reduction by HCN and NH₃ cases.

4. Discussion

In this study, we investigated the influence of CH₄, CO and H₂ on the NO reduction performance by HCN and NH₃ via ReaxFF MD simulations. Results indicate that the concentrations of different nitrogen-free species can modify the nitrogen distribution of products, which suggests the adjustment of nitrogen-free species in coal pyrolysis gas could be a

feasible way to improve NO reduction performance. The effects of nitrogen-free additives are summarized in Fig. 5.

Regarding NO reduction, our simulation results, together with previous studies, suggest that hydrocarbons have better performance in NO decrease than H₂ and CO [24,25]. The main reason is that the reactive H radicals in CH₄ could enhance the conversion from NO to HNO. The influence of CO on the NO content on products is insignificant. Considering the nitrogen-containing intermediates (HCN/CN, NH_i and C_xN_yO_z) in the reburn zone will be oxidized to NO_x in the burnout zone, N₂ can be chosen as an indicator for NO reduction performance.

For N₂ formation, H₂ molecules present the best performance of the three nitrogen-free additives, and CH₄ the worst. Both CO and CH₄ show inhibition effects on N₂ formation; by contrast, H₂ benefits the generation of N₂. Therefore, reducing the CH₄ and CO contents can be an effective method to improve NO reduction efficiency, which can be achieved by adjusting operating conditions during coal pyrolysis process

[26,27]. Also, the contribution of the nitrogen-free species on N_2 generation is significantly lower than nitrogen-containing intermediates from HCN and NH_3 , which is consistent with previous experimental results that nitrogen species play dominant roles in the NO_x reduction process in coal pyrolysis gas [2,3].

5. Conclusions

A series of ReaxFF MD simulations were conducted to investigate the influence of nitrogen-free components (CH_4 , CO and H_2) on the NO_x reduction performance by coal pyrolysis gas. The nitrogen distribution in the products was studied in the presence of different nitrogen-free compounds. Additionally, the reaction pathways of NO reduction by HCN and NH_3 with different additives were scrutinized at the atomic scale. The present research provides new insights into the effects of nitrogen-free species on the NO_x reduction performance by HCN and NH_3 , which will be helpful for developing strategies for NO_x emission control via the adjustment of nitrogen-free components in coal pyrolysis gas.

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 Nos. EP/R029598/1 and EP/X035075/1) 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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