

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

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## 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 N<sub>2</sub>. Nitrogen-containing compounds (HCN and NH<sub>3</sub>) play dominant roles in the NO reduction performance. In this study, we investigated the influence of nitrogen-free species (CH<sub>4</sub>, CO and H<sub>2</sub>) in coal pyrolysis gas on the NO reduction by HCN and NH<sub>3</sub> 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 NH<sub>3</sub> under different additives. In addition, mechanisms of NO reduction by HCN and NH<sub>3</sub> 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 CH<sub>4</sub>, CO and H<sub>2</sub> on the NO reduction by HCN and NH<sub>3</sub>, which may be helpful to reduce the NO<sub>x</sub> emissions during coal combustion by optimising the nitrogen-free components of coal pyrolysis gas.

## 1. Introduction

NO<sub>x</sub> 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 NO<sub>x</sub> 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 NO<sub>x</sub> is formed. In the reburn zone, pyrolysis gas is injected to convert NO<sub>x</sub> from the main zone to clean N<sub>2</sub> 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 NO<sub>x</sub> reduction behaviours of this technology.

Previous studies have reported the feasibility of using nitrogen-containing species (HCN and NH<sub>3</sub>) to reduce NO<sub>x</sub> in coal pyrolysis gas [2,3]. The presence of nitrogen-free compounds (CH<sub>4</sub>, CO and H<sub>2</sub>) also influences NO<sub>x</sub> performance by nitrogen-containing species in pyrolysis gas. NO is the main component of NO<sub>x</sub> emissions, accounting for about

95% of the total [4,5]. To explore the influence of CH<sub>4</sub>, CO and H<sub>2</sub> on NO removal by HCN and NH<sub>3</sub> will be helpful to understand the NO<sub>x</sub> control mechanism and lay theoretical foundations for NO<sub>x</sub> 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 NH<sub>3</sub>, its processes have long been researched in selective non-catalytic reduction (SNCR), in which NH<sub>3</sub> is employed to reduce NO<sub>x</sub> emissions in flue gas under fuel lean circumstances [6–8]. The results showed that NH<sub>2</sub> radicals derived from NH<sub>3</sub> are the key intermediate for NO abatement. Also, a few studies have investigated the NO reduction by NH<sub>3</sub> in the SNCR process with CO and CH<sub>4</sub> [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 NH<sub>3</sub>, 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

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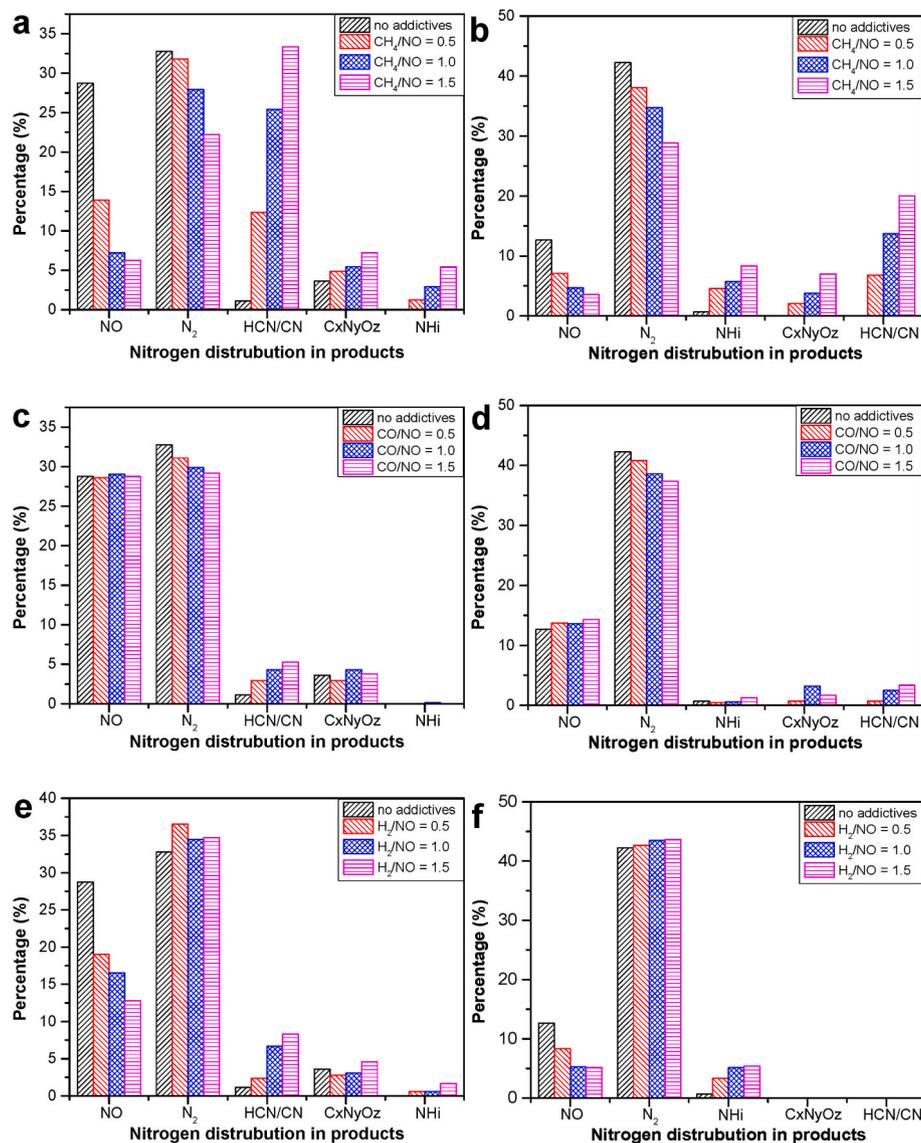
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<https://doi.org/10.1016/j.joei.2023.101172>

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 CH<sub>4</sub> addition. (b) NH<sub>3</sub> with CH<sub>4</sub> addition. (c) HCN with CO addition. (d) NH<sub>3</sub> with CO addition. (e) HCN with H<sub>2</sub> addition. (f) NH<sub>3</sub> with H<sub>2</sub> addition. C<sub>x</sub>N<sub>y</sub>O<sub>z</sub> present species containing C, N and O elements. NH<sub>i</sub> is an umbrella term of NH<sub>3</sub>, NH<sub>2</sub> 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]:

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

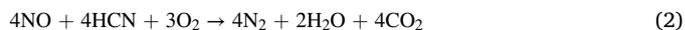
where  $E_{\text{system}}$ ,  $E_{\text{bond}}$ ,  $E_{\text{over}}$ ,  $E_{\text{under}}$ ,  $E_{\text{lp}}$ ,  $E_{\text{val}}$ ,  $E_{\text{tor}}$ ,  $E_{\text{vdW}}$ , and  $E_{\text{Coulomb}}$  represent total energy, bond energy, overcoordination energy penalty, undercoordination stability, lone 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 CH<sub>4</sub>, CO and H<sub>2</sub> addition on NO reduction performance by HCN and NH<sub>3</sub>. The nitrogen distribution of products is

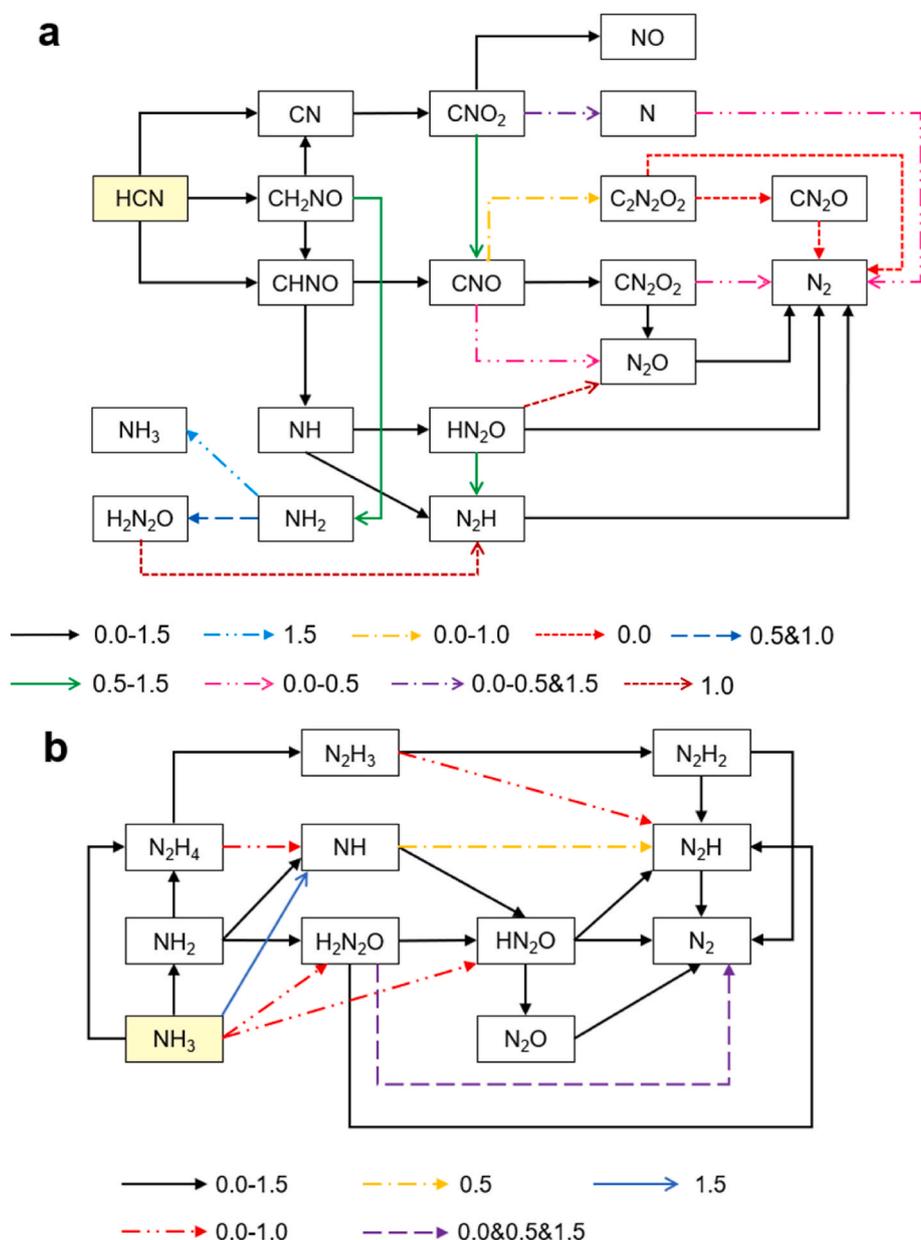
studied firstly under varying numbers of CH<sub>4</sub>, CO and H<sub>2</sub>. Then, the mechanisms of NO removal by HCN and NH<sub>3</sub> with different additives are explored. The present simulation results and previous experimental results are discussed, and proposed strategies regarding adjustment of nitrogen-free components in pyrolysis gas to improve NO<sub>x</sub> 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 NH<sub>3</sub>, MD simulations are performed, each simulation box contains 120 NO and 120 HCN or NH<sub>3</sub>. To study effects of nitrogen-free species on NO reduction by HCN and NH<sub>3</sub>, CH<sub>4</sub>, CO and H<sub>2</sub> molecules are added to the simulation system with molar ratios of CH<sub>4</sub>/NO, CO/NO and H<sub>2</sub>/NO being 0.5, 1.0 and 1.5. The



**Fig. 2.** Reaction pathways of NO reduction by (a) HCN and (b) NH<sub>3</sub> with CH<sub>4</sub> addition. The numbers in the figure are the molar ratios of CH<sub>4</sub> to NO. HCN and NH<sub>3</sub> 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/cm<sup>3</sup> 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 NH<sub>3</sub> 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 NH<sub>3</sub> under different additives

Fig. 1 shows nitrogen distribution in the NO removal process by HCN and NH<sub>3</sub> with different additives. Overall, the nitrogen-free additives significantly influence the yields of main nitrogen-containing products (NO, N<sub>2</sub>, HCN/CN, C<sub>x</sub>N<sub>y</sub>O<sub>z</sub> and NHi).

Specifically, as observed in Fig. 1a and b, CH<sub>4</sub> benefits NO reduction in both HCN and NH<sub>3</sub> cases. On the other hand, the conversion from NO to N<sub>2</sub> formation is inhibited in the NO reduction by HCN and NH<sub>3</sub> with CH<sub>4</sub> addition. The proportion of HCN/CN, NHi and C<sub>x</sub>N<sub>y</sub>O<sub>z</sub> is promoted by CH<sub>4</sub> molecules in both HCN and NH<sub>3</sub> cases.

Fig. 1c and d illustrate the influence of CO on nitrogen distribution when NO is removed by HCN and NH<sub>3</sub>. The influence of CO addition on

**Table 1**Net flux (NF) of main pathways for NO consumption and N<sub>2</sub> formation in the NO removal process by HCN and NH<sub>3</sub> with varying CH<sub>4</sub>/NO molar ratios.

NO reduction with HCN	0	0.5	1	1.5	NO reduction with NH <sub>3</sub>	0	0.5	1	1.5
CNO → CN <sub>2</sub> O <sub>2</sub>	46	9	14	14	NH → HN <sub>2</sub> O	34	27	18	15
CNO → N <sub>2</sub> O	18	11	0	0	NH → N <sub>2</sub> H	0	10	0	0
NH <sub>2</sub> → H <sub>2</sub> N <sub>2</sub> O	0	10	19	0	NH <sub>3</sub> → HN <sub>2</sub> O	7	9	6	0
NH → HN <sub>2</sub> O	17	17	9	22	NH <sub>3</sub> → H <sub>2</sub> N <sub>2</sub> O	18	12	10	0
NH → N <sub>2</sub> H	11	9	9	8	NH <sub>2</sub> → H <sub>2</sub> N <sub>2</sub> O	60	36	30	59
N → N <sub>2</sub>	6	5	0	0	NO consumption	119	94	64	74
NO consumption	98	61	51	44	HN <sub>2</sub> O → N <sub>2</sub>	53	45	37	31
CNO <sub>2</sub> → NO	60	28	22	7	N <sub>2</sub> H → N <sub>2</sub>	58	67	64	59
Net NO consumption	38	33	29	37	N <sub>2</sub> H <sub>2</sub> → N <sub>2</sub>	18	22	15	19
N <sub>2</sub> O → N <sub>2</sub>	54	33	16	12	N <sub>2</sub> O → N <sub>2</sub>	15	14	14	5
HN <sub>2</sub> O → N <sub>2</sub>	19	24	15	17	H <sub>2</sub> N <sub>2</sub> O → N <sub>2</sub>	18	3	0	6
N <sub>2</sub> H → N <sub>2</sub>	8	11	23	17	N <sub>2</sub> formation	162	151	130	120
CN <sub>2</sub> O → N <sub>2</sub>	19	0	0	0					
C <sub>2</sub> N <sub>2</sub> O <sub>2</sub> → N <sub>2</sub>	19	0	0	0					
CN <sub>2</sub> O <sub>2</sub> → N <sub>2</sub>	17	6	0	0					
N → N <sub>2</sub>	6	5	0	0					
N <sub>2</sub> 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 NH<sub>3</sub> cases. The yields of N<sub>2</sub> decrease with CO addition in both HCN and NH<sub>3</sub> cases. When NO is removed by HCN, the percentage of HCN/CN increases slightly with CO addition. The numbers of C<sub>x</sub>N<sub>y</sub>O<sub>z</sub> and NH<sub>i</sub> almost remain the same in Fig. 1c. For NO removal with NH<sub>3</sub>, CO addition promotes the formation of C<sub>x</sub>N<sub>y</sub>O<sub>z</sub> and HCN/CN, but has insignificant influence on the NH<sub>i</sub> production.

Regarding the effects of H<sub>2</sub> addition on NO reduction process as shown in Fig. 1e and f, H<sub>2</sub> molecules promote the NO consumption significantly and N<sub>2</sub> formation slightly in both HCN and NH<sub>3</sub> cases. In NO removal by HCN cases, the H<sub>2</sub> addition also increases the percentages of HCN/CN and NH<sub>i</sub>, but the C<sub>x</sub>N<sub>y</sub>O<sub>z</sub> content remains the same with H<sub>2</sub>/NO ratios changing from 0 to 1.5. The NH<sub>i</sub> content shows an upward trend with H<sub>2</sub> addition during NO reduction with NH<sub>3</sub>.

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 NH<sub>3</sub>. To further explore mechanisms, the reaction pathways are scrutinized.

### 3.2. Effects of CH<sub>4</sub> addition on mechanisms of NO reduction by HCN and NH<sub>3</sub>

Fig. 2a shows reaction pathways of NO reduction by HCN with the addition of CH<sub>4</sub>. N, CNO, NH and NH<sub>2</sub> are key intermediates initiating the oxidation and decomposition of HCN, which can react with NO molecules forming N<sub>2</sub> eventually. The pathway from N to N<sub>2</sub> occurs in molar ratios of CH<sub>4</sub>/NO being 0 and 0.5. CNO participates in reactions with NO generating CN<sub>2</sub>O<sub>2</sub> and N<sub>2</sub>O, and generates N<sub>2</sub> eventually. The pathway CNO → CN<sub>2</sub>O<sub>2</sub> is found in all cases, but CNO → N<sub>2</sub>O only happens when the CH<sub>4</sub>/NO molar ratios are 0 and 0.5. The N<sub>2</sub> formation from CNO occurs when molar ratio CH<sub>4</sub>/NO is 0. CH<sub>4</sub> shows insignificant changes for N<sub>2</sub> formation from reactions where NH reacts with NO generating HN<sub>2</sub>O and N<sub>2</sub>H. CH<sub>4</sub> promotes the generation of NH<sub>2</sub> intermediates, and the consumption of NO molecules by NH<sub>2</sub> is observed in cases where CH<sub>4</sub>/NO molar ratios are 0.5 and 1.0.

According to Fig. 2b, in NO reduction with NH<sub>3</sub> cases, NO molecules are consumed by reactions with NH<sub>3</sub>, NH<sub>2</sub> and NH species generating intermediates, such as H<sub>2</sub>N<sub>2</sub>O, HN<sub>2</sub>O and N<sub>2</sub>H, which will convert to N<sub>2</sub> finally. CH<sub>4</sub> has no influence on NO consumption via NH<sub>2</sub> → H<sub>2</sub>N<sub>2</sub>O and NH → HN<sub>2</sub>O. The pathways NH<sub>3</sub> → H<sub>2</sub>N<sub>2</sub>O and NH<sub>3</sub> → HN<sub>2</sub>O are not observed when molar ratio CH<sub>4</sub>/NO is 1.5. The conversion from NH to N<sub>2</sub>H occurs when the molar ratio of CH<sub>4</sub>/NO is 0.5. Regarding N<sub>2</sub> formation, N<sub>2</sub>H<sub>2</sub>, N<sub>2</sub>H, HN<sub>2</sub>O are main precursors in all cases, but the conversion from H<sub>2</sub>N<sub>2</sub>O to N<sub>2</sub> is not observed in the case where the molar ratio CH<sub>4</sub>/NO is 0.5. The reaction pathways suggest that N<sub>2</sub>H<sub>2</sub> and part of N<sub>2</sub>H can be generated directly from NH<sub>i</sub> (NH<sub>3</sub>, NH<sub>2</sub> and NH)

species without NO removal.

To further identify how CH<sub>4</sub> affects the NO reduction performance with HCN and NH<sub>3</sub>, the NF of main pathways is explored as shown in Table 1. In the NO removal with HCN cases, CH<sub>4</sub> inhibits the N<sub>2</sub> formation from reactions CNO + NO or CNO via pathways CNO → CN<sub>2</sub>O<sub>2</sub>/N<sub>2</sub>O → N<sub>2</sub> and CNO → C<sub>2</sub>N<sub>2</sub>O<sub>2</sub>/CN<sub>2</sub>O → N<sub>2</sub>. The NFs of NH → HN<sub>2</sub>O/N<sub>2</sub>H → N<sub>2</sub> almost remain the same under varying CH<sub>4</sub> to NO molar ratios. Also, the NFs of CN → CNO<sub>2</sub> → NO and CN → CNO<sub>2</sub> → N → N<sub>2</sub> decrease with CH<sub>4</sub> addition. Overall, CH<sub>4</sub> suppresses the conversion of HCN to both NO and N<sub>2</sub>. Due to the inhibition influence of CH<sub>4</sub> 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 CH<sub>4</sub> addition increases, the NO abatement by NH and NH<sub>3</sub> is weakened in NO reduction with NH<sub>3</sub> cases. The NF of NH<sub>2</sub> → H<sub>2</sub>N<sub>2</sub>O reaches the lowest point when molar ratio CH<sub>4</sub>/NO is 1. Regarding N<sub>2</sub> formation, the contribution of HN<sub>2</sub>O, N<sub>2</sub>O and H<sub>2</sub>N<sub>2</sub>O decreases with CH<sub>4</sub> addition, by contrast, the NFs of N<sub>2</sub>H → N<sub>2</sub> and N<sub>2</sub>H<sub>2</sub> → N<sub>2</sub> fluctuate with molar ratio CH<sub>4</sub>/NO rising. To sum up, the behaviours for NH<sub>3</sub> and HCN to convert NO to N<sub>2</sub> are inhibited by CH<sub>4</sub> molecules addition. Such trends account for the changes of N<sub>2</sub> yield in Fig. 1a and b. The chemical effects of CH<sub>4</sub> on nitrogen-containing species are investigated subsequently to elucidate the N content on other products like NO, HCN/CN, C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> and NH<sub>i</sub> under varying CH<sub>4</sub>/NO molar ratios.

When NO is removed by HCN, the addition of CH<sub>4</sub> promotes the consumption of NO by generating HNO via R1 and R2.

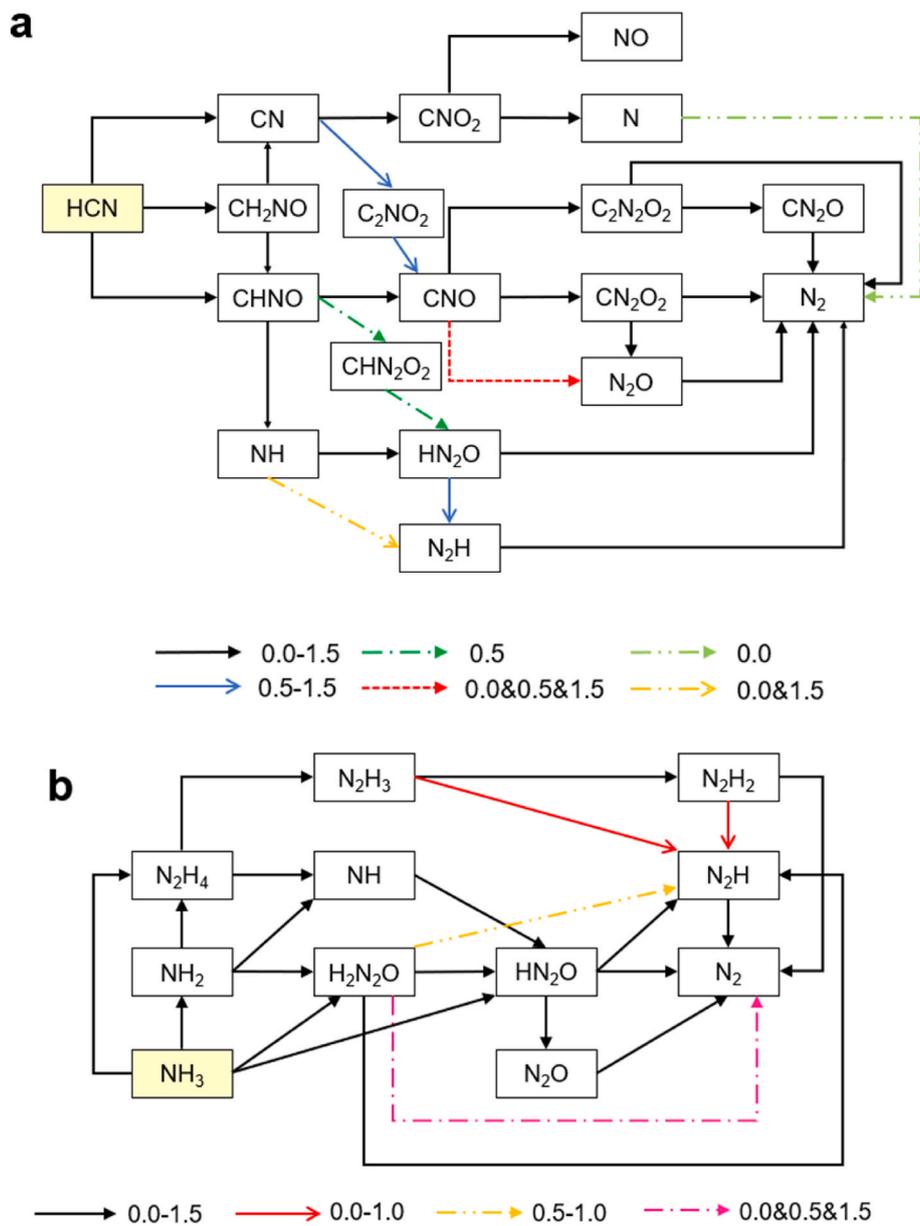


CH<sub>4</sub> promotes the generation of NH<sub>i</sub> by the pathway CH<sub>2</sub>NO → NH<sub>2</sub>, and HNO benefits the NH formation.

CH<sub>3</sub> radicals can react with CNO and form C<sub>2</sub>H<sub>3</sub>NO (R3), which will be converted to HCN/CN by pathways C<sub>2</sub>H<sub>3</sub>NO → CH<sub>2</sub>N/CH<sub>3</sub>N → HCN/CN. The addition of CH<sub>4</sub> reduces the numbers of OH, O and O<sub>2</sub> species by the generation of CO, inhibiting the consumption of HCN and CN by pathways CN → CNO<sub>2</sub>, HCN → CHNO and HCN → CH<sub>2</sub>NO. Therefore, the quantities of HCN and CN at the end of reactions are promoted by CH<sub>4</sub> molecules. In addition, CH<sub>4</sub> promotes the reactions between hydrocarbons (C<sub>x</sub>H<sub>y</sub>) and nitrogen-containing species like NO, HNO, HCN/CN, increasing the C<sub>x</sub>N<sub>y</sub>O<sub>z</sub> content on products.



In the NO removal with NH<sub>3</sub> cases, CH<sub>5</sub>N is formed in CH<sub>4</sub> addition cases via R4, which can be converted to HCN and CN eventually. And the

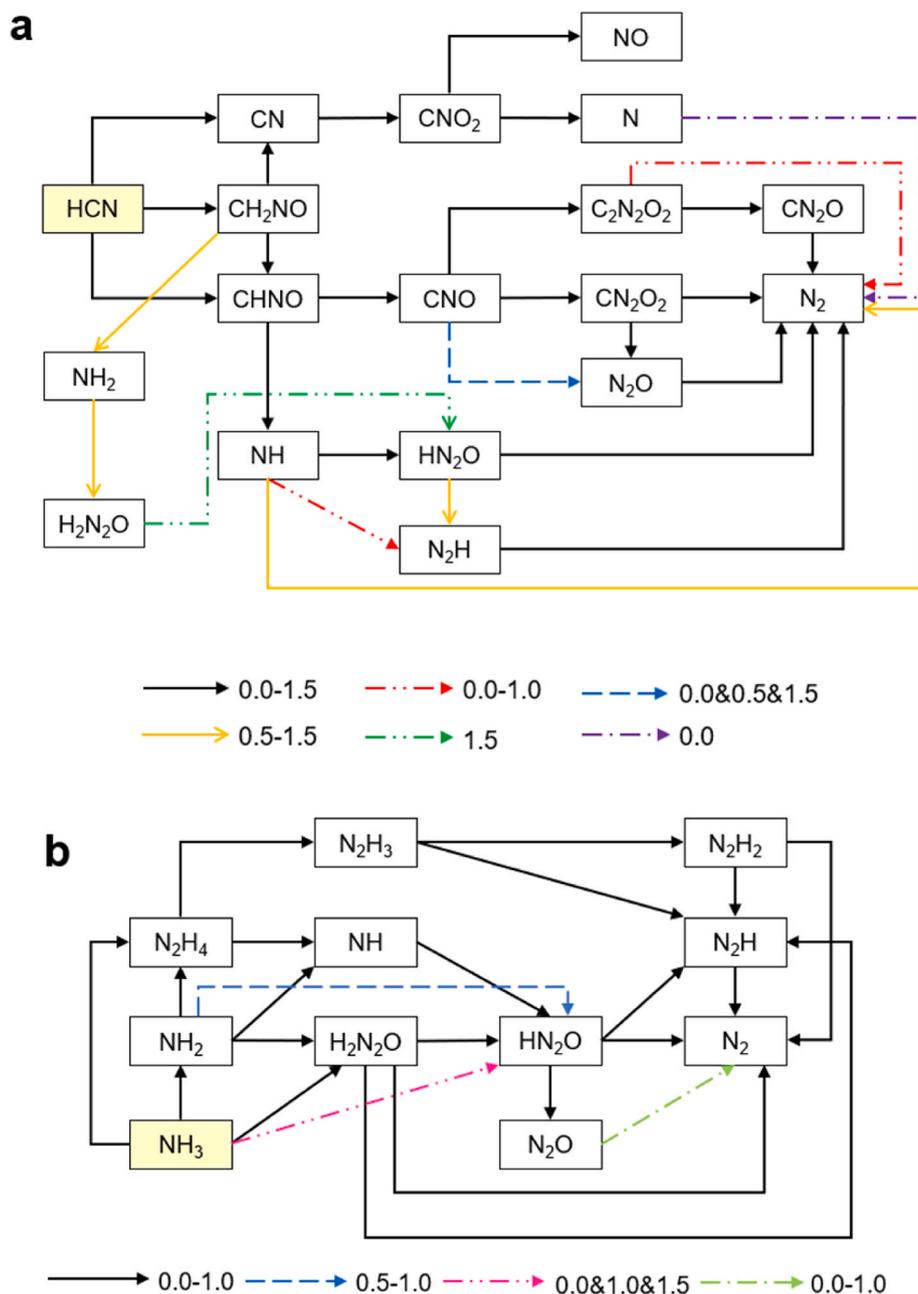


**Fig. 3.** Reaction pathways of NO reduction by (a) HCN and (b) NH<sub>3</sub> with CO addition. The numbers in legends are the molar ratios of CO to NO. Boxes in the yellow indicate species at the start of reactions. (For interpretation of the references to color in this figure legend, the reader is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

**Table 2**

Net flux (NF) of main pathways for NO consumption and N<sub>2</sub> formation in the NO removal by HCN and NH<sub>3</sub> with varying molar ratios of CO to NO.

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



**Fig. 4.** Reaction pathways of NO reduction by (a) HCN and (b)  $\text{NH}_3$  with  $\text{H}_2$  addition. The numbers in legends are the molar ratios of  $\text{H}_2$  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  $\text{NH}_i$  radicals, leading to the decrease of NO reduction performance. The reactions of hydrocarbons ( $\text{C}_x\text{H}_y$ ) 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 $\text{NH}_3$

In Fig. 3, the CO molecules modify the reaction pathways in NO reduction by both HCN and  $\text{NH}_3$ . 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  $\text{N}_2\text{O}$  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  $\text{CO}/\text{NO}$  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  $\text{N}_2$  formation from reactions between N and NO is

not found in CO addition cases. Regarding the influence of CO on NO reduction process by  $\text{NH}_3$ , 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  $\text{CO}/\text{NO}$  is less than  $1.5$ . The conversion from  $\text{H}_2\text{N}_2\text{O}$  to  $\text{N}_2\text{H}$  happens in molar ratio  $\text{CO}/\text{NO} = 0.5$ – $1.0$ . The  $\text{N}_2$  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  $\text{N}_2$  at the end of reactions is further illustrated in terms of NFs reactions related to the formation of NO and  $\text{N}_2$ .

In NO removal with HCN cases, CO molecules react with oxygen-containing species (such as  $\text{O}_2$ , O and OH) and generate  $\text{CO}_2$ .  $\text{CO}_2$  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.



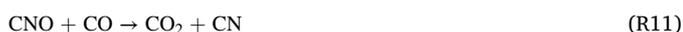
**Table 3**Net flux (NF) of main pathways for NO consumption and N<sub>2</sub> formation during NO removal with HCN and NH<sub>3</sub> with varying molar ratios of H<sub>2</sub> to NO.

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



The decrease of O<sub>2</sub> inhibits in the conversion of CN to CNO<sub>2</sub>. Thus the NFs of CNO<sub>2</sub> → NO and CNO<sub>2</sub> → N → N<sub>2</sub> 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 N<sub>2</sub> formation, the NFs of C<sub>2</sub>N<sub>2</sub>O<sub>2</sub> → N<sub>2</sub> and CN<sub>2</sub>O → N<sub>2</sub> decrease slightly with CO addition. CO inhibits N<sub>2</sub> formation via the pathway CNO → CN<sub>2</sub>O<sub>2</sub>/N<sub>2</sub>O → N<sub>2</sub>. CO enhances the conversion from N<sub>2</sub>H to N<sub>2</sub>, but mitigates the conversion of HN<sub>2</sub>O to N<sub>2</sub> slightly. The consumption of oxygen-containing species by CO suppresses the conversion from HCN/CN to intermediates, such as CNO<sub>2</sub>, CH<sub>2</sub>NO and CHNO. The effects of CO on C<sub>x</sub>N<sub>y</sub>O<sub>z</sub> and NHi formation and consumption are insignificant, and the C<sub>x</sub>N<sub>y</sub>O<sub>z</sub> and NHi contents almost remain the same in all cases.

When NO is removed by NH<sub>3</sub> molecules, CO will react with NH<sub>2</sub> and form CH<sub>2</sub>NO, which will finally be converted to CNO and CN (R7-R11). As a result, the contents of C<sub>x</sub>N<sub>y</sub>O<sub>z</sub> and HCN/CN increase.



The ability of C<sub>x</sub>N<sub>y</sub>O<sub>z</sub> to convert NO to N<sub>2</sub> 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 N<sub>2</sub> formation reduces in CO addition cases as shown in Table 2. Specifically, CO has insignificant influence on NO consumption by NH<sub>3</sub> via pathways NH<sub>3</sub> → HN<sub>2</sub>O and NH<sub>3</sub> → H<sub>2</sub>N<sub>2</sub>O. The conversion from NH to HN<sub>2</sub>O is inhibited with molar ratio CO/NO. The NF of NH<sub>2</sub> → N<sub>2</sub> first increases with the CO addition and then decreases, and the peak NF occurs at molar ratio CO/NO of 0.5. As for N<sub>2</sub> formation, the conversion from HN<sub>2</sub>O, N<sub>2</sub>H and H<sub>2</sub>N<sub>2</sub>O to N<sub>2</sub> is inhibited as the number of CO addition increases. CO has insignificant influence on the NFs of pathways N<sub>2</sub>H<sub>2</sub> → N<sub>2</sub> and N<sub>2</sub>O → N<sub>2</sub>.

### 3.4. Effects of H<sub>2</sub> addition on mechanisms of NO reduction by HCN and NH<sub>3</sub>

Fig. 4 illustrates reaction pathways of NO reduction by HCN and NH<sub>3</sub> with H<sub>2</sub> addition. The addition of H<sub>2</sub> promotes the conversion from NH<sub>2</sub>

to H<sub>2</sub>N<sub>2</sub>O, NH to N<sub>2</sub> and HN<sub>2</sub>O to N<sub>2</sub>H. N → N<sub>2</sub> and H<sub>2</sub>N<sub>2</sub>O → HN<sub>2</sub>O are detected in molar ratio H<sub>2</sub>/NO of 0 and 1.5 cases, respectively. The pathways NH to N<sub>2</sub>H and C<sub>2</sub>N<sub>2</sub>O<sub>2</sub> to N<sub>2</sub> occur when H<sub>2</sub>/NO molar ratios change from 0 to 1.0. In the NO reduction by NH<sub>3</sub> cases, the conversion from NH<sub>2</sub> to HN<sub>2</sub>O is observed in molar ratio H<sub>2</sub>/NO = 0.5–1.0. NH<sub>3</sub> → HN<sub>2</sub>O is not found when the molar ratio of H<sub>2</sub>/NO is 0.5. N<sub>2</sub> generation from N<sub>2</sub>O takes place with H<sub>2</sub>/NO molar ratio ranging from 0.0 to 1.0.

To further account for changes of nitrogen distribution in products with H<sub>2</sub> addition during NO abatement process, we investigated the NFs of main pathways related to NO reduction and N<sub>2</sub> formation as shown in Table 3. In NO removal with HCN cases, the H<sub>2</sub> addition reduces the NFs of CNO → CN<sub>2</sub>O<sub>2</sub>/N<sub>2</sub>O and N → N<sub>2</sub>, but slightly promotes the NO consumption by NH radical and the formation of HN<sub>2</sub>O, N<sub>2</sub> and N<sub>2</sub>H. The pathway CH<sub>2</sub>NO → NH<sub>2</sub> → H<sub>2</sub>N<sub>2</sub>O is enhanced by H<sub>2</sub> molecules in the NO removal process. As for the NO formation, the addition of H<sub>2</sub> significantly inhibits the channel CN → CNO<sub>2</sub> → NO. In addition, the contribution of CNO intermediate to N<sub>2</sub> formation via CNO → C<sub>2</sub>N<sub>2</sub>O<sub>2</sub>/CN<sub>2</sub>O/CN<sub>2</sub>O<sub>2</sub>/N<sub>2</sub>O → N<sub>2</sub> decreases with H<sub>2</sub> addition during NO abatement process. The NFs of N<sub>2</sub> generation from the NH radical via NH → N<sub>2</sub>, NH → HN<sub>2</sub>O/N<sub>2</sub>H → N<sub>2</sub> increase in H<sub>2</sub> addition cases. When NO is reduced by NH<sub>3</sub>, the NFs of NO consumption increase considerably with the number of H<sub>2</sub> added, but the contributions of NH and NH<sub>2</sub> on NO abatement are diminished in H<sub>2</sub> addition cases. Moreover, H<sub>2</sub> has insignificant influence on N<sub>2</sub> generation from HN<sub>2</sub>O and N<sub>2</sub>H, but promotes the conversion from N<sub>2</sub>H<sub>2</sub> to N<sub>2</sub>. The NF of H<sub>2</sub>N<sub>2</sub>O → N<sub>2</sub> decreases in H<sub>2</sub> addition cases. Regarding the pathway N<sub>2</sub>O → N<sub>2</sub>, the NF almost remains the same in molar ratio H<sub>2</sub>/NO = 0.0–1.0, but decreases to 0 in the molar ratio H<sub>2</sub>/NO of 1.5 case. The total NF changes of NO consumption and N<sub>2</sub> formation in both HCN and NH<sub>3</sub> cases are inconsistent with that of NO and N<sub>2</sub> content on products in Fig. 1e and f. To explain this phenomenon, the chemical effects of H<sub>2</sub> linked with NO and N<sub>2</sub> are investigated subsequently.

The addition of H<sub>2</sub> 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 NH<sub>3</sub> cases.



H<sub>2</sub> molecules also benefit the formation of HN<sub>2</sub>O<sub>2</sub>, which will be converted to N<sub>2</sub> eventually (R13-R15). Such pathways reveal the mechanisms for the enhancement of H<sub>2</sub> on N<sub>2</sub> formation in the NO reduction process.



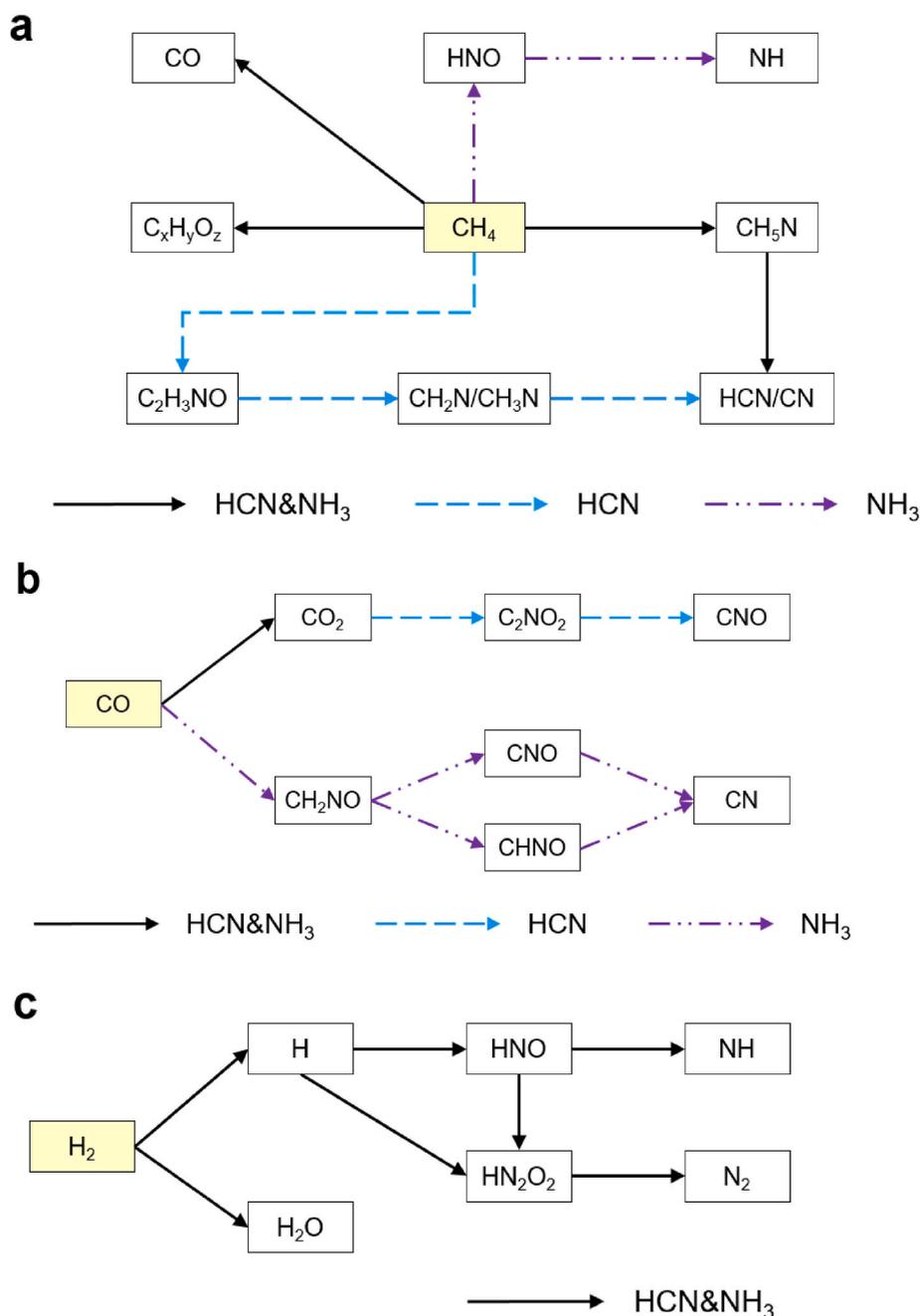


Fig. 5. Diagram of (a) CH<sub>4</sub>, (b) CO, (c) H<sub>2</sub> affecting NO reduction by HCN and NH<sub>3</sub> processes.



Compared with NO, HNO is less reactive with nitrogen-containing intermediates and reduced numbers of N<sub>2</sub> and NH<sub>i</sub> are formed. H<sub>2</sub> decreases the number of active species, such as OH, O and O<sub>2</sub>, by the generation of H<sub>2</sub>O, which inhibits the conversion of HCN/CN to CNO<sub>2</sub>, CHNO and CH<sub>2</sub>NO. The increase of HNO with H<sub>2</sub> addition also benefits the formation of NH in NO reduction by HCN and NH<sub>3</sub> cases.

#### 4. Discussion

In this study, we investigated the influence of CH<sub>4</sub>, CO and H<sub>2</sub> on the NO reduction performance by HCN and NH<sub>3</sub> 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 H<sub>2</sub> and CO [24,25]. The main reason is that the reactive H radicals in CH<sub>4</sub> 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<sub>i</sub> and C<sub>x</sub>N<sub>y</sub>O<sub>z</sub>) in the reburn zone will be oxidized to NO<sub>x</sub> in the burnout zone, N<sub>2</sub> can be chosen as an indicator for NO reduction performance.

For N<sub>2</sub> formation, H<sub>2</sub> molecules present the best performance of the three nitrogen-free additives, and CH<sub>4</sub> the worst. Both CO and CH<sub>4</sub> show inhibition effects on N<sub>2</sub> formation; by contrast, H<sub>2</sub> benefits the generation of N<sub>2</sub>. Therefore, reducing the CH<sub>4</sub> 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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