Full Length Article

Effect of HCl and CO on nitrogen oxide formation mechanisms within the temperature window of SNCR

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ABSTRACT

Selective non-catalytic reduction (SNCR) is an effective way to limit NO emissions in power plants. However, the concentration of HCl in the flue gas may be relatively high for some chloride-containing solid fuels combustion. HCl may play an important role in adjusting NO formation within the temperature window of SNCR. In addition, the various combustion atmospheres (from oxidizing to reducing) can influence pollutant formation. To reveal the effect mechanism of HCl and CO on NO emission, the reaction system is simplified as a $CO/NH_3/O_2/H_2O/HCl$ system with N_2 as the balance gas. The experiments are investigated in a tube flow reactor for CO/NH_3 combustion under the temperature window of SNCR (from 1173 to 1423 K). Different inlet concentrations of HCl, CO, NH_3, O_2, and H_2O with N_2 as the balance gas are used to simulate the process of fuel combustion. The results obtained from the experiments show that HCl addition can decrease the temperature window. HCl can inhibit NH_3 oxidation to NO at 1173 K and exhibits promotion at higher temperatures (> 1173 K). The concentration of NO tends to increase with a slight fluctuation when the concentration of CO increases from 1% to 6% under an oxidizing atmosphere. However, CO inhibits NO emission under lean oxidation conditions. The modeling predictions are in good agreement with the experimental results. The calculated results demonstrate that HCl and CO addition can affect NO formation by the recombination of H, O and OH radicals. The competitive relationships among various elementary reactions determine the final results.

1. Introduction

Chlorine is abundant in some solid fuels used in industrial furnaces, and the content of chlorine in some types of biomass, municipal solid waste (MSW) and coals is often relatively high. Cl mainly exists in organic and inorganic matter and is associated with rock and soil conditions and the growing process of plants. According to researchers [1,2], chloride (Cl) concentrations in fuels can reach 1%. Chloride can be released as HCl or Cl_2 during combustion and can catalyze the recombination of the radicals H, O, OH, etc., which can influence pollutant formation [3–8]. Therefore, it is important to study the effect mechanisms of HCl on nitric oxide (NO) formation during high chlorine fuel combustion and to give guiding opinions on controlling the concentration of NO in the flue gas.

In recent years, the effect of halogens on NO formation has been widely studied; in addition, researchers have found that temperature, carbon monoxide (CO), and H_2O can influence NO formation:

• Chloride: Glarborg [9] pointed out that hidden interactions (Cl, S, N, etc.) can affect pollutant formation and emissions. Due to the interaction of chloride with the combustion process and with other trace species, there is renewed interest in the elementary reactions of chloride. Julien et al. [10] found that the content of Cl in fuels can influence NO, N_2O, SO_2, etc., formation and emission in circulating fluidized bed combustion (CFBC). Chloride addition can inhibit the fuel-nitrogen conversion to NO and N_2O. Gokulakrishana et al. [11] described that the addition of HCl to the fluidizing gas mixture decreased the concentration of NO_x in an electrically heated bed of fluidized sand. The addition of HCl consumes the radical pool of H, OH and O and then inhibits the oxidation of the nitrogen source to form NO_x. The same conclusions were also confirmed in a previous study by our group on a laboratory scale [6,12,13]. The experimental results indicated that HCl tended to inhibit NO formation at lower temperatures (< 1223 K). In addition, a few researchers confirmed that halogens can promote NO emission in fluidized bed combustion (FBC) [14,15].

- Temperature: Temperature has a strong impact on NO formation. The temperature range at which ammonia is most likely to react, causing optimum net reduction of NO, is usually defined as the temperature window. Kang et al. [16] found that the de-NO$_x$ efficiency first increases and then decreases, and the SNCR de-NO$_x$ reaction temperature window is 1123–1323 K. Daood et al. [17] studied NO$_x$ control in coal combustion and found that NH$_3$ tended to be oxidized to form NO rather than being reduced to N$_2$ at a higher temperature (> 1473 K).
- CO concentration: Oxygen-rich or oxygen-lean conditions can also influence NO formation. Guo et al. [18] conducted experiments in an electrical heating horizontal tube furnace and suggested that CO could react with O$_2$ to generate more O radicals. Wargadalam et al. [19] found that CO and CH$_4$ were important to promote homogeneous NO formation in a flow tube reactor of quartz glass. An increase in the CO concentration could increase NO formation. In addition, our group [13] confirmed that sufficient CO combustion might enhance the oxidation of NH$_3$ to NO in an entrained flow reactor.
- Steam: H$_2$O is a vital component of flue gas. Toops et al. [20] studied the effect of CO$_2$, H$_2$O and SO$_2$ on the kinetics of NO formation and thought that H$_2$O can increase the rate of NO reduction. Mueller et al. [21] conducted a kinetic modeling study in a postcombustion modeling study and indicated that increasing the H$_2$O concentration led to an increase in the amount of NO converted to NO$_2$.

In addition, fly ash, metal elements, residence time, etc., can influence NO formation [22]. In general, NO formation can be influenced by many parameters, making it very complicated. The interactions among CO, NO and HCl show that NO formation is sensitive to the influence of HCl and CO. HCl plays a catalytic role in the oxidation of CO and the formation of NO in combustion [23–25]. To date, many researchers have studied the effect of halogens and CO on the formation of NO in FBC, CFBC and electrically heated tube reactors. The reaction temperature is usually lower than that for SNCR denitrification. The main conclusions show that HCl addition can inhibit NO formation [10–13]. However, few works have systematically studied the effect of HCl on NO formation at higher temperatures (higher than the optimum temperature of SNCR). When the reaction temperature is increased, how do HCl and CO influence NO formation—by inhibition or promotion? This effect will be investigated in detail because the reaction mechanisms are found to be very sensitive to the air/fuel ratio, temperature and concentrations of gaseous components.

The real combustion atmosphere is complicated, and the concentrations of HCl and NO precursors (NH$_3$) are determined by the fuel types. In addition, the catalysis of ash or bed materials can interfere with the effects of HCl and CO on NO formation. To explore the effect and reveal the mechanisms of the interactions between NO and HCl or CO, homogeneous experiments and simulation studies are designed and conducted in a tube flow reactor at 1173–1473 K. Therefore, we simplify the combustion atmosphere as a CO/NH$_3$/O$_2$/H$_2$O/HCl system with N$_2$ as the balance gas. Based on the elementary reactions, the effect mechanism of HCl and CO on NO formation during CO/NH$_3$ combustion is analyzed through CHEMKIN.

2. Experimental

2.1. Experimental procedure

The experiments are investigated in a tube flow reactor (TFR) (shown in Fig. 1). The velocity of the gas is low, the temperature is uniform and the viscosity is small. Reaction tube dimensions are selected that minimize axial dispersion in the reactors at given laminar flow conditions (Re ≈ 30). Therefore, the operation condition is similar to the plug flow mode. The length of the reaction zone is 600 mm, and the inner diameter is designed as 20 mm. The reaction temperature can

be controlled by a temperature controller. Heat loss is minimized with a resistance heater that maintains the reactor at a stable reaction temperature. CO, NH$_3$, O$_2$, N$_2$, HCl and H$_2$O are used in the simulated flue gas, and the total gas flow rate is kept at 4 L/min at 293 K and 0.1 MPa. In the experiments, the mixture of gases consists of 3% O$_2$ and 1% H$_2$O, and CO, NH$_3$, and HCl are adjusted as required. N$_2$ is used as the balance gas.

The main gas (N$_2$/O$_2$) flows through the quartz tube reactor and carries reactants (HCl and H$_2$O). The reactant gas (CO/NH$_3$) is added into the reactor via an independent entrance. The reactants can be thoroughly mixed through free diffusion before entering the intermediate main reaction zone. In the experiments, NH$_3$ as a precursor for NO formation is an important nitrogen-containing component released from solid fuels (coal, biomass, MSW, etc.). The concentrations of gaseous CO, NH$_3$, O$_2$ and N$_2$ are each controlled by mass flow controllers (MFCs) with a 1% error. The HCl and H$_2$O can be generated via an acid liquid gasification device [13]. The acid liquid can be added through the injection pump and is heated to gasification through the heater. The acidic liquid can be gasified completely by controlling the flow speed. When the system operates stably, the mole ratio of HCl to H$_2$O in the gas phase is equal to that in the liquid phase.

The concentration of flue gas is determined by using an online gas analyzer (Gasmet DX-4000, Finland), which can precisely measure H$_2$O, CO, CO$_2$, NO, NO$_2$, N$_2$O, SO$_2$, HCl, HF, NH$_3$, HCN, CH$_4$, C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$ and COS with a 2% error. An interference compensation device is added to the gas analyzer to eliminate the error caused by the presence of H$_2$O since the absorption lines of NO and H$_2$O coincide. The average of the data within 60 s under stable conditions is selected as the reference value, and the difference between the maximum or minimum value and the reference value is the value of the error bar.

The operating conditions of the experiment are listed in detail in Table 1. The pressure is 0.1 MPa, and the measured times are 180 s for all various experimental conditions. Before reactants are introduced, N$_2$ is added into the total reaction system to ensure that there is no impurity gas present. N$_2$ can also be used as the balance gas.

2.2. Kinetic analysis

The chemical kinetic behavior of the reactants is modeled via CHEMKIN subroutines to study the effect of HCl and CO on NO formation. According to the simulation results, the distance from the inlet to the reaction region is approximately 5–10 mm, which is less than the initial region length (approximately 35 mm) of laminar flow under the experimental conditions. Therefore, the velocity distribution of the reaction region is still close to a uniform distribution due to not reaching the fully developed region, and the reaction model can be approximately simplified as a plug flow reactor (PFR). The homogeneous reaction system is simulated under real experimental conditions. The program solves the conservation equations for mass and energy for a homogeneous mixture in a closed reactor at 0.1 MPa. According to the design parameters and shape of the reactor, it can be calculated that the mixing time of reactants is approximately 2 ms and heat transfer coefficient is designed as 3 J/m^2·K·s. The reaction mechanisms include 1,112 reversible reactions and 181 species. Simple hydrocarbons (C1-C4) and the detailed nitrogen subset are documented in Refs. [22,26,27]. The chloride reactions are selected from Refs. [24,28] and are incorporated into the mechanism. Sensitivity analysis is conducted to determine the rate-dominating reactions for NO formation in the presence of HCl and CO in the experiments. In the simulation, the sensitivity function is opened, and the data will be calculated through the normalized coefficients. The operating conditions of the simulation are listed in detail in Table 2. The reaction times are 0.25 s for all simulation conditions due to fast rate of gaseous reactions. N$_2$ is used as the balance gas.
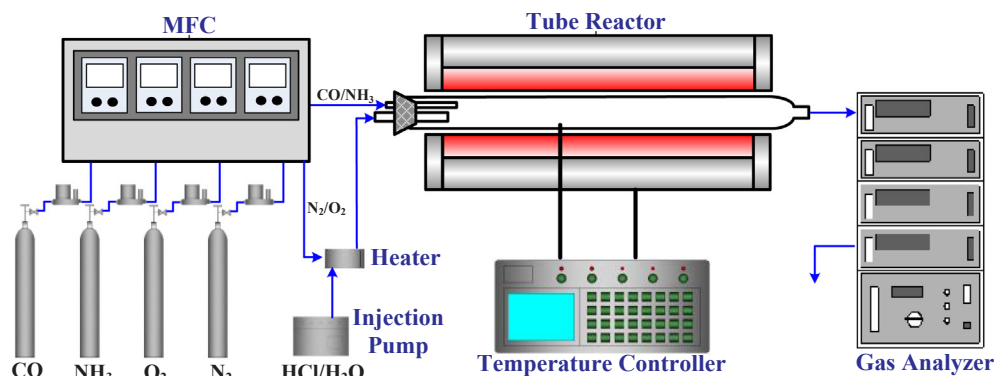
Fig. 1. Schematic diagram of the experimental system.

Table 1
Inlet gas compositions of the experiments.

Test	T (K)	NH$_3$ (ppm)	H$_2$O (%)	O$_2$ (%)	HCl (ppm)	CO (%)	Time (s)
Effect of temperature on NO formation							
1	1173–1423	500	1	3	0	3	180
2					600		
Effect of HCl on NO formation							
3	1273	500	1	3	0–1200	3	180
4		1000					
5		1500					
6	1373	500	1	3	0–1200	3	180
7		1000					
8		1500					
Effect of CO on NO formation							
9	1273	1000	1	3	0	1–8	180
10	1373						

Table 2
Operating conditions of the simulation.

Test	T (K)	NH$_3$ (ppm)	H$_2$O (%)	O$_2$ (%)	HCl (ppm)	CO (%)	Time (s)
Effect of HCl on NO formation							
1	1173	1000	1	3	0–1200	3	0.25
2	1273						
3	1373						
Effect of CO on NO formation							
4	1273	1000	1	3	0	1–8	0.25
5	1373						

3. Results and discussion

3.1. Behavior of HCl during CO/NH$_3$ combustion

When the reaction system reaches a steady state, the concentration variation of HCl is measured by a gas analyzer in 1 min with 600 ppm HCl addition at 1273 K, 0.1 MPa, 3% CO, 3% O$_2$, 1% H$_2$O, 1000 ppm NH$_3$ and 600 ppm HCl and N$_2$ as the balance gas. Fig. 2(a) shows that the concentration of HCl is not changed significantly after the combustion reaction. The results indicate that HCl might act as a "catalyst" in the CO/NH$_3$ combustion system. HCl can indirectly influence NO formation by changing the radical pool. The simulation results are shown in Fig. 2(b) and illustrate that HCl can react with other components to form Cl during combustion as HCl + M = Cl + H (M). After a series of chemical reactions, Cl can be consumed and can regenerate HCl.

3.2. Effect of reaction temperature and HCl addition on NO emission

3.2.1. Effect of temperature on NO formation

Fig. 3 illustrates NO emission in flue gas with increasing temperature. The reaction temperatures from 1173 to 1423 K cover the temperature window of DeNO$_x$ (SNCR) [16,29,30]. The symbols denote the experimental data, while the solid lines denote calculated values. Although there are some differences between the measured concentrations of NO and those of the modeling predictions, they exhibit common variation trends with increasing reaction temperature. At lower temperatures (< 1273 K), NO formation decreases and then increases as the temperature rises from 1273 to 1423 K. As shown in Fig. 3, without HCl addition, significant NO reduction starts at 1223 K and reaches its maximum reduction of approximately 39% at 1273 K. Moreover, with 600 ppm HCl addition, the temperature window can be diminished, and the maximum reduction ratio increases. Therefore, due to significant inhibition of NO formation by HCl at a lower temperature (at 1173 K), the effect of SNCR on NO reduction is weakened. In addition, at higher temperatures (> 1173 K), HCl begins to exhibit a promotion effect on NO formation. A previous study [12,13] showed that HCl addition tends to inhibit NO formation when the reaction temperature is lower than 1223 K. The effect mechanisms of HCl on NO formation when the reaction temperature is on the right side (> 1223 K) of the temperature window of SNCR will be discussed in detail in the next section.

3.2.2. Effect of HCl on NO formation

A previous study [13] indicated that HCl addition mainly inhibits NO formation at 1023–1173 K and exhibits promotion effects at 1223 K. To further clarify the effect of HCl on NO production at higher temperatures, experiments are carried out at 1273 and 1373 K while changing the concentration of HCl from 0 to 1200 ppm. Fig. 4 illustrates the measured and calculated NO emission at different HCl concentrations and reaction temperatures in CO/NH$_3$ combustion. The symbols denote the experimental data, while the solid lines denote calculated values. At 1273 K, as shown in Fig. 4(a), the measured concentrations of NO are 112, 147 and 187 ppm without HCl addition; when 200 ppm HCl is added to the gas, NO concentrations drop gently by 15%, 12%, and 13%, respectively. However, when the inlet concentration of HCl increases to 600 ppm or above, the NO emission begins to increase sharply, which indicates that HCl promotes the transformation from NH$_3$ to NO. For example, with 1000 ppm HCl addition, the NO increase rate with initial NH$_3$ concentrations of 500, 1000, and 1500 ppm is 10.7%, 19.7% and 37.4%, respectively. The effect of HCl on NO formation is more obvious at higher initial concentrations of NH$_3$. In addition, the variation trends of the modeling predictions are consistent with those of the experimental results. NO emission is inhibited when the concentration of HCl is lower than 400 ppm. The generation amount of NO gradually begins to increase with higher concentrations of HCl addition (> 400 ppm). This observation indicates that a small
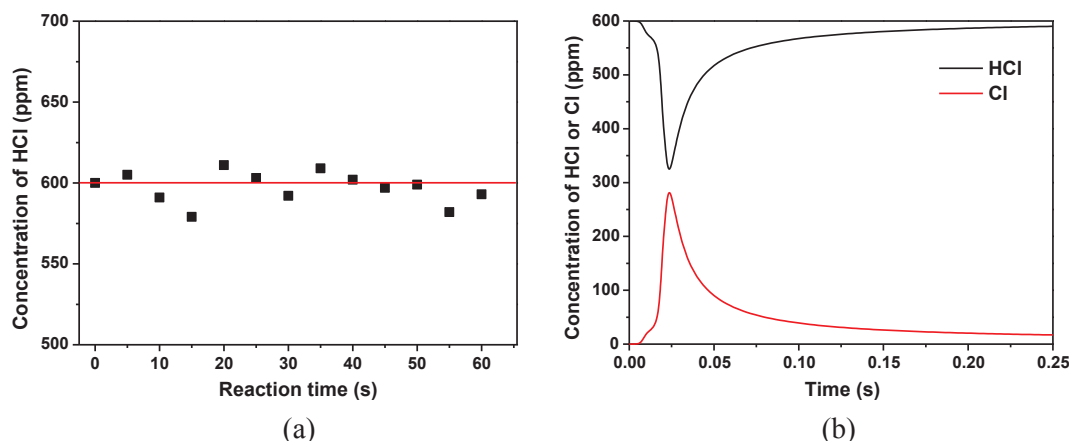
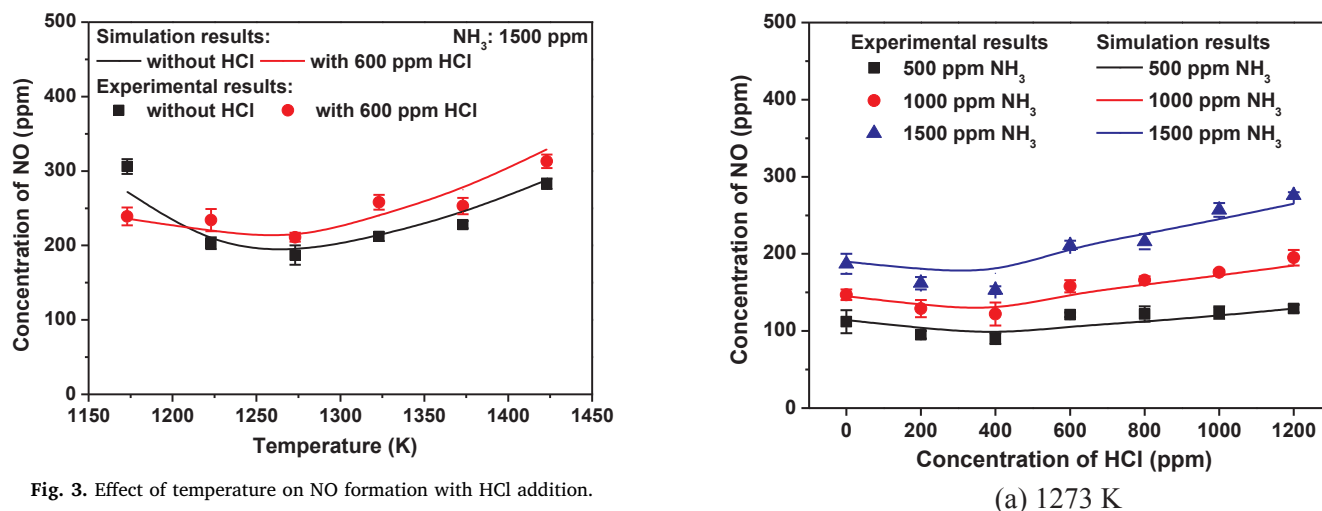Fig. 2. Concentration variation of HCl in the reaction exit.

Fig. 3. Effect of temperature on NO formation with HCl addition.

amount of HCl addition exhibits an inhibitory effect on NO formation; however, as the concentration of HCl increases, the inhibition effect reaches saturation, and the promotion effect of HCl begins to gradually become dominant.

As shown in Fig. 4(b), at 1373 K, when the HCl concentration increases from 0 to 400 ppm, the variation in the NO emission rate is not obvious. This result indicates that a higher temperature can increase the promotion effect of HCl on NO formation and balance the inhibition and promotion effects of HCl. However, HCl begins to promote NO formation when the injection concentration of HCl is over 400 ppm, for example, with 1000 ppm HCl addition; although the measured concentration of NO is reduced gently at an initial 500 ppm of NH_3, the increase rate is 10% and 30.2% at an initial 1000 and 1500 ppm of NH_3, respectively. The calculated results also indicate that HCl addition can promote NO formation and exhibits a more obvious effect at higher concentrations of HCl. In addition, compared with the results gained from 1273 K, the calculated results via modeling predictions exhibit more significant variation trends at 1373 K, which indicates that the promotion effect of HCl on NO formation may be further enhanced at higher temperatures.
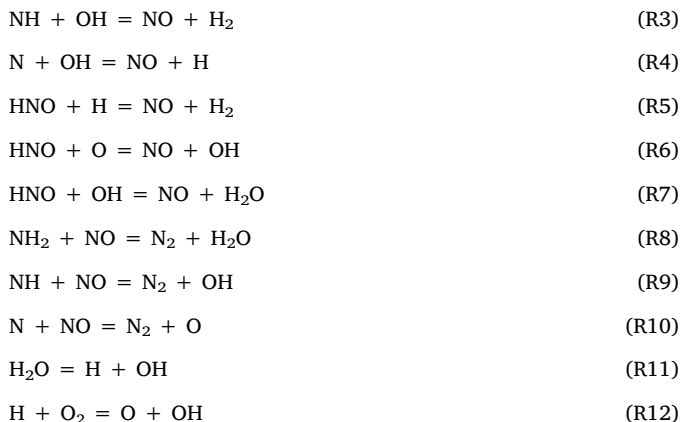
3.2.3. Mechanism analysis of HCl influencing NO formation

The NO formation mechanism includes interactions between the nitrogen source and other components in the radical pool. The pathways of NO formation are mainly through NH and HNO oxidation (R1–R7) [13,19]. The source of NH and HNO comes from NH_3 or NH_2 conversion through radicals of H, O and OH [19,31]. Thus, the concentrations of H, O, and OH are important for controlling NO formation.

(a) 1273 K

(b) 1373 K
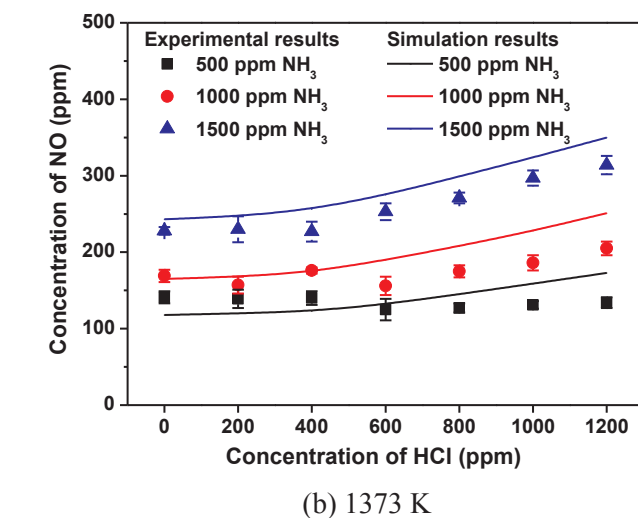
Fig. 4. Comparison of experimental data and modeling predictions for NO formation in a TFR at 0.1 MPa, 3% CO, 3% O_2, and 1% H_2O with N_2 as the balance gas.

In addition, R8-R10 are the major reactions of SNCR that reduce the concentration of NO. The main radical pool comes from R11–R12.

$$NH + H = N + H_2 \tag{R1}$$

$$NH + O = NO + H \tag{R2}$$

$$NH + OH = NO + H_2 \tag{R3}$$

$$N + OH = NO + H \tag{R4}$$

$$HNO + H = NO + H_2 \tag{R5}$$

$$HNO + O = NO + OH \tag{R6}$$

$$HNO + OH = NO + H_2O \tag{R7}$$

$$NH_2 + NO = N_2 + H_2O \tag{R8}$$

$$NH + NO = N_2 + OH \tag{R9}$$

$$N + NO = N_2 + O \tag{R10}$$

$$H_2O = H + OH \tag{R11}$$

$$H + O_2 = O + OH \tag{R12}$$

With HCl addition, sensitivity analysis is performed in the presence of HCl in the reactor, and the sensitivity coefficients are presented in Fig. 5 at 0.1 MPa, 3% CO, 3% O_2, 1% H_2O, and 1000 ppm NH_3 with N_2 as the balance gas. The sensitivity coefficient of R12 is the largest according to CHEMKIN analysis. Fig. 5 illustrates the relative sensitivity coefficients of R13-R15 compared with that of R12 (sensitivity coefficient is 100%). The effect of HCl on NO formation is determined by the competitive relationships between two groups of reactions.
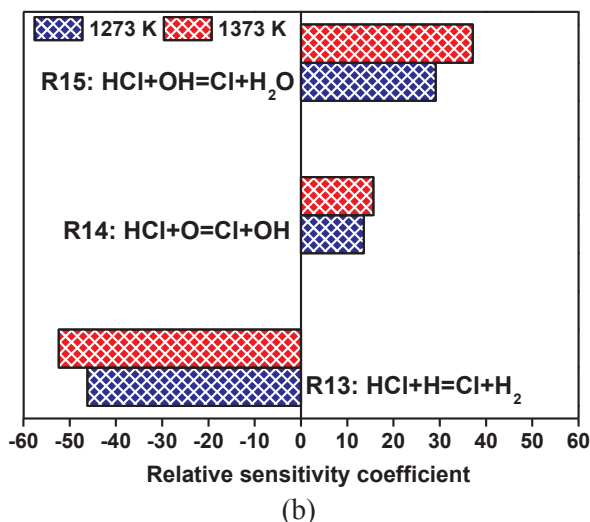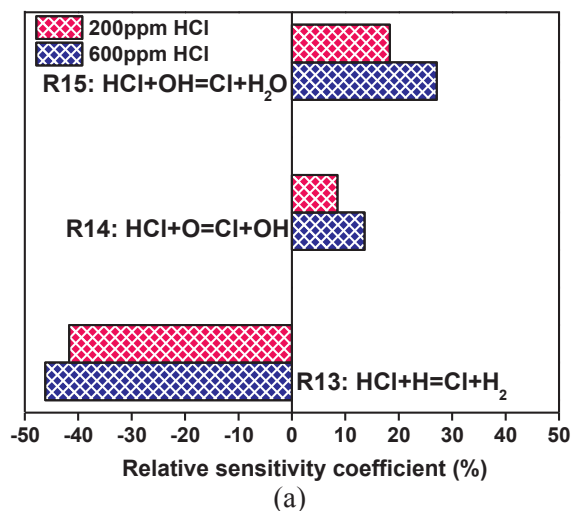

(a)

(b)

Fig. 5. Relative sensitivity coefficients for NO formation in the presence of HCl: (a) T = 1273 K; (b) HCl = 600 ppm.

Inhibition reaction:

$$HCl + H = Cl + H_2 \tag{R13}$$

Promotion reactions:

$$HCl + O = Cl + OH \tag{R14}$$

$$HCl + OH = Cl + H_2O \tag{R15}$$

Negative sensitivity for NO generation is determined by R13 with HCl addition. The H radicals can be consumed, and the radical concentration decreases via R11. R1–R7 will be inhibited, which results in a decline in NO emission. As the reaction temperature and HCl concentration increase, the inhibition effect of R13 begins to be balanced. R14 and R15 gradually become more dominant, and the radical concentrations of Cl and OH are enriched. Although R15 consumes OH radicals, it also generates Cl radicals and promotes NO formation via R16.

$$Cl + HNO = HCl + NO \tag{R16}$$

To explain the results in Fig. 4, it can be seen in Fig. 5 that R13 plays an important role and that the radical pool of H, O and OH is consumed when a small amount of HCl is injected. With increasing HCl concentration, the inhibitory effect of HCl on NO formation is close to saturation. Furthermore, as shown in Fig. 5 (a), the effect of R14 and R15 on NO formation is enhanced. Therefore, the effect of HCl on NO formation exhibits inhibition first and then promotion with increasing HCl concentration at 1273 K, as shown in Fig. 4(a). At the same time, Fig. 5(b) shows that increasing temperature can enhance the impact of R14 and R15 on NO formation. When the HCl concentration is < 400 ppm, the effect of HCl is not obvious due to the interaction effect of R13 and R14 and R15 at 1373 K, as shown in Fig. 4 (b). When the HCl concentration exceeds 600 ppm, the effect of R14 and R15 is enhanced, and NO formation is promoted.

OH radicals have a significant effect on the combustion reaction and NO formation, and the effect of HCl on OH radicals is shown in Fig. 6. At 1173 K, with the concentration of injected HCl varying from 0 to 1200 ppm, the amount of OH radicals gradually decreases because of R13 (HCl + H = Cl + H_2), which results in inhibition of the oxidation of NH_3 to NO. With elevated temperature, the inhibition of OH radical formation by HCl will be weakened at 1273 K. At the same time, HCl addition exhibits a slight promotion of OH radical formation. At 1373 K, the amount of OH radicals generated gradually increases with the concentration of HCl, and NO formation is promoted. The reason for this effect is that R14 (HCl + O = Cl + OH) is promoted at higher temperatures, which can directly lead to OH radical generation, as shown in Fig. 5(b). Moreover, a small amount of HCl addition can
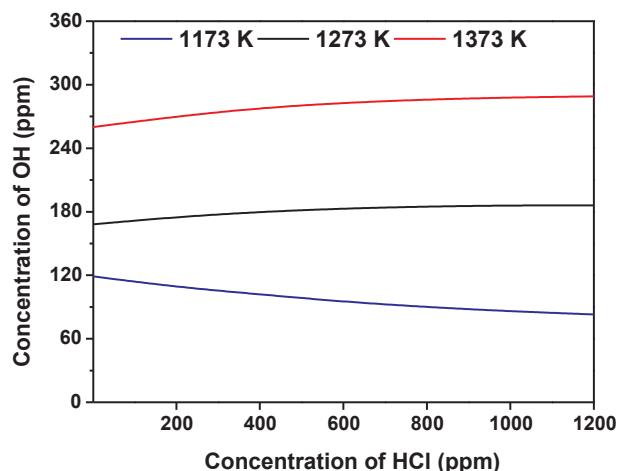

Fig. 6. Effect of HCl content on the concentration of OH radical.
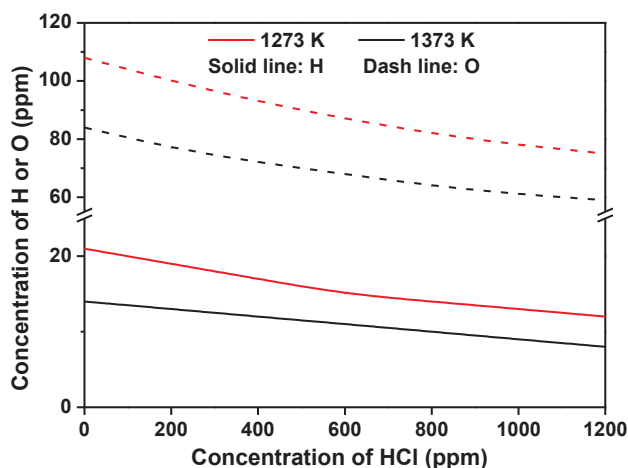
Fig. 7. Effect of HCl content on the concentration of H and O radicals.

balance the inhibition of R13 via R14. If the concentration of HCl is over 600 ppm, the effect of R14 will be further strengthened, as shown in Fig. 5(a), and the balance will be destroyed. R14 will dominate to promote NO formation due to the generation of more OH radicals.

At the same time, as shown in Fig. 5, when the reaction temperature is over 1273 K, HCl addition can consume H and O radicals via R13 and R14, respectively. To clearly show the effect of HCl on the concentration of H and O radicals, the modeling calculation is carried out at 1273 and 1373 K, and the results are illustrated in Fig. 7. The generation amounts of H and O radicals increase at higher temperatures, and the oxidation process of NH_3 to NO is enhanced. However, with HCl addition, the generation amount of H and O radicals will be inhibited. These results are consistent with the conclusions in Fig. 5. Although HCl addition decreases the concentration of H and O radicals, it increases the concentration of OH and Cl radicals, which can directly or indirectly promote NO formation. In addition, the inhibition of H and O radical generation by HCl slightly increases because the relative sensitivity coefficients of R13 (HCl + H = Cl + H_2) and R14 (HCl + O = Cl + OH) strengthen with increasing temperature.

3.3. Effect of CO on NO formation

To study the effect of an oxidizing or reducing atmosphere on NO formation, the CO concentration is varied from 1% to 8% without HCl addition. The O_2 concentration is held constant at 3% (equivalent ratio = 1 at 6% CO). Fig. 8 shows the concentration of NO during CO/
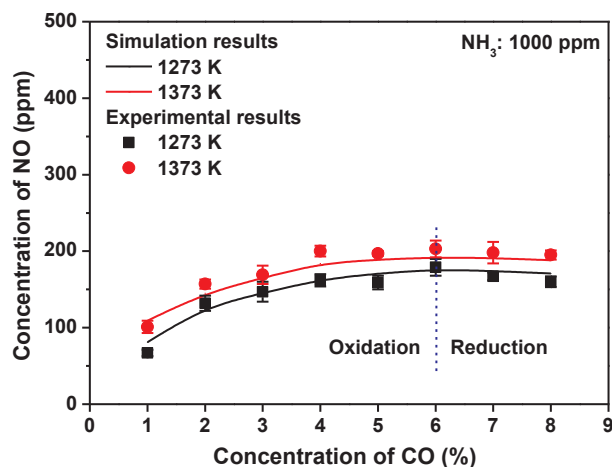
NH_3 combustion. The symbols denote the experimental data, while the solid lines denote calculated values. The measured results indicate that the amount of NO emission significantly increases from 17 to 147 ppm at 1273 K and from 51 to 169 ppm at 1373 K when the concentration of CO increases from 1 to 3%. While the concentration of CO continues to increase to 6%, the amount of NO generated also increases. These results are consistent with the studies reported by Suhimann and Rotzoll [32]. In their experiments, adding CO to the $NH_3/NO/O_2$ system led to more NO release. However, the increasing rate becomes gentle because of the saturation of the radical concentration. Although oxygen is lean for combustion when the concentration of CO is over 6%, NH_3 still tends to form NO. However, excessive CO will compete with NH_3 oxidation for radicals, and CO may also react with NO to form N_2 under a reducing atmosphere [33,34]. Therefore, the NO emission begins to decrease. The modeling predictions match the experimental results at 1273 and 1373 K. The simulation results indicate that a small amount of CO can significantly promote NO emission when the concentration of CO is lower than 4%. However, CO exhibits a slight inhibitory effect when the CO concentration is higher than 6%.

The sensitivity analysis is conducted in the presence of 3% CO in the reactor. Fig. 9 illustrates each relative sensitivity coefficient of R17–R20 [18] at 1273 and 1373 K. The effect of CO on NO formation is determined by the competitive relationships between two groups of reactions.

Inhibition reactions:

$$CO + OH = CO_2 + H \tag{R17}$$

$$CO + O\,(+M) = CO_2\,(+M) \tag{R18}$$

Promotion reactions:

$$CO + O_2 = CO_2 + O \tag{R19}$$

$$CO + HO_2 = CO_2 + OH \tag{R20}$$

Negative sensitivity for NO formation is shown by R17 and R18, via which the radicals of O and OH are consumed. Positive sensitivity is shown by R19 and R20. O radicals are generated through R19, and OH radicals are generated through R20, which has a positive effect on NO formation. The sensitivity coefficients of R19 and R20 are larger than those of R17 and R18 under these conditions. Therefore, a large number of O and OH radicals can be generated, and the oxidation process of NH_3 to NO is promoted. Fig. 10 illustrates that increasing the concentration of CO in the reactor is positive for OH radical generation. By increasing the concentration of CO from 1% to 3%, the generation amount of OH radicals increases sharply and enhances the oxidation of NH_3 to NO. When the concentration of CO is over 4%, the concentration
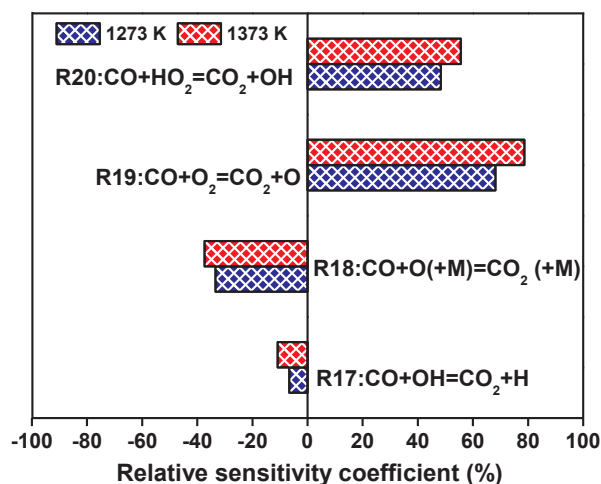

Fig. 8. Comparison of experimental data and modeling predictions for NO formation at different concentrations of CO without HCl addition.

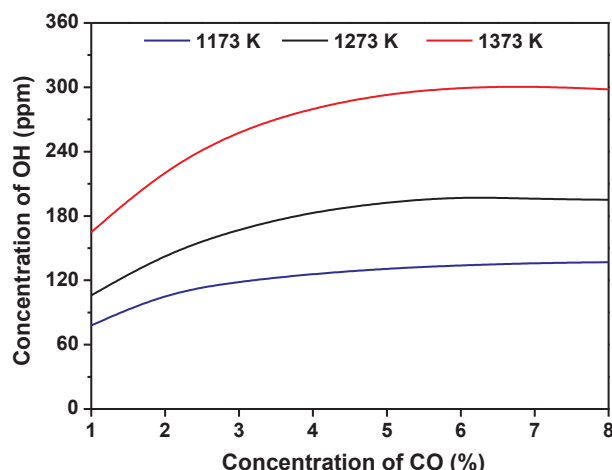**Fig. 9.** Relative sensitivity coefficients for NO formation in the presence of CO.

Fig. 10. Effect of CO content on the concentration of OH radicals.

of OH radicals begins to increase gently, which indicates that the competition for radicals between R17 ($CO + OH = CO_2 + H$) and R20 ($CO + HO_2 = CO_2 + OH$) becomes more balanced.

3.4. Reaction pathway analysis

Based on the above experimental and modeling predictions, the main reaction pathway flux analysis for NO formation is shown in Fig. 11 at 1273 K, 3% CO, 3% O_2, 1% H_2O, 1000 ppm NH_3, and 600 ppm HCl with N_2 as the balance gas. The relative widths of the arrows indicate the importance of the reaction pathway [13,31]. First, NH_3 will react with H, O, and OH radicals to form NH_2. When the reaction temperature is under the window of SNCR, NH_2 can react with NO to form N_2. Second, NH_2 will continue to react with H and O radicals to form NH and HNO at higher temperatures (far from the optimum $DeNO_x$ temperature). Finally, NH will be oxidized to NO by H, O and OH radicals, and HNO can react with H radicals to form NO. In addition, some NH_2 and NH may react with NO to form N_2O, but compared with NO, the amount generated is relatively small. No large amount of N_2O generation is detected during the experiments, and our previous paper [12] also reports the same conclusion.

With HCl addition, the radical pool will be influenced. On the one hand, HCl can consume H, O, and OH radicals to form Cl and other components or radicals. This process will lead to the inhibition of NH_3 oxidation to form NO. On the other hand, HCl can also promote OH radical formation and then promote NO formation. In addition, Cl can directly react with HNO to form NO. Therefore, the concentration of NO emission may be increased with HCl addition. Whether NO formation is

inhibited or promoted will depend on the competitive relationships among various elementary reactions. R13 ($HCl + H = Cl + H_2$) can significantly inhibit the concentration of O and OH radicals by consuming H radicals at lower temperatures or with less HCl addition. At this time, HCl addition inhibits the formation of NO. As the temperature or the concentration of HCl increases, the inhibition effect reaches saturation. HCl addition will strengthen the influence of R14 ($HCl + O = Cl + OH$), which will dominate to promote NO formation due to the generation of more OH and Cl radicals. In addition, sufficient CO can promote the oxidation of NH_3 to NO by generating more radical sources. However, excessive CO may also compete with NH_3 oxidation for radicals.

4. Conclusions

In this paper, the formation of NO in the presence of HCl and CO during CO/NH_3 system combustion is investigated in a tube flow reactor (TFR) under laboratory-scale conditions with temperatures varying from 1173 to 1423 K. The results indicate that NO formation is sensitive to the temperature and the concentration of HCl or CO. The modeling predictions can match the measured results. The main conclusions are as follows:

1. NO formation decreases and then increases as the temperature increases from 1173 to 1423 K. HCl has a negative effect on NO formation at 1173 K and exhibits a positive effect at higher temperatures (> 1173 K). HCl addition can also decrease the temperature window.
2. As the concentration of HCl increases from 0 to 1200 ppm at 1273 and 1373 K, HCl addition mainly tends to promote NO formation. The simulation results indicate that HCl can influence the radical pools and then promote NO formation directly or indirectly by generating Cl and OH radicals. Inhibition of NO formation by HCl is mainly through "$HCl + H = Cl + H_2$", and promotion of NO formation is via "$HCl + O = Cl + OH$", "$HCl + OH = Cl + H_2O$" and "$Cl + HNO = NO + HCl$".
3. As the concentration of CO increases from 1% to 6%, the oxidation process of NH_3 to NO is promoted under an oxidizing atmosphere. However, excessive CO (over 6%) may inhibit NO emission due to the competition for O_2 between CO and NH_3 oxidation and may react with NO to form N_2 under a reducing atmosphere. The calculated results indicate that CO can promote NO formation by generating a large number of O and OH radicals.

CRediT authorship contribution statement

Jing Zhao: Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing - original draft. **Xiaolin Wei:** Conceptualization, Supervision, Validation, Writing - review & editing. **Teng Li:** Conceptualization, Methodology, Supervision. **Sen Li:** Methodology, Formal analysis, Supervision.

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.
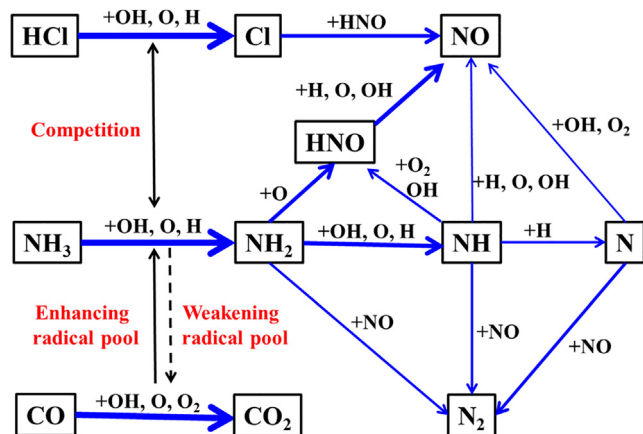
Acknowledgements

Fig. 11. Reaction pathway diagram of NO formation.

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