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Experimental and Numerical Study of the Nitrogen Transformation Mechanism in the Reburning Zone

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by using image spectroscopy. The results of image spectroscopy showed that the simultaneous presence of NO and NH_3 led to the decrease of OH and the increase of NH and CN. It was also found that the reduction of NO occurred earlier than the oxidation of NH. In addition, the spatial distribution of the reaction rate between NH and OH was obtained by calculating the product of spontaneous emission intensity of NH and OH. The rate of production (ROP) of NO was used to generate the mechanism of NH_3 and NO coexistence on nitrogen transformation. The results showed that in NO + NH_3 flames, the acceleration of the oxidation reaction rate of nitrogenous intermediates was limited, but the reduction reaction rate of NO increased rapidly relative to other flames, which led to the decrease of NO when NO and NH_3 coexist. This study revealed the mechanism of the coupling effect of NO reduction and NH_3 oxidation on the nitrogen conversion, which provides theoretical guidance for improving the NOx removal effect in the reburning zone.

1. INTRODUCTION

Nitrogen oxides (NOx) are inevitably produced during fuel combustion and cause harm to the environment. A number of techniques have been implemented in industrial production to reduce NOx generated during fuel combustion. Among the alternatives, reburning is regarded as one of the promising and cost-effective NOx reduction strategies. The removal effect of NOx in the reburning zone is jointly affected by various operational parameters. The results of Liu et al.¹ showed that the concentration of NO released during coal combustion was $700-2000 \text{ mg/m}^3$. They also indicated that reduction of particle size was beneficial for eliminating NO. Chae et al.² compared the reduction effect of CH₄/CO/H₂ on NO and found that the promotion effect of CH₄ on NO reduction was stronger than that of CO and H₂. Munir et al.³ declared that addition of biomass to coal coupled with air-staging and fuelstaging techniques was significant to reduce NOx and improve the char burnout efficiency. Hu et al.⁴ proposed that CO₂ had a significant inhibitory effect on NO reburning by syngas independent of variations in reaction temperatures, equivalence ratios, and initial ratios of hydrogen to carbon monoxide. Li et al.⁵ also showed that NO reduction efficiency

in a CO_2 atmosphere was lower than that in a N_2 atmosphere. It can be seen that the application of appropriate operational parameters could effectively improve the removal efficiency of NOx in the reburning zone.

The effect of operational parameters on the nitrogen conversion is realized by changing the main reaction path and key groups. There are many studies to reveal the key groups and main reaction pathways in the reburning zone. Wang et al.⁶ pointed out that C_2H_2 was the key hydrocarbon in the NO reduction when methane was the reburning fuel. They indicated that the reaction between CH₃ and NO had a significant effect on the conversion of NO to HCN, NH₃, and HNCO. The interactions of NO with H and OH radicals mainly occurred in the weak reducing atmosphere, which

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Figure 1. (a) Schematic diagram of the premixed flame experimental platform and (b) diagram of gas flow in the burner.

contributed to remove a small part of NO to N₂.⁷ Yamamoto and Kajimura⁸ indicated that HCCO played a major role in NO reduction and that the most important reactions for NO reduction were HCCO + NO = HCN + CO₂ and NCO + NO = N₂ + CO₂ when using dimethyl ether as a reburning fuel. He et al.⁹ claimed that NO was mainly reduced by NH₂ and NH as a result of the enhancement of the NCO \rightarrow HNCO \rightarrow NH₂ \rightarrow NH channel under fuel-rich and stoichiometric conditions in O₂/H₂O atmospheres. Under fuel-lean conditions, NCO had an important influence due to the strength of the HNCO \rightarrow NCO channel. It can be concluded that, in the reburning zone, the conversion of NO is a chemically complex process, which is affected by the partial oxidation of the reburning fuel, reaction between hydrocarbon radicals and NO, and subsequent conversion of the intermediate nitrogenous species.

The above studies only analyzed the formation and transformation of NO in the reburning zone, but volatile nitrogen released from reburning fuel also affected the nitrogen transformation. The pyrolysis results showed that NH₃ was the main volatile nitrogen released from biomass and low-rank coal.¹⁰⁻¹² The results of Anca-Couce et al.¹³ showed that the concentrations of NH₃ released during the combustion of miscanthus pellets and corncob pellets were 1000 and 1400 ppm, respectively. With the increase of nitrogen content in fuel, the conversion yield of fuel nitrogen to NH₃ increased. Therefore, the oxidation of NH₃ also plays an important role in the nitrogen transformation of the reburning zone. On the basis of numerical simulation, Liu et al.¹⁴ analyzed the oxidation of NH₃ in the counterflow flame with a premixed CH₄/NH₃/O₂/CO₂ combustible mixture and N₂. It was concluded that the NH₃ reaction path was mainly NH₃-NH₂-NH-N₂/NO and the secondary reaction path was NH₃-NH₂-HNO-NO. In addition, with the increase of equivalence ratio, NH₂ tended to convert to NH. Meanwhile, Mendiara and Glarborg¹⁵ proposed that, in the $CH_4/NH_3/O_2/N_2$ premixed

flame, NO was mainly generated by the oxidation of HNO, and the major source of HNO was $NH_2 + O$. The secondary intermediate was NH, mainly formed by $NH_2 + H$. The formation of N_2 was mainly via the reaction of NH_2 and NH with NO. The study conducted by Tian et al.¹⁶ confirmed that NH_2 , NH, and HNO were the key species in the oxidation of NH_3 , and the conversion of NO and N_2 was mainly affected by the reactions $H + O_2 = O + OH$, $NH_2 + O = HNO + H$, $NH_2 + NO = N_2 + H_2O$, and $NH + NO = N_2O + H$. It can be seen that the oxidation of NH_3 is a coupling of multiple pathways involving a variety of reactions and groups.

The joint interaction between NH₃ issued from N-fuel oxidation and NO issued from either thermal NOx or fuel NOx in the reburning zone can be expected. There are some reports on the effects of NO and NH₃ coexistence on nitrogen transformation. Lamoureux et al.¹⁷ investigated the nitrogen conversion in the $CH_4/O_2/N_2$ flame doped with NO, NH₃, or $NH_3 + NO$ via molecular beam mass spectrometry (MBMS). The NO conversion yield in the front flame doped with NH₃ + NO was higher than that in the flame doped with NH₃, indicating that NH₃ had a certain interaction with NO. Sun et al.¹⁸ analyzed the interaction between NH₃ and NO by using FTIR to detect NO concentration in flue gas. The results showed that the reduction of NO by gas-phase reaction was enhanced by NH₃ in fuel-lean conditions at a higher temperature. In fuel-rich conditions, the reduction of recycled NO by hydrocarbon radicals played an important role. On the basis of MBMS, Bian et al.¹⁹ discovered that, in lean flames, NH₃ was converted into NO with a conversion yield of 0.5 independently of the presence of NO in the reactants. In stoichiometric flames, the conversion yield of NH3 was quasi null in the presence of NO. Therefore, the coupling of NH₃ oxidation and NO reduction in the reburning zone will lead to a more complicated nitrogen transformation mechanism.

Overall, the effect of coexistence of NH_3 and NO on NO removal efficiency was analyzed according to the component information by sampling gas through MBSM or FTIR, but the nitrogen conversion mechanism in the presence of NH_3 and NO was not fully revealed. Moreover, during the sampling process, the change of temperature and other conditions may lead to reaction or attenuation of radicals. Therefore, it is crucial to obtain the in situ components and radical information in the flame to reveal the mechanism of nitrogen transformation.

As a kind of noninvasive optical detection technology, combined with image processing algorithms, image spectroscopy has been widely used in combustion diagnosis,^{20–31} such as alkali release,²⁶ flame temperature,²⁹ and stoichiometry.³⁰ Image spectroscopy is also a typical technology to obtain excited-state radicals. Zhang et al.²⁰ characterized the reaction zone by measuring OH, CH, and C₂ in CH₄/O₂ co-flow jet diffusion flames. By means of image spectroscopy, Hu et al.²¹ claimed that the OH radicals could be considered as a good indicator of the heat release rate in the coal-water slurry diffusion flames. Smith et al.³¹ used image spectroscopy to determine the absolute excited-state concentrations and extracted rate constants of groups in three low-pressure premixed methane–air flames.

In this work, the concentration of NO or NH_3 doped in the flame (2000 ppm) was set to be similar to the concentration of NO released by solid fuel combustion and NH_3 released by biomass combustion to characterize the reduction of NO and oxidation of NH_3 , respectively. The above two flames were further compared with the methane flame doped with the mixture of NH_3 and NO (2000 ppm) to reveal the influence on NO reduction and NH_3 oxidation when NO and NH_3 coexist so as to obtain the NH_3/NO conversion in the reburning zone. Image spectroscopy was used to reveal the change of spatial distribution characteristics of radical spontaneous emission in the flame. The reaction path and reaction rate of N species were analyzed in detail on the basis of the results of numerical simulation.

2. METHODS

2.1. Experimental Setup. Figure 1a shows the experimental setup of the premixed flame experimental platform. The flow of gas was controlled by a mass flow meter. The gas was uniformly mixed in a gas mixing tank and then passed into a co-flow burner. The fuel was introduced from the inlet at the lower part of the burner and ejected from the pipe with a diameter of 10 mm at the center of the burner. To avoid fuel contact with the atmosphere, nitrogen was introduced as a co-flow gas from the upper inlet of the burner and ejected from the annular flow straightener at the top of the burner. The diagram of gas flow in the burner is shown in Figure 1b. Stable methane premixed laminar jet flame was obtained by artificial ignition. NO/NH₃/NO + NH₃ were added to the premixed gas to obtain the methane premixed flame doped with $NO/NH_3/NO + NH_3$. The total inlet flow rates of the three flames were 5.33 L/min. To avoid the effect of different N_2 flow rates on nitrogen conversion, the N2 flow rates in the three flames were set to be the same. Ar was introduced to ensure the consistency of total gas flow. Compositions and flow rates of gases are shown in Table 1.

An ICCD (DH734, Andor) camera was coupled with different filters to detect key radicals in the nitrogen conversion. The results of Zhang et al.²⁰ and Mashruk et al.³² showed that obvious NH/CH/CN/OH spontaneous emission peaks could be observed in the N-species-doped methane flame in the wavelength range of 300-450 nm. The wave peaks of each radical was far apart, so the cross talk between the spontaneous radiation of radicals was not obvious in this

Table 1. Flow Rates of Gases in Flames (mL/min)

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CH_4	O ₂	N_2	NH ₃	NO	Ar
475	950	3700	10	0	190
			0	10	190
			10	10	180
			0	0	200

work. The spontaneous emission of CH was specifically obtained by using a filter with a center wavelength of 434 nm (FF01-434/17-25, Semrock). A filter with a central wavelength of 340 nm (FF01-340/ 26-25, Semrock) was selected to specifically obtain the spontaneous emission of NH. The spontaneous emission of CN was specifically obtained by using a filter with a central wavelength of 390 nm (FF01-390/18-25, Semrock). A filter with a central wavelength 315 nm (FF01-315/15-25, Semrock) was selected to obtain the spontaneous emission of OH, and a bandwidth filter (FGUV11, Thorlabs) was used to reduce the interference of yellow-green light on the spontaneous emission of OH.

2.2. Abel Inversion. As shown in Figure 2, the spectra observed from an inhomogeneous and axisymmetric spectroscopic source are



Figure 2. Sketch map of Abel inversion.

integrated along the line of sight. To obtain the spectroscopic radiation with spatial resolution, it is necessary to carry out a deconvolution technique that allows the emissivity to be deduced from different regions. For the infinitesimally narrow probe beam, the relationship between the line-of-sight integral projection data I(y) and the emissivity X(r) is shown in eq 1.

$$I(y) = 2 \int_0^x X(r) dx \tag{1}$$

Equation 1 can be converted into polar coordinates to obtain eq 2, which is called Abel transformation.

$$I(y) = 2 \int_{y}^{R} \frac{X(r)r}{\sqrt{r^{2} - y^{2}}} dr$$
(2)

The analytic inversion of the projection data to the emissivity X(r) is well known as Abel inversion.

$$X(r) = -\frac{1}{\pi} \int_{r}^{K} \frac{dI(y)/dy}{\sqrt{y^{2} - r^{2}}} dy$$
(3)

However, there are two drawbacks. The first one is the difficulty in making a precise determination of the derivative dI(y)/dy from experimental data with random errors, and the other is the divergence of the integrals for y = r.³³ Therefore, numerical transformation methods are usually used to avoid these drawbacks. The cubic spline function³⁴ is one of the most common numerical transformation methods applied in Abel inversion and was chosen in this work.

2.3. Contour Extraction Algorithm. Image contour is the most obvious spatial position of image intensity change. The upper and

lower boundaries of the group could be obtained by contour extraction of the radiation images of each group so as to obtain the spatial information of the generation and transformation of each group.

The most common method of image contour extraction, i.e., edge detection, is used to detect the discontinuity of brightness value. Generally, it could be obtained by detecting the image gradient.

$$G[f(x, y)] = \left[\left(\frac{\partial f}{\partial x} \right)^2 + \left(\frac{\partial f}{\partial y} \right)^2 \right]^{1/2}$$
(4)

where f(x, y) is the gray value of pixel, $\frac{\partial f}{\partial x}$ is the partial derivative of the gray value of the pixel to the *x* axis, and $\frac{\partial f}{\partial y}$ is the partial derivative of the gray value of the pixel to the *y* axis.

The product of the edge detection operator and pixel gray value is often used to characterize image gradient. Common simple edge detection filters include the Sobel,³⁵ Prewitt,³⁶ and Roberts³⁷ operators. Because of the advantages of simple operation and rapid computation, the Sobel operator was used to detect the edge of the image and extract contour features.

2.4. Kinetic Modeling. Sensitivity analysis, rate of production (ROP) analysis, as well as the main compound concentrations were modeled relying on a detailed kinetic database using the Premixed Laminar Flame-Speed Calculation program from the Chemkin PRO package. The parameters GRAD = 0.02 and CURV = 0.02 resulted in a grid of ~650 points. Although methane premixed jet flame was applied in this paper, it had been shown that the spatial distribution of the radicals in the multidimensional flame was consistent with the results of the one-dimensional simulation.³⁰ The mechanism proposed by Okafor et al.³⁸ had been shown to be reliable in a wide range of NH₃ concentrations (0–0.3) and equivalence ratios (0.8–1.3) and was applied in this work.

3. RESULTS AND DISCUSSION

3.1. NO Concentration of Flue Gas in Flames. To obtain the influence of coexistence of NH₃ and NO on NOx production and conversion yield, the NO concentrations in different flames' flue gases were detected by a portable ultraviolet flue gas analyzer (HGA-OES-P01, CN Test, resolution 0.1 ppm, measurement error 2%). The measurement range of NO of the equipment is only 0-500 ppm, which is lower than the NO concentrations of flue gas in this work. Therefore, 48.6 L/min of Ar was injected into the flue gas to dilute the NO concentration to the original 1/10 to facilitate detection. When detecting the flue gas, a protective cover with a height of 500 mm was added to the burner, and the flue gas was transmitted to the flue gas analyzer through the outlet at the upper end of the protective cover. Equation 5 was used to calculate the conversion yield of NO to eliminate the interference of prompt NOx and thermal NOx on nitrogen conversion. The actual NO concentration, fluctuations of NO concentrations, and NO conversion yield in flue gas are shown in Table 2. All NO concentrations were the average of 3 min after the flue gas analyzer readings became relatively stable. The temperatures of methane flame measured by thermo-

Table 2. NO Production in Flue Gas

	NH3-doped flame	NO-doped flame	NH ₃ + NO- doped flame	non-N- doped flame
concentration (ppm)	1370 ± 10	1850 ± 20	2710 ± 20	50 ± 10
conversion yield	66.0%	90.0%	66.5%	

couples were about 1250 K. The results of the flue gas analyzer showed that the concentration of NOx generated in the non-N-doped flame was 50 ppm, which also indicated that thermal and prompt NOx generation was less.

$$\phi = \frac{c(\text{NO}_{\text{out}}) - c(\text{NO}_{\text{none}-\text{N}})}{c(\text{N}_{int})} \times 100\%$$
(5)

where $c(NO_{out})$ represents the concentration of NO in flue gas, $c(N_{int})$ is the sum of NH₃ concentration and NO concentration added in the premixed gas, and $c(N_{none - N})$ represents the NO generated in the flame without the addition of NH₃ or NO.

It can be seen from Table 2 that only 66.0% of NH_3 is converted into NO through oxidation reaction, indicating that a considerable proportion of NH_3 is finally converted into N_2 . In the NO-doped flame, 10% of NO is converted into N_2 and other N species, indicating that CH_4 has an effective effect on NO reduction. The NO concentration in the flue gas of the NO + NH_3 -doped flame is higher than that of the other two flames. However, the NO conversion yield of the NO + NH_3 doped flame is significantly lower than that of the NO-doped flame, which is similar to that of the NH_3 -doped flame, indicating that the simultaneous presence of NH_3 and NO would inhibit the production of NO.

3.2. NO Sensitivity Analysis of Different Flames. The positive and negative values of the sensitivity coefficient represent the promotion and inhibition of NO formation, respectively. The larger the absolute value is, the more significant is the effect of the reaction on the formation or transformation of NO. It can be seen in Figure 3 that the reactions with a significant influence on NO generation and transformation are mainly R1-R15. The positive sensitivity coefficient of R1 is the largest in all flames, indicating that it has the most significant promoting effect on NO generation. This is attributed to the fact that R1 is the main reaction to generate OH and O, which are the key groups to oxidize N. It can be corroborated by the positive sensitivity coefficient of the OH/O-consuming reactions (R2/R3/R4/R5). The oxidation reactions of NH₂/NH/N (R2/R3/R5) are important paths for NO generation, so these reactions could promote the generation of NO. Compared with the NH₃-doped methane flame, in the NO-doped flame, the promotion effect of R4 on NO formation is weaker and that of R6/R7 is stronger. It can be seen that the promotion effect of R4/R6/R7 of the flame doped with NO + NH_3 on NO formation is greater than that of the other two flames.

In all flames, R8 and R9 have the largest negative sensitivity coefficient, indicating that the NO reduction reactions are the most important for the inhibition of NO formation in the three flames. Compared with the flame doped with NH₃₁ in the flame doped with NO + NH_3 , the inhibitory effect of R8/R9 is stronger and that of R15 is weaker. Because NH₂ and NH would reduce NO to N2, R10 and R11 exhibit a negative sensitivity coefficient. It is worth noting that the inhibitory effect of R10 and R11 on NO formation in NH₃-doped flame is stronger than that in NO + NH₃-doped flame. In NO- and NO + NH₃-doped flames, reactions R12 and R13 play an important role in NO formation inhibition, especially for NOdoped flame. Therefore, when NO and NH₃ coexist, the formation of NO is jointly inhibited by reaction of NO with CH_i, NO reduction reactions, and stepwise hydrogen desorption reaction of NH₃.



Figure 3. Sensitivity bar chart of NO in flames: (a) positive sensitivity coefficient and (b) negative sensitivity coefficient.





$H + O_2 = OH + O$	(R1)	$N + NO = N_2 + O$	(R8)
$NH_2 + O = HNO + H$	(R2)	$NH + NO = N_2O + H$	(R9)
NH + O = NO + H	(R3)	$\mathrm{NH}_3 + \mathrm{OH} = \mathrm{NH}_2 + \mathrm{H}_2\mathrm{O}$	(R10)
$OH + CH_4 = CH_3 + H_2O$	(R4)	$\rm NH_2 + \rm H = \rm NH + \rm H_2$	(R11)
N + OH = NO + H	(R5)	$CH_2 + NO = H + HNCO$	(R12)
$O + CH_3 = H + H_2 + CO$	(R6)	CH + NO = HCN + O	(R13)
$CH + O_2 = O + HCO$	(R7)	$OH + CH_3 = CH_2(S) + H_2O$	(R14)



Figure 5. Spatial distribution of the radiation intensity of OH in NO + NH₃-doped flame after Abel inversion.

 $NH_2 + NO = N_2 + H_2O$ (R15)

3.3. Radical Measurements by Image Spectroscopy. According to the results of NO sensitivity analysis, OH, CH, and NH are key groups for the generation and transformation of NO, so their distribution characteristics have important significance for the study of nitrogen transformation. As an important intermediate nitrogen-containing group for nitrogen transformation, CN was also analyzed in this work. Thus, the spontaneous emissions of OH/CH/NH/CN in flames were collected in different flames, and the results are shown in Figure 4. It can be seen that the gray value of different radicals in flames obtained by image spectroscopy is stronger at the flame edge. However, the gray value directly collected by ICCD is integral along the line of sight. Therefore, the images of radicals were processed by Abel inversion to obtain the real spatial radiation distribution of radicals. Because the spatial distribution of different radicals is similar, only the spatial distribution of OH in the flame doped with NO + NH₃ is taken as an example, which is shown in Figure 5. It could be found that radicals are mainly distributed near the flamelet, and the radiation intensity of radicals in different regions of the flame is different, where it is weak at the top of the flame and near the burner nozzle and larger in the area 3-15 mm from the nozzle.

To obtain the effect of NO and NH₃ on radicals, the total radiation intensity of radicals after Abel inversion in different flames was compared. The results are shown in Figure 6. The error bar in the figure is the standard deviation of the total intensity of 10 images. In the three flames, the order of CH total radiation intensity is NH₃-doped flame > NO + NH₃doped flame > NO-doped flame; that of CN total radiation intensity is NO + NH3-doped flame > NH3-doped flame > NO-doped flame; that of NH total radiation intensity is NO + NH₃-doped flame > NH₃-doped flame > NO-doped flame; and that of OH total radiation intensity is NO-doped flame > NH₃doped flame > NO + NH₃-doped flame. The total radiation intensity of CH in the three flames indicates that the addition of NO inhibits the formation of CH and the addition of NH₃ boosts the formation of CH. The total radiation intensity of nitrogen-containing intermediate radicals (NH/CN) is the smallest in NO-doped flame and largest in NO + NH₃-doped flame. The reason is that only part of NO is converted into nitrogen-containing intermediates by reaction of NO and CH_i whereas most of NH₃ is converted into nitrogen-containing



Figure 6. Comparison of the total radiation intensity of radicals in flames.

intermediates.¹⁷ NH and CN will be further oxidized by radicals such as OH. Therefore, the difference of the concentration of radicals has an important effect on nitrogen conversion in flames.

The spatial distribution of radicals in NO + NH₃-doped flame was compared to reveal the spatial distribution of the main reactions involved in the nitrogen conversion when NO and NH₃ coexisted. The contours of the spatial distribution of radicals were extracted to obtain the upper and lower boundaries of its distribution. The lower boundary was taken as the spatial position where radicals began to be generated in large quantities, and the upper boundary was the spatial position where the radicals were basically consumed. Figure 7 shows the contour extraction results of OH in NO + NH₃doped flame. The upper and lower lines formed by discontinuous yellow pixels represent the upper and lower boundaries of radicals, respectively. The contour spatial distribution of other radicals in the flame is similar to OH in NO + NH₃-doped flame.

Owing to the limited resolution of ICCD, the boundary in the Figure 7 is composed of only a few independent pixels. Therefore, the quadratic polynomial function (ploy4) was used to fit the upper and lower boundaries of each group to obtain the continuous boundary. Figure 8 shows the function fitting



Figure 7. Extracted profile of OH in the NO + NH₃-doped flame.



Figure 8. Fitting results of the lower boundary of OH in the flame doped with NO + NH_3 .

results of the lower boundary of OH in NO + NH₃-doped flame. The fitting function is $z_i = 0.0055x_i^4 + 0.4513x_i^3 - 0.0816x_i^2 - 6.6500x_i + 10.5900$, the correlation coefficient (R^2) reaches 0.9981, and the relative deviation (RMSE) is 0.2488. The fitting results show that all R^2 values are higher than 0.99, indicating that the fitting function could well reflect the spatial distribution characteristics of the group boundary.where $x_i = (R_i - \text{mean})$, std, R_i is the radial coordinate of each pixel after contour extraction, mean is the mean value of R_i , and std is the variance of R_i .

The upper and lower boundaries of OH/CH/NH/CN in NO + NH_3 -doped flame fitted by *ploy4* are shown in Figure 9.

It can be seen that the radicals are generated with the sequence NH, CH, CN, and OH, where NH and CH are almost generated simultaneously, and consumed with the sequence CH, NH, CN, and OH. Owing to the simultaneous existence of NO and NH₃, intermediate N species are generated by both reactions of NO with CH_i and NH_3 oxidation reactions. OH is present at a distance from the nozzle, indicating that NH and CN are oxidized late. Because NO was added to the premixed gas, NH would react with NO to produce N₂. Therefore, in the coexistence of NH₃ and NO, the reduction reactions of NO occur earlier than the oxidation reactions of intermediate N species.

NH participates in both the formation and reduction of NO, so its spatial distribution characteristics could reflect nitrogen transformation. It can be seen from Figure 5 that the groups are mainly distributed on the flamelet 3-15 mm away from the nozzle. In this region, the relative spatial distribution of each group is basically the same. To further reveal the spatial distribution characteristics of NH, the spatial gradient (first derivative) of it along the axial direction and the axial spatial distribution of radicals on the same cross section (R = 2.76 mm) in the flame doped with NO + NH₃ were compared, as shown in Figure 10.

It can be found that in the NO + NH_3 -doped flame, the maximum spatial gradient of NH occurs at the axial height of 15.29 mm, indicating that the growth rate of NH starts to slow down significantly at this position. The lower boundary of OH also appears at this position, indicating that the oxidation reaction of NH begins to be significant from here. The reaction between NH and OH is an important reaction affecting the conversion of NH, which is also an important way of NO generation. Therefore, obtaining the reaction rates between NH and OH is of great significance for the study of NO generation and conversion. The reactions involved in the combustion are mainly bimolecular reactions. According to the molecular collision theory, the reaction rate of bimolecular reactions can be calculated from eq 6.

$$\frac{d[A]}{dt} = -R_{\text{bimolec}} \times [A] \times [B]$$
(6)

where [A] denotes the concentration of reactant A, [B] denotes the concentration of reactant B, and R_{bimolec} denotes the reaction rate constant.



Figure 9. Spatial distribution of the upper and lower boundaries of different radicals in $NO + NH_3$ -doped flames: (a) lower boundary and (b) upper boundary.



Figure 10. Spatial gradient of NH and spatial distribution of radicals on the cross section of R = 2.76 mm in the flame doped with NO + NH₃.



Figure 11. Spatial distribution of NH \times OH radiation intensity of NO + NH₃-doped flame.



Figure 12. ROP bar chart of NO in flames: (a) positive ROP and (b) negative ROP.

The radiation intensity of radicals could qualitatively characterize the concentration distribution, so the chemical reaction rate of NH oxidation reaction could be characterized by the product of radiation intensity of NH and OH. The results are shown in Figure 11. The reaction between NH and OH occurs mainly at the edge of the flame. However, there are differences in reaction rates in different flame edge regions. The reaction rate in the region near the nozzle is faster than that far from the nozzle. It is also noteworthy that the reaction rate is slower at the region close to the burner rim (z = 1-2 mm). A possible reason is that the higher thermal conductivity of the copper burner nozzle leads to a lower temperature in its vicinity and a slower chemical reaction rate.

3.4. Rate of Production (ROP) Analysis of NO. The spatial distribution characteristics of OH/CH/NH/CN in the presence of NO and NH_3 were obtained by using image spectroscopy, and the influence mechanism of NO and NH_3 coexistence on the main reactions involved in nitrogen



Figure 13. The proportions of reaction rates in NO total consumption or formation rates in flames: (a) NO formation reaction and (b) NO consumption reaction.

conversion could be further revealed by combining ROP analysis. The results are shown in Figure 12. The positive and negative values of ROP represent NO generation and consumption, respectively, and the absolute value represents the rate of reaction. The proportions of reaction rates in NO total generation or consumption rates in the three flames were compared to analyze the influence of NH_3 and NO coexistence on NO generation and transformation. The results are shown in Figure 13, and the calculation method is shown in eq 7.

$$\eta = \frac{\text{ROP}_i}{\sum_{i=1}^{n} \text{ROP}_i}$$
(7)

where ROP_i represents the reaction rate of the *i*th reaction involving NO and $\sum_{i=1}^{n} \text{ROP}_{i}$ represents the total rate of reactions that consume or generate NO.

R16/R17 and R18/R19/R20 have larger ROP values, indicating that there is a strong equilibrium between NO and HNO as well as between NO and NO₂ in the flame. It can be seen from Figure 12a that HNO is the main source of NO generation. As shown in Figure 12b, in addition to R19/R20, NO reduction reactions are the main pathways for NO consumption, especially R8. Compared with NO- or NH₃doped flame, NO + NH3-doped flame has a faster NO reduction reaction rate. The reason is that the simultaneous addition of NO and NH₃ increases the concentration of NO and NH₃ in the flame compared to adding NO or NH₃, and NH₃ further generates nitrogen-containing components such as NH/N/NCO/NNH through dehydrogenation and oxidation reactions. Thus, the concentration of the reactants in the NO reduction reaction is increased, resulting in a rapid acceleration of the NO reduction reaction rate. Because the reactants of NO reduction reaction and nitrogenous intermediates' oxidation reaction are NH/N, there is a competitive relationship between the two types of reactions. It can also be found that the formation rate of NO in the NO + NH₃-doped flame is faster than that in other flames and less than the sum of the reaction rates of the other two flames. As shown in Figure 6, the reduction of OH in NO + NH₃-doped flame is one of the reasons for limiting the HNO/NH/N/ NCO oxidation reaction rate. The NO reduction reaction rate in NO + NH_3 -doped flame is significantly faster than that in the other two flames; especially, the reaction rate of R8, R9, R22, and R23 is faster than the sum of the other two flames. In other words, the limitation of accelerating the oxidation rate of nitrogenous intermediates in NO + NH₃-doped flame and the substantial acceleration of NO reduction reaction rate are the

main reasons for the reduction in NO when NO and NH_3 coexist.

As shown in Figure 13, compared with the flame doped with NH₃, the proportion of R16 in the flame doped with NO + NH₃ is larger, and the proportion of R3 and R5 is smaller. It shows that the simultaneous addition of NO and NH₃ promotes the conversion of HNO to NO and inhibits the conversion of NH/N to NO. According to the work conducted by Liu et al.¹⁴ and Mendiara and Glarborg,¹⁵ the NH₃ oxidation pathway is mainly NH₃-NH₂-NH-NO/N₂ or NH₃-NH₂-HNO-NO/N₂, so the coexistence of NO and NH₃ promotes the reaction pathway NH₃-NH₂-HNO-NO.

 $HNO + H = H_2 + NO \tag{R16}$

$$NO_2 + H = NO + OH$$
(R17)

$$H + NO + M = HNO + M$$
(R18)

$$NO + O + M = NO_2 + M \tag{R19}$$

$$HO_2 + NO = NO_2 + OH$$
(R20)

$$NNH + NO = N_2 + HNO$$
(R21)

$$NH + NO = N_2 + OH$$
(R22)

$$NCO + NO = N_2O + CO$$
(R23)

By ROP analysis of NO, the influence of NO and NH_3 coexistence on the main reactions of NO generation and consumption was obtained. The sensitivity analysis of NO also showed that the reactions $NO + CH_i$ have a significant effect on NO consumption. Therefore, the ROP analysis of reactions of NO + CH_i was also conducted, and the result is shown in Figure 14. It shows that the main reactions of NO and CH_i are the same in all flames, and the proportion of R13 is the largest. Nevertheless, the reactions rates in three flames are different: NO + NH_3 -doped flame > NH_3 -doped flame > NO-doped flame. It indicates that the coexistence of NO and CH_i .

4. CONCLUSIONS

In this work, the $CH_4/O_2/N_2$ premixed flame with simultaneous addition of NO and NH₃ was used to reveal the nitrogen conversion mechanism in the coexistence of NH₃ and NO in the reburning zone and compared with the NH₃- or NO-doped methane flame to obtain the influence of the coexistence of NO and NH₃ on NH₃ oxidation and NO reduction. The spatial distribution characteristics of OH/CH/

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Figure 14. ROP bar chart of the reactions NO + CH_i in flames.

CN/NH radiation intensity in flames were obtained by image spectroscopy. Numerical simulation was used to analyze the influence mechanism of NH_3 and NO on the reaction in the flame. The following conclusions are derived from the Results and Discussion.

- (1) ROP analysis of NO shows that the oxidation reaction rate of nitrogenous intermediates in NO + NH_3 flame is faster than that in other flames but slower than the sum of the other two flames, and the NO reduction reaction rate is faster than the sum of the other two flames. That is the main contribution to NO reduction when NH_3 and NO coexist in the reburning zone.
- (2) Results of image spectroscopy show that NH appears before OH in the NO + NH₃ flame, indicating that the reduction reaction of NO occurs earlier than the oxidation reactions of HNO/NH/N. In addition, it was found that the OH in the NO + NH₃-doped flame was reduced compared to that in the other flames, which is an essential reason for the limitation of the acceleration of oxidation of nitrogenous intermediates in this flame.
- (3) In this work, it is proposed that the product of spontaneous emission intensity of NH and OH could be used to qualitatively characterize the spatial distribution characteristics of NH oxidation reaction.

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Gangfu Rao was responsible for conceptualization, methodology, investigation, and writing the original draft. Meirong Dong was responsible for supervision, writing, reviewing, editing, and resources. Wei Nie was responsible for supervision, reviewing, and editing. Xiao Lin was responsible for investigation. Youcai Liang was responsible for reviewing, editing, and resources. Jidong Lu was responsible for reviewing, editing, and resources.

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Notes

The authors declare no competing financial interest.

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