

Effects of ethylene on NO conversion and product distributions in an rf discharge reactor

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Abstract

In the previous study, high concentration of NO in N₂/O₂ mixtures could be converted mainly into N₂ via a radio-frequency discharge approach at a low pressure (4 kPa). To enhance the efficiency of NO removal, C₂H₄ was added to elevate significantly the NO conversion in this study. The results showed that at inlet C₂H₄/NO molar ratio of 1 and 120 W in the C₂H₄/NO (1%)/O₂ (6%)/N₂ mixtures, the NO conversion reached 93.7% with a C₂H₄ conversion of 100%, to much higher than without C₂H₄ condition (NO conversion = 77.6%). Moreover, as high as 99.8% of the fraction of total N atoms converted from NO into N₂ was achieved. In addition, the relationship between the major active species observed in the optical emission spectra at different inlet C₂H₄ concentration and the important reactions for NO removal and N₂ formation were discussed. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Nitrogen oxide (NO), produced primarily by diesel engines and coal-burning power plants, is known to be the precursor of urban ozone and acid rain. In industry, concentrations of nitrogen oxides for tail gas streams of nitric acid plants can be as high as 2000 ppm, and can even be as much as 10,000 ppm when emitted from a high temperature oven for the manufacture of automotive catalyst [1,2]. Emission control strategies have been intensively implemented, such as the selective catalytic reduction of NO with adding reductant, such as ammonia, urea, hydrocarbons, and alcohols, to remove NO [2–4]. However, the effective temperature range of the catalysts is relatively narrow.

Recently, one method attempted to improve the catalyst feasibility at lower temperatures is by using the nonthermal plasma

approach. Particularly, plasma seems effective when the flow rate of effluents is small, e.g., gases emitted by the mobile combustion process. Plasmas are usually dry process and can be generated by different gaseous discharges, such as electron beams, dielectric-barrier discharge [5–7], corona discharge [8–11], and microwave discharge [12], all of which methods have been actively studied in reference to the removal of NO.

However, most of the conversions of NO via cold plasmas are due to the oxidation reaction, with only a small fraction being caused by the reduction process, leading to the most common final product primarily NO₂, HNO₃, N₂O and HNO₂ [5,11,13]. Although NO₂ and HNO₃ are water soluble and amenable for removal with scrubbers, it would be very beneficial to develop a process for reducing NO into N₂ to avoid the corrosion problem.

In order to enhance NO conversion, the process includes the addition of ammonia or the injection of Ca(OH)₂ into the stream to neutralize the acids and terminate the reverse-reactions [5,10,14]. Different hydrocarbon additives, such as CH₄, C₂H₄, C₃H₆, and C₃H₈, are also utilized to play a part in the NO remedi-

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ation. Following this, it was found that C_2H_4 is the more efficient additive [6,15–17]. However, when C_2H_4 is used as an additive, the common products are still higher oxidized nitrogen species [6,13]. Hence, it is beneficial to develop a discharge approach for reducing NO into N_2 .

Due to easy coupling, the radio-frequency (rf) discharge of the industrial frequency of 13.56 MHz, is very commonly used to generate plasma and has been applied to recover elemental sulfur from SO_2 , and to convert CH_4 into syngas [18,19]. In addition, the rf discharge has also been utilized to convert NO mainly into N_2 in $N_2/O_2/H_2O$ mixtures in our preliminary study [20]. However, the NO conversion was lower. Hence, the addition of C_2H_4 into the $NO/O_2/N_2/(H_2O)$ mixtures for enhancing the NO conversion apparently with mainly converted NO into N_2 is demonstrated in this study.

2. Experimental section

The similar experimental system was shown in Fig. 1 and in the previous study [19,20]. In a laboratory-scale rf discharge reactor, C_2H_4 was added into simulated $NO/O_2/N_2/H_2O$ mixtures to evaluate the feasibility for enhancing the NO conversion and converting NO into N_2 . The experimental flowcharts are passing the gaseous reactants that metered by mass flow controller into a mixing vessel and then introducing into a temperature-controlled water tank for entering the cylindrical glass reactor. A 13.56 MHz rf generator (PFG 600, Fritz Hüttinger Elektronik GmbH) coupled with a matching network (Matchbox PFM) was used to apply the rf powers which delivered to the plasma reactor that wrapped two outer copper electrodes to generate an inductively coupled glow discharge. The net power to the discharge was determined by obtaining an optimum match via reading the difference between the forward and reflected power.

The qualitative and quantitative analyses of reactants and effluents were mainly performed by an on-line Fourier transform infrared (FTIR) spectrometer (Nicolet, Avator 370) with a gas cell of 10 m-light path. For FTIR, the analysis condition was at a resolution of 1 cm^{-1} , velocity = 0.6329, aperture = 10, and number of scan = 8 using BaF2 windows. The gas sampling lines, including the gas cell of FTIR are heated and kept at about 330 K by wrapping a heated belt coupling with a temperature controller in order to measure HNO_2 and HNO_3

that vaped in the overall close system (reactor, sampling lines, and gas cell are at the same pressure) until pumping out.

Before the experiment running, a mechanical pump was used to exhaust the effluents for cleaning contaminations. For each designed experimental run, the system was kept at working pressure and all reactants and byproducts were measured more than three times in order to assure the plasmachemical reactions being at steady state. Furthermore, the accuracy of the concentration of NO_x was also checked by a commercially available analyzer (Land, Lancom III). In addition, the amounts of N_2 converted from inlet NO were calculated based on the mass balance of N atoms by quantifying all N-species.

Studies of the optical emission spectra (OES) were carried out by the commercial optical spectrometer (Ocean Optics, Model HR 4000CG) with OOIBase32 software. The emission light (200–1100 nm) was collected through an optical fiber, which was put in the rear part of the discharge at the center of the reactor, and analyzed via a scanning monochromator.

The operational parameters and conditions are as follows: applied rf power = 30–120 W, inlet concentration of NO ($[NO]_{in}$) = 10,000 ppm, inlet $[C_2H_4]/[NO]$ molar ratio = 0–5, inlet concentration of oxygen ($[O_2]$) = 2%, or 6%, inlet volume concentration of steam = 0% or 10%, carrier gas = nitrogen, and total flow rate = 200 standard $ml\text{ min}^{-1}$. The feeding temperature of reactants was at about 300 K. The effluent gas temperature measured by a thermocouple that was put at the rear of discharge zone in the reactor was in the range of 400–800 K at 30–120 W and the gas mean residence times in the physical discharge zone was computed and ranged between 0.2 and 0.4 s in all test runs. In addition, the pressure was operated at 4 kPa in order to start the discharge easily and keep the discharge was in a stable state.

The conversion of NO (C_{NO}) and the fraction of total N atoms converted from NO into N_2 (F_{N_2}) are calculated by the following equations:

$$C_{NO} = \frac{\text{NO converted}}{\text{NO fed to the reactor}} \times 100\%$$

$$F_{N_2} = \frac{2 \times N_2 \text{ formed from decomposed NO}}{\text{NO converted}} \times 100\%$$

where NO and N_2 are, respectively, the moles of compounds NO and N_2 . However, it is impossible to distinguish N_2 produced by NO conversion from the carrier gas (N_2) via direct measurement. The amounts of N_2 converted from inlet NO were calculated based on the mass balance of N atoms by quantifying all N-species detected, including NO, NO_2 , N_2O , HNO_2 , and HNO_3 .

Similarly, F_C , including F_{CO} , F_{CO_2} , F_{CH_4} , $F_{C_2H_2}$, and $F_{C_2H_6}$, was defined as the fraction of total C atoms converted from C_2H_4 into C-containing compound:

$$F_C = \frac{\text{C atom number in C-containing compound}}{C_2H_4 \text{ converted} \times 2} \times 100\%$$

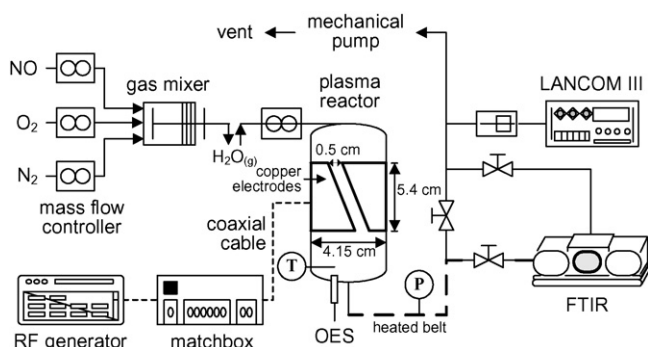


Fig. 1. Sketch of the radio-frequency plasma system.

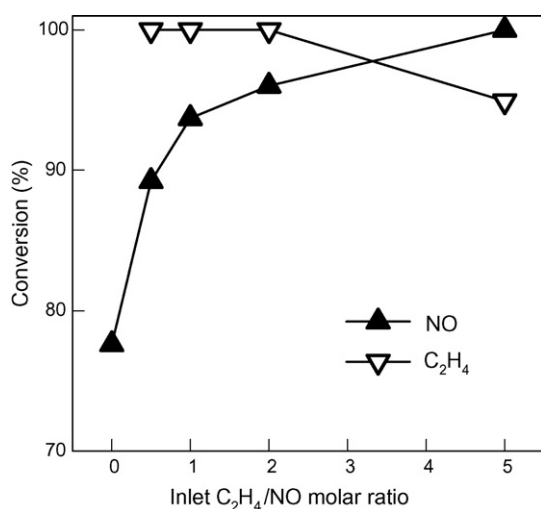


Fig. 2. Conversions of NO and C₂H₄ in the NO/C₂H₄/N₂/O₂ (6%) mixtures for various inlet C₂H₄/NO molar ratios at 120 W.

3. Results and discussion

3.1. Enhancement of NO conversion at various inlet C₂H₄/NO molar ratios

Fig. 2 shows that in NO/N₂/O₂ (6%) mixtures, adding C₂H₄ enhances the conversion of NO apparently. In the absence of C₂H₄ (that is [C₂H₄]/[NO]=0), C_{NO} was only 77.6%. However, C_{NO} increased significantly from 89.2% to 100% with increasing inlet [C₂H₄]/[NO] molar ratio (R) from 0.5 to 5 at 120 W.

As for the conversion of C₂H₄ kept at 100% at 120 W when R was in the range of 0.5–2, it decreased to 94.9% at R = 5 (Fig. 2). Hence ethylene was utilized, not only because it is one of the major combustion products in exhaust gases, but also because of its effectiveness in the NO reduction process.

In order to evaluate the improvement efficiency per mole feed of C₂H₄ on the C_{NO}, the %C_{NO}-enhanced/[C₂H₄] was calculated, and reached 23.1, 16.1, 9.2 and 4.5 (%C_{NO}-enhanced) at R = 0.5, 1, 2, and 5, respectively. Though the best utilization efficiency of C₂H₄ was obtained at R = 0.5 with a C_{NO} of 89.2%,

R = 1 with a higher C_{NO} of 93.7% and completely consumed C₂H₄ was set up to improve the C_{NO} effectively and examine the influences of power, oxygen content, and steam after adding C₂H₄ on the NO conversion.

3.2. Effects of power, oxygen contents, and steam on the NO conversion

Table 1 shows that though C_{NO} apparently decreased when oxygen or steam was added, the addition of C₂H₄ improved the C_{NO}. At R = 1, increasing the applied power from 30 to 120 W, C_{NO} increased from 74.8% to 100% at [O₂] = 2%, to be higher 7.2–24.7% as compared to that which had no C₂H₄. A greater level of applied power led to a higher plasma density to provide more transformations of energies and higher probabilities of electron-impact dissociation, thus leading to the production of higher concentration of energetic species produced to enhance the C_{NO}.

When [O₂] was 6%, C_{NO} rose from 67.0% to 93.7% when the power increased from 30 to 120 W (Table 1). C_{NO} enhanced 16.1–22.2% than that of no C₂H₄ condition. The lower C_{NO} at a higher oxygen content because of large amounts of O₂ molecules attached the energetic species to decrease the concentration of active species and inhibit the processing of NO decomposition reactions. Moreover, parts of O₂ were excited or dissociated into atomic O would elevate the rate of NO recombination. However, the addition of C₂H₄ yielded many C_xH_y fragments, to react with not only the excited O₂ or atomic O, but also the NO, leading to a decrease of the possibility of NO recombination.

When H₂O (10 vol.%) existed in the NO/N₂/O₂ (6%) environment, C_{NO} decreased due to the steam rapidly quenched the active N₂. However, the addition of C₂H₄ improved the C_{NO}, which increased from 55.7% to 92.7% with power ranging from 30 to 120 W (Table 1). C_{NO} elevated 12.4–21.4% than that of no C₂H₄ condition. The existence of H₂O consumed the energies of the active species via reaction or energy transformation. Moreover, H₂O reacted with N or N₂ to form OH and HN, and further bringing about an NO recombination via the reactions, such as N + OH, O + HN, OH + HN, etc. [7,16] to lead to the reduction of C_{NO}. The addition of C₂H₄ showed that C_{NO} increased dras-

Table 1
Conversions of NO (C_{NO}) and C₂H₄ for various applied powers at with/without C₂H₄ and steam [O₂] = 2% or 6%, and N₂ balanced mixtures

Applied power (W)	[O ₂] (%)	Steam (vol.%)	C _{NO} (%) without C ₂ H ₄ condition	C _{NO} (%) at [C ₂ H ₄]/[NO] = 1	Conversion of C ₂ H ₄ (%)
30	2	0	50.1	74.8	80.9
60	2	0	84.3	98.9	100.0
90	2	0	88.7	100.0	100.0
120	2	0	92.8	100.0	100.0
30	6	0	44.8	67.0	86.0
60	6	0	69.9	89.7	100.0
90	6	0	75.8	92.6	100.0
120	6	0	77.6	93.7	100.0
30	6	10	43.3	55.7	81.5
60	6	10	64.2	85.6	100.0
90	6	10	72.9	90.9	100.0
120	6	10	74.2	92.7	100.0

tically from 74.2% (at no C₂H₄ condition) to 92.7% at 120 W (Table 1), thus revealing that C₂H₄ plays an important role in the process of the enhancement of C_{NO} at reducing NO into N₂.

The results also showed that the conversion of C₂H₄ was as high as 100% when a power greater than 60 W was applied (Table 1). Interestingly, we found that at 30 W, a higher conversion of C₂H₄ occurred when [O₂] = 6% than when [O₂] = 2%. This is because the higher oxygen concentration enabled the oxidation rate of C₂H₄ to proceed faster under the lesser electron density caused by the lower power supplied.

3.3. Fractions of total N atoms converted from NO into N₂ when adding C₂H₄

Importantly, besides a significant enhancement of NO conversion, a very high fraction of total N atoms converted from NO into N₂ (F_{N_2}). The amount of N₂ converted from inlet NO was calculated based on the mass balance of N atoms by quantifying all N-species. Table 2 shows that as high as 99.7–99.9% of the total N atoms converted from NO into N₂ for NO/C₂H₄/N₂/O₂ mixtures at $R=0-5$ and 120 W. These results reveal that the rf discharge approaches reduced NO primarily into N₂.

When elevating the applied power from 30 to 120 W at $R=1$, F_{N_2} increases from 95.5% to 99.8% for NO/C₂H₄/N₂/O₂ mixtures (Table 2). The results indicate that a larger power supply could provide a higher plasma density to dissociate the weaker bonds of N-containing species and keep the highly thermodynamically stable N₂ as the only major products.

When 10 vol.% steam was added in the reactor, no HNO₃ could be identified. However, several tens ppm of HNO₂ was produced to lead the F_{N_2} reduce slightly, but F_{N_2} was still in the range of 95.8–99.6% at 30–120 W and $R=1$ (Table 2). The high F_{N_2} was obtained because there was no NO₂ formed. NO₂ cannot be detected because it may be caused by the lower rate of NO₂ formation ($NO + O + M \rightarrow NO_2 + M$) [26], as well as NO₂ would be re-dissociated owing to its weaker binding energies ($D_0=301.6$ kJ/mol). As a result, no HNO₃ was detected because there was no NO₂ as the precursor to form HNO₃ via $NO_2 + OH \rightarrow HNO_3$, though OH radicals

could be generated through electron-impact dissociation reaction ($H_2O + e \rightarrow OH + H + e$) [13].

3.4. Other byproducts

When C₂H₄ is added into the NO/N₂/O₂/H₂O mixtures, NO was converted mainly into N₂ with CO₂ and CO as the major C-containing products. In addition, only several to tens ppm of other N-containing species, including HNO₂, NO₂, and N₂O, as well as other trace amounts of C-containing byproducts, such as CH₄, C₂H₂, C₂H₆, CH₂O and CH₃OH could be detected. Interestingly, no HNO₃, toxic HCN or O₃ were found. The results are fairly different from those found in the previous discharge approaches that produced NO₂, N₂O, and HNO₃ as the major products [5,6,21,22].

3.4.1. N-containing compounds

The results of product analyses revealed that from 0% to 0.33% of total N atoms converted from NO into HNO₂ (F_{HNO_2}) was found (Table 2), that is, 0–33.0 ppm of HNO₂ formed, when the inlet C₂H₄/NO molar ratio was elevated from 0 to 5 at 120 W due to the species dissociated from C₂H₄ reacting with oxygen to form OH radicals, thus leading to the formation of HNO₂ via the reaction of $NO + OH + M \rightarrow HNO_2 + M$ [5,11,21,23]. Hence, F_{N_2} decreased slightly with elevated R . However, at a fixed R , the F_{HNO_2} seemed to decrease with an increase in the applied power, from 0.68% to 0.18% and from 1.56% to 0.40% for the NO/C₂H₄/N₂/O₂ and NO/C₂H₄/N₂/O₂/H₂O conditions, respectively (Table 2). As for more HNO₂ being produced in the steam-containing environment as opposed to the no-steam environment would seem to be caused by an increase in OH yielded from H₂O, in addition to C₂H₄ reacting with oxygen.

Besides HNO₂, the only other N-containing byproducts that could be detected were trace amounts of NO₂ and N₂O. Surprisingly, though NO₂ is usually the major final product in corona discharge plasma, regardless of added C₂H₄ [6,24,25], the concentration of NO₂ was usually under the detection limit for most of test runs except at a lower power supplied in this rf plasma process. This is because the reaction of $NO + O + M \rightarrow NO_2 + M$ did

Table 2
Fraction of total N atoms converted from NO into N-containing compounds, and fraction of total C atoms converted from C₂H₄ into C-containing compounds for C₂H₄/NO/N₂ (balance)/O₂ (6%) mixtures with/without steam at different powers and inlet [C₂H₄]/[NO] molar ratios

Power (W)	[C ₂ H ₄]/[NO] ratio	H ₂ O (%)	F_{N_2} (%)	F_{NO_2} (%)	F_{N_2O} (%)	F_{HNO_2} (%)	F_{CO} (%)	F_{CO_2} (%)	F_{CH_4} (%)	$F_{C_2H_2}$ (%)	$F_{C_2H_6}$ (%)
120	0	0	99.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
120	0.5	0	99.9	0.0	0.0	0.09	2.2	97.8	0.0	0.0	0.0
120	1	0	99.8	0.0	0.0	0.18	3.6	96.6	0.0	0.0	0.0
120	2	0	99.7	0.0	0.0	0.31	11.9	87.9	0.25	0.0	0.0
120	5	0	99.7	0.0	0.0	0.33	45.9	43.9	4.2	0.18	0.27
30	1	0	95.5	1.1	2.8	0.68	53.3	42.7	2.5	0.09	0.64
60	1	0	99.6	0.0	0.0	0.41	12.0	87.2	0.0	0.10	0.33
90	1	0	99.7	0.0	0.0	0.27	8.2	91.4	0.0	0.0	0.0
120	1	0	99.8	0.0	0.0	0.18	3.6	95.5	0.0	0.0	0.0
30	1	10	95.8	0.8	1.9	1.56	48.2	49.0	2.2	0.08	0.21
60	1	10	99.4	0.0	0.0	0.59	8.1	91.9	0.0	0.0	0.0
90	1	10	99.5	0.0	0.0	0.54	6.4	93.9	0.0	0.0	0.0
120	1	10	99.6	0.0	0.0	0.40	2.9	97.1	0.0	0.0	0.0

Table 3

List of the main bands and peaks detected by OES

Species (system)	Transition	Band/peak position (nm)
N ₂ (second positive)	C ³ Π → B ³ Π	337.1, 357.7, 375.5, 380.5
NO (γ-band)	A ² Σ ⁺ → X ² Π	226.9, 237.0, 247.9, 259.6, 271.5, 285.0
N	3s ⁴ P → 3p ⁴ S ⁰	745.2
N	3d ⁴ P → 3p ⁴ P ⁰	674.5
N ₂ ⁺ (first negative)	B ² Σ _u ⁺ → X ² Σ _g ⁺	391.4, 427.8
CN (violet system)	B ² Σ → A ² Π	359.0, 388.3 , 421.6
OH (3064-Å system)	A ² Σ ⁺ → X ² Π	306.4, 307.7, 307.8, 308.9
C ₂ (swam system)	A ³ Π _g → X ³ Π _u	512.9, 516.5
CH (4300 system)	³ Π → ³ Π	431.2 –494.0
H	² P ⁰ → ² D	656.3 , 486.1, 434.1
O	³ S ⁰ → ³ P	777.2, 777.4, 844.6
CO (third positive system)	b ³ Σ → a ³ Π	266.5 , 283.3, 297.7

not proceed very fast [26]. Moreover, almost no emission peak of atomic O could be identified, exhibiting that the reaction of O + NO was not able to play an important role. In addition, NO₂ would be re-dissociated owing to its weaker binding energies in a high power environment. Hence, NO₂ was only detected at 30 W, and F_{NO_2} was about 1.1% (without H₂O) and 0.8% (with H₂O-containing condition) at $R=1$ (Table 2).

Similarly, N₂O was also yielded only at a lower applied power (30 W), having levels of about 2.8% of $F_{\text{N}_2\text{O}}$ (NO/C₂H₄/N₂/O₂) and 1.9% of $F_{\text{N}_2\text{O}}$ (NO/C₂H₄/N₂/O₂/H₂O) (Table 2). N₂O decomposes easily from the weak N–O bond ($D_0 = 161.3$ kJ/mol) into N₂ and O [27], resulting in the rapid disappearance of N₂O.

Although both NO₂ and N₂O were yielded at 30 W, resulting in a slight decrease of F_{N_2} , the F_{N_2} level was still higher than 95.5%.

3.4.2. C-containing compounds

Table 2 shows that increased power provides a thermodynamically favorable sink for C atoms in their oxygen-rich condition (at a lower R), mainly converting C₂H₄ into CO₂. With elevating R from 0.5 to 5 at 120 W, the molar fraction of CO and CO₂ elevated apparently because added C₂H₄ reacted with oxygen, however, F_{CO} increased from 2.2% to 45.9%, but F_{CO_2} decreased from 97.8% to 43.9%. At $R=1$, F_{CO} decreased sharply from 53.3% to 3.6% (without steam) and from 48.2% to 2.9% (with steam) with an increase in the applied rf power going from 30 to 120 W (Table 2). Contrary to the F_{CO} , F_{CO_2} increased from 42.7% to 95.5% (NO/C₂H₄/N₂/O₂) and from 49.0% to 97.1% (NO/C₂H₄/N₂/O₂/H₂O). These results indicate that adding steam favors slightly the formation of CO₂, although the molar fraction of CO and CO₂ are similar whether steam is present or not.

The formation pathways of CH₄, C₂H₆, and C₂H₂ in plasma are usually via CH₃ + H → CH₄, CH₃ + CH₃ → C₂H₆, and C₂H₄ + e → C₂H₂ + 2H (or H₂), respectively [28]. Table 2 shows that CH₄, C₂H₆, and C₂H₂ were produced at either a higher R ($R \geq 2$) or lower applied power (≤ 60 W), as well as the fraction of total C atoms converted from C₂H₄ into hydrocarbons was usually in the orders of $F_{\text{CH}_4} > F_{\text{C}_2\text{H}_6} > F_{\text{C}_2\text{H}_2}$. No complex molecules such as C₃-hydrocarbons were detected, while

trace amount of CH₂O and CH₃OH were detected at the similar conditions with that of the hydrocarbons yielded. However, when a higher C_{NO} was performed, hydrocarbons, CH₂O and CH₃OH were not found to conduct to the major C-containing products were CO₂ and CO. Moreover, no obvious carbon black and depositions were observed, due that the active species had a short lifetime and quenching time to limit the probabilities of formation of complex compounds in the afterglow zone.

3.5. OES of NO/C₂H₄/N₂/O₂ plasma

The plasma diagnosis was obtained via observations of optical emission spectra (OES) with the main bands and peak positions listed in Table 3 [29–34]. Fig. 3 shows that in the NO/N₂/O₂/C₂H₄ rf discharge environment, N₂ (second positive band) and NO (γ system) are the major active species with very weak peaks of CN, CH and H are detected in the C₂H₄ (5%)-containing plasma. Since O₂ molecule is a very efficient quencher via destructive processes [35], hence some atomic lines

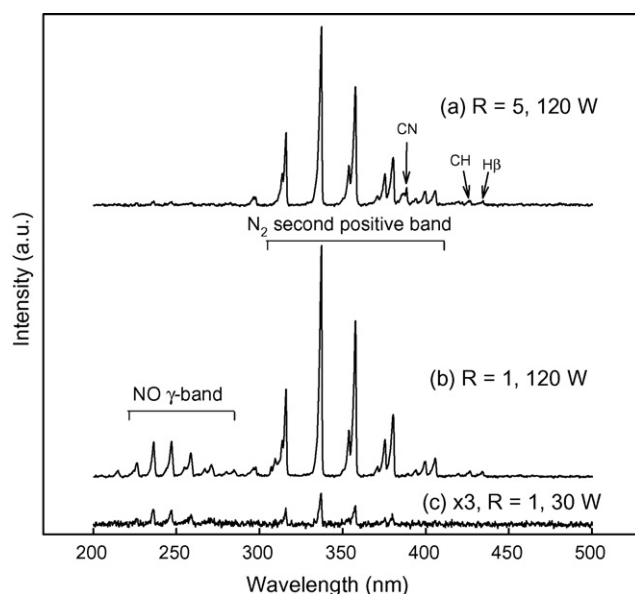


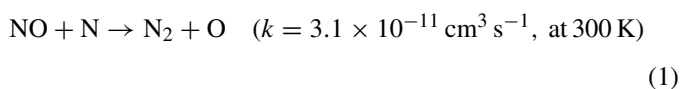
Fig. 3. Optical emission spectra of NO/C₂H₄/N₂/O₂ (6%) mixtures at inlet C₂H₄/NO molar ratio (R) = 1 or 5 with applied power = 30 or 120 W.

(O, N and C), electronically excited species, C₂H₄-related peak, and N₂⁺ were difficult to be observed.

Fig. 3 shows that at 120 W and with 1% C₂H₄ condition, the peak intensities of NO, N₂ and other active species appear stronger than those at 30 W, due to a higher electron density providing the gaseous molecules with more energy transformation to excite or dissociate the reactants. Interestingly, at $R=5$, the peak intensities of NO and N₂ are lower than when $R=1$ (Fig. 3). Notice that the NO γ -band almost disappears because of the complete conversion of NO achieved at $R=5$. The lower N₂ intensity indicates that excited N₂ is consumed by colliding with NO, thus reducing NO or transferring energy. Moreover, quenching of the active species by C₂H₄ and its fragments leads to a decrease of the N₂ peak intensity.

However, the elevation of NO conversion is apparently enhanced by dissociating C₂H₄ into abundant active species, leading it to react with NO and its fragments to form highly stable products, including N₂, CO, CO₂ and H₂O, resulting in a significant improvement of NO conversion. Moreover, the carbon atoms of C₂H₄ molecules are able to consume the O atoms of NO and not only inhibit the recombination of NO via forming CO and CO₂ but also to simultaneously elevate NO conversion. Modeling shows that abundant radicals such as H, OH, and CH₃O produced by the C₂H₄ reacting with O₂ oxidizes NO to NO₂ with an HNO₂ byproduct to enhance the NO conversion [21]. Hence, the higher inlet C₂H₄ concentration elevates the C_{NO} .

Previous studies indicated that the major pathways of NO removal, including the reduction reaction (equation (1)), and/or the oxidation reaction equation (2) [26,27,31], are as follows:



As for long-lived excited N₂ in plasma jets did not seem to play an important role in NO destruction, although N₂(A³Σ_u⁺) and N₂(a¹Σ_u⁻) could dissociate NO directly into N and O via Penning dissociation reaction: NO + N₂ → N₂ + N + O [36,37]. Because N₂(A) was easily quenched by the NO molecules and returned to the N₂ ground state with NO excited to NO(A).

Hence, N(⁴S) produced from electron-impact dissociation (e + NO → N + O + e) or Penning process reduce NO into N₂ via Eq. (1), playing a decisive role on the formation N₂. However, the rate of electron-impact rate is dependent on discharge types owing to their different electron mean energy and plasma density.

Usually NO₂ and N₂O are produced via the reactions of NO + O + M → NO₂ + M (Eq. (2)), 2NO + O₂ → 2NO₂, and NO₂ + N → N₂O + O [38]. However, a very few parts of NO₂ and N₂O formed may be caused by high concentrations of N₂(A) and atomic N that may not only reduce NO into N₂, but also control the evolution of NO₂ and NO₂ via the following reactions: N₂(A) + N₂O → 2N₂ + O, N(⁴S) + NO₂ → N₂ + O₂, and

N(⁴S) + NO₂ → N₂ + 2O, leading to more N₂ formation and inhibiting the yield of NO₂ and N₂O [37,38]. Moreover, due to the large amounts of CO₂ and CO formed, the active O-containing species are consumed inhibiting the recombination of NO, N₂O and NO₂.

In addition, a large amount of C₂H₄ is dissociated and reacts with other species in the rf plasma, resulting in the weak peak intensities of CN, CH and H which are detected (Fig. 3). CH, CH₂, and H radicals are able to react rapidly with NO to form HCN, HCO and NCO, thus yielding further CN, NH or N, finally reducing NO mainly to N₂ [13,16]. Therefore, these results are very different from the final products, which are usually NO₂ and HNO₃ when the other plasma approaches using C₂H₄ as additive are utilized.

4. Conclusion

NO conversion can be enhanced apparently by adding C₂H₄ in the C₂H₄/NO/N₂/O₂ (6%) mixtures, increasing from 77.6% (without C₂H₄) to 89.2% and 100% for inlet [C₂H₄]/[NO] ratio = 0.5 and 5, respectively, at 120 W and 4 kPa. To operate the discharge at a higher inlet C₂H₄/NO ratios or a higher applied power could lead to a higher conversion of NO. In addition, NO was converted mainly into N₂. The fraction of total N atoms converted from NO into N₂ was in the range of 95.8–99.6% for C₂H₄/NO/N₂/O₂/H₂O mixtures at 30–120 W and inlet [C₂H₄]/[NO] = 1.

From the observation of optical emission spectra, a large amount of N₂ and NO were excited, suggesting the electron-impact dissociation and Penning dissociation for yielding N atoms, and then the NO + N → N₂ + O and N + N → N₂ reactions, played important roles in the removal of NO and the formation of N₂.

However, the rf discharge approach is not practical in this stage due to its lower operating pressure and lower energy efficiency though the addition of C₂H₄ enhances apparently the NO conversion. The further research for plasma process operating at atmospheric pressure with a higher flow rate should be proceeded. In addition, the other atmospheric pressure, lower electron temperature and gas temperature plasmas are also in developing for converting NO mainly into N₂.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2007.04.120.

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