Influence of Argon Addition on NO Conversion Efficiency and Optical Emission Spectroscopy in NO/N₂/O₂ Mixture by Non-thermal Plasma

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The experimental set-up of NO conversion in NO/N₂/O₂/Ar mixture by non-thermal plasma was established. The effects of applied voltage and Ar concentration on NO conversion efficiency, NO₂ concentration and O₃ concentration were studied. The chemical mechanism of NO conversion was also analyzed by combining with emission spectroscopy diagnosis. The results show that adding Ar in the NO/N₂/O₂ mixture can enhance the activation probability of the molecules at low V_{pp} due to the penning effect. Furthermore, the electron density of NTP increases with Ar additive, which promotes the formation of N, O atoms. The conversion efficiency of NO rises with the increasing of Ar concentration. With high V_{pp}, Ar additive has a negative effect on O₃ generation and O₃ concentration reduces with the increasing of Ar concentration. The variation of NO₂ concentration is similar to that of O₃ concentration.

Key Words: Non-thermal Plasma, NO conversion, Argon, Emission spectroscopy, Electron density.

INTRODUCTION

With the increase of automobile population, how to reduce the NO_x emission in automobile exhaust has become a global problem. Since the non-thermal plasma (NTP) technology do not affect the engine performance and has the advantage of reducing NO_x and particulate matter simultaneously by comparison to other treating methods, it is considered as one of the most promising techniques to solve the problem of the automobile exhaust pollution^{1,2}. Dielectric barrier discharge (DBD) as one of the most common ways to obtain non-thermal plasma under atmospheric pressure, can produce high chemical active substances such as ions, atoms, radicals and excited molecules which are difficult to obtain in usual conditions. Then these active substances can enable the chemical reaction to proceed smoothly. The atoms, radicals and excimers produced in discharge process can radiate characteristic spectrum when they move from the excited state to ground state. Therefore, the relevant information about radicals and excimers can be obtained through the analysis of emission spectroscopy, which is helpful to analyze the chemical mechanism of non-thermal plasma³.

The collision of the high energy metastable argon with other particles would lead to Penning effect and produce seed electrons which can reduce the discharge field. As a result, the discharge become more easily and uniform⁴, which is beneficial to diesel emission treatment. Some research results have

shown that NO conversion efficiency in the argon as background gas is greater than that in the nitrogen as background gas⁵ and argon added in the mixture can increase the electron density of the discharge plasma⁶. In this paper, the non-thermal plasma and the optical emission spectroscopy technologies were used to study the effect of argon additive on electron density and the NO conversion process in NO/N₂/O₂ mixture, which can provide reference for efficient treatment of NO_x by non-thermal plasma technology.

EXPERIMENTAL

Fig. 1 shows the arrangement of experimental system for NO conversion by non-thermal plasma technology, composed of gas supply unit, non-thermal plasma reactor, TDGC2-2kVA voltage regulator, CTP-2000 K intelligent electron impact machine (plasma power supply), TDS3034B Tektronix oscilloscope, Interscan 4480 ozone analyzer, Test 350-XL gas analyzer and Maya 2000-Pro emission spectrometer. In this experiment, the mixture of NO/N₂/O₂/Ar with different concentration can be obtained by inputting wanted data on the panel of program-controlled gas mixture (PCGM). The discharge frequency of non-thermal plasma reactor was 12.2 kHz and the flow rate of the mixture was 10 L/min with the initial concentration of O₂ 2.3 % and the initial concentration of NO 880 × 10⁻⁶. Concentration of various gases in the NO/N₂/O₂/Ar mixture and emission spectroscopy were measured and analyzed when the Ar concentration was 0, 5.6 and 9.0 %, respectively.

The structure parameters of DBD-type non-thermal plasma reactor used in the experiment are shown as follows. A stainless steel tube with the external diameter 32 mm was used as the inner electrode. The dielectric barrier was quartz tube (inner diameter 36 mm, external diameter 40 mm) and the external electrode was stainless steel wire with the length of 100 mm which wrapped outside the quartz tube tightly.

Fig. 1. Schematic diagram of experiment system

RESULTS AND DISCUSSION

Effect of argon concentration on NO conversion: The NO concentration as a function of applied voltage (V_{p-p}) for the different Ar concentrations is shown in Fig. 2. As shown in Fig. 2, with V_{p-p} less than 15.5 kV, the NO concentration decreases dramatically with the increasing of V_{p-p} and the NO conversion efficiency increases with the increasing of Ar concentration. When V_{p-p} is 14 kV, the NO conversion efficiency is only 51.98 % at the Ar concentration of 0, whereas it is about 61.98 % at that of 5.6 % and it can reach 67.50 % at that of 9.0 %. When V_{p-p} exceeds 15.5 kV, the NO concentration slightly decreases with the increasing of V_{p-p} and the NO conversion efficiency for different Ar concentration are roughly the same. The highest NO conversion efficiency can reach 76.38 %. It is thus clear that the Ar additive can improve the NO conversion in NO/N₂/O₂ mixture when V_{p-p} is low.

Fig. 2. NO concentration as a function of V_{p-p}

The O₃ concentration as a function of V_{p-p} for the different Ar concentrations is shown in Fig. 3. In Fig. 3, the O₃ concentration grown up at first and then goes down with the increasing

of V_{p-p} when the Ar concentration is 0 or 5.6 % and reaches their maximum at 14.5 kV and 13.5 kV, respectively. But for the mixture with Ar concentration 9 %, the O₃ concentration gradually decreases with the increasing of V_{p-p} . The O₃ concentration increases with the increasing of Ar concentration at the V_{p-p} of 13 kV. However, the existence of Ar inhibits the generation of O₃ with V_{p-p} above 14 kV. The higher Ar concentration is, the less O₃ molecules will be produced.

Fig. 3. O₃ concentration as a function of V_{p-p}

The NO₂ concentration as a function of V_{p-p} for different Ar concentration is shown in Fig. 4. It is obvious that the variation of NO₂ concentration is similar to that of O₃.

Fig. 4. NO₂ concentration as a function of V_{p-p}

Effect of argon concentration on emission spectroscopy:

When V_{p-p} is set to 14 kV and 15.5 kV, respectively, the effect of Ar concentration on the emission spectroscopy of NO/N₂/O₂/Ar plasma is shown in Fig. 5(a) and Fig. 5(b). The NO- γ band ($A^2\Sigma^+ \rightarrow X^2\Pi_r$) and N₂ second positive band ($C^3\Pi_u \rightarrow B^3\Pi_g$)⁷ were observed in our experiment. It is shown that NO- γ band and N₂ second positive band are mainly located in the range of 200-300 nm and 300-450 nm, respectively.

It can be seen from the Fig. 5(a) that the spectral intensity of NO- γ band and N₂ second positive band increase with the increasing of Ar concentration and the growth rate of N₂ second

positive band is higher than that of NO- γ band. With the increasing of Ar concentration, the full width at half maximum (FWHM) of N₂ second positive band is enhanced. The larger version of N₂ spectral line at 337.19 nm can be viewed in the upper left corner of Fig. 5(a). The analysis shows that the FWHM of N₂ spectral line at 337.19 nm is 2.32 nm, 2.362 nm and 2.445 nm, respectively, corresponding to Ar concentration of 0, 5.6 and 9 %. Generally, the broadening mechanisms of spectral line emitted from plasma include natural broadening, doppler broadening, stark broadening, collision broadening caused by neutral particles and instrument broadening⁸. Since this test was carried out in the same condition which means the atmospheric pressure and ambient temperature is invariant, the impact of doppler effect, collision effect and instrument effect on FWHM of spectral line can be basically considered to maintain invariable and the variation of FWHM of spectral line was mainly caused by the stark broadening. Stark broadening is associated with electron density rather than with whether the plasma satisfies the local thermodynamic equilibrium⁹. Therefore, adding Ar in the NO/N₂/O₂ mixture causes the increase in electron density of non-thermal plasma and

then the number of the excited N₂(C³Πu) and metastable N₂(A³Σu⁺) particles rises, leading to simultaneously increase in spectral intensity of NO- γ band and N₂ second positive band (the emission spectrum of NO- γ band is excited by the collision of the N₂ metastable state). The rise in electron density is related to the reactions as follows¹⁰:

In addition, the metastable argon can also cause the change in N₂(C³Πu) population during the discharge of mixture. The excitation potential of Ar_m4³P₂ and Ar_m4³P₀ were 11.55 eV and 11.72 eV respectively and just above that of the first excitation potential of nitrogen molecules (11.05 eV)¹¹. Therefore, Ar_m4³P₂ and Ar_m4³P₀ can transfer their energy to the ground state of N₂ easily, causing its excitation and the population of N₂(C³Πu) would be enlarged by the Penning effect when Ar was added in the NO/N₂/O₂ mixture. Consequently, the growth rate of the spectral intensity of N₂ second positive band is more obvious than that of NO- γ band. The related reaction mechanism is shown as follow:

In Fig. 5(b), when V_{p-p} reaches 15.5 kV, there was no apparent change in FWHM of the spectral line of 337.19 nm with the increasing of Ar concentration and the spectral lines of N₂ second positive band under different Ar concentrations almost overlap. That is to say the three different mixtures have nearly equal electron density. It can also be seen from the Fig. 5(b) that the spectral intensity of NO- γ band gradually decreases with the increasing of Ar concentration, which is different from the phenomenon of Fig. 5(a). Since the electron densities of three different mixtures are almost equal, the electron density has little effect on spectral intensity of NO- γ band. Therefore, spectral intensity of NO- γ band is mainly affected by NO concentration and it also verifies that the conversion efficiency of NO in NO/N₂/O₂/Ar mixture is higher than that in NO/N₂/O₂ mixture with V_{p-p} 15.5 kV. Through the contrast of Fig. 5(a) and Fig. 5(b), it is found that effect of Ar concentration on the electron density is great with low V_{p-p}, while it is small with high V_{p-p}. This shows that with the increasing of V_{p-p}, the effect of Ar concentration on the electron density begins to weaken and the effect of applied voltage on the electron density gradually increases.

Fig. 6 shows the emission spectra of argon in the pure Ar and NO/N₂/O₂/Ar mixture. It is clearly that several spectral lines of Ar with energy level transition 4P to 4S are observed in pure Ar discharge, while only a spectral line of Ar at 751 nm can be observed clearly in NO/N₂/O₂/Ar mixture until V_{p-p} exceeds 16 kV. This is because the emission spectrum of Ar can easily be quenched while Ar atoms transfer their energy to nitrogen molecules in the Penning ionization process¹¹.

Reaction mechanism: The main chemical reactions of NO/N₂/O₂/Ar mixture occurring in the discharge interval of DBD reactor can be drawn as follows^{10,12-14}:

Fig. 5. Effect of Ar concentration on emission spectrum of NO/N₂/O₂/Ar plasmas

Fig. 6. Optical emission spectrum of Ar atom for various gas plasmas

When breakdown of NO/N₂/O₂ mixture happens, the electrons in discharge space are accelerated with the action of external electric field and then impact N₂ molecules and O₂ molecules to form ground particles of N(⁴S), O(³P) and excited state particles of N(²D), O(¹D). These particles are the important reaction components in the non-thermal plasma process and trigger the subsequent reactions. With the increasing of V_{p-p}, the number of N and O radicals dissociated by N₂ and O₂ molecules rise and then an increasing number of NO molecules are reduced to N₂ or oxidized to NO₂ through reaction (6) to (8). As a result, NO concentration decreases. When the V_{p-p} is higher than 15.5 kV, the number of N radicals goes up sharply and additional NO molecules are generated by reaction (9). Consequently, the NO concentration changes slowly. O₃ is prone to thermal decomposition and chemical decomposition for its weak chemical bond and the temperature of discharge space is rising with the continuous discharge, so the production of O₃ is suppressed when V_{p-p} is high. In addition, O₃ can also be decomposed according to reactions (11) and (12). Therefore, the O₃ concentration increases at first and then decreases with the increasing of V_{p-p}. Since NO₂ is mainly produced by the reaction of O₃ and NO, the variation of NO₂ is similar to that of O₃.

In the presence of argon, a significant decrease of breakdown voltage of the mixture is observed, which indicates that discharge occurs more easily. (With Ar concentration increasing from 0 to 9 %, the breakdown voltage reduces from 11.76 kV to 10.64 kV.) When V_{p-p} is low, Ar⁺ and the metastable argon Ar_m can dissociate NO, N₂, O₂ effectively through reaction (13) to (15) because of Penning effect. Therefore, with the increasing of Ar concentration, the activation probability of these molecules increases. Besides, the increase in electron density improves the collision probability of N₂, O₂ molecules and then the role of reaction (4) and reaction (5) enhances, which promotes the production of N and O atoms. The growth of the number of N atoms allows more NO molecules to be reduced, while the increased O atoms promotes the production of O₃ and more NO molecules are oxidized to NO₂. As a result, the NO conversion efficiency increases with the increasing of Ar concentration for low V_{p-p}. When V_{p-p} exceeds 15.5 kV, the effect of Ar concentration on electron density reduces, so the Ar concentration has little influence on NO conversion efficiency.

High V_{p-p} and high Ar concentration acting on the mixture may cause inordinate production of N and O atoms and subsequently enhances the effect of reaction (10) to (12). In addition, the thermal conductivity of Ar is lower than that of the other three gases, so Ar additive could improve the temperature rise rate of the mixture¹³. Consequently, O₃ and NO₂ concentration decrease with the increasing of Ar concentration when V_{p-p} is high.

Conclusions

The experimental system of NO conversion in NO/N₂/O₂/Ar mixture by non-thermal plasma technology was carried out. The effects of V_{p-p} and Ar concentration on NO conversion efficiency, NO₂ and O₃ concentration were studied and conversion mechanism of NO was also analyzed by combining with emission spectroscopy diagnosis. From the above discussions, the following conclusions can be drawn:

(1) When V_{p-p} is low, with the increasing of Ar concentration, the FWHM of N₂ spectral line at 337.19 nm gradually increases, indicating an increase in electron density of the discharge space. The conversion efficiency of NO rises with the increasing of Ar concentration.

(2) With the increasing of V_{p-p}, the NO concentration firstly decreases and then goes to be flat. With high V_{p-p}, the NO concentration is roughly same among the mixtures with three Ar concentration values and Ar additive has a negative effect on O₃ generation. O₃ concentration reduces with the increasing of Ar concentration and the variation of NO₂ concentration is similar to that of O₃ concentration.

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