Asian Journal of Chemistry; Vol. 25, No. 18 (2013), 10546-10550

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.15874

Influence of Argon Addition on NO Conversion Efficiency and Optical Emission Spectroscopy in $NO/N_2/O_2$ Mixture by Non-thermal Plasma

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(*Received*: 6 June 2013; *Accepted*: 26 November 2013) AJC-14444

The experimental set-up of NO conversion in $NO/N_2/O_2/Ar$ mixture by non-thermal plasma was established. The effects of applied voltage and Ar concentration on NO conversion efficiency, NO_2 concentration and O_3 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 $NO/N_2/O_2$ mixture can enhance the activation probability of the molecules at low V_{p-p} 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_{p-p}, Ar additive has a negative effect on O_3 generation and O_3 concentration reduces with the increasing of Ar concentration. The variation of NO_2 concentration is similar to that of O_3 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 plasma[3].

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 uniform[4], 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 gas[5] and argon added in the mixture can increase the electron density of the discharge plasma[6]. 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 $NO/N_2/O_2$ 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 $NO/N_2/O_2/Ar$ 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 O_2 2.3 % and the initial concentration of NO 880×10^{-6}. Concentration of various gases in the $NO/N_2/O_2/Ar$ 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.

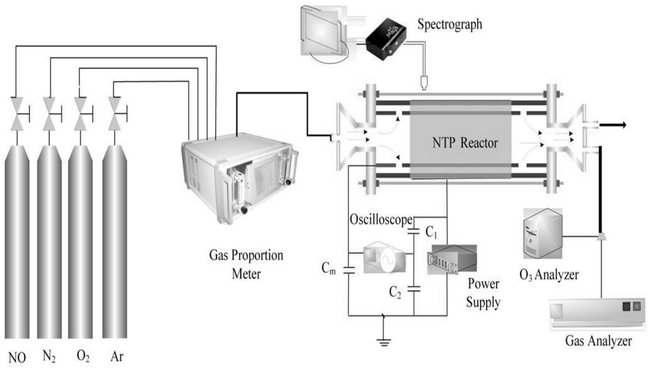


Fig. 1. Schematic diagram of experiment system

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 $NO/N_2/O_2$ mixture when V_{p-p} is low.

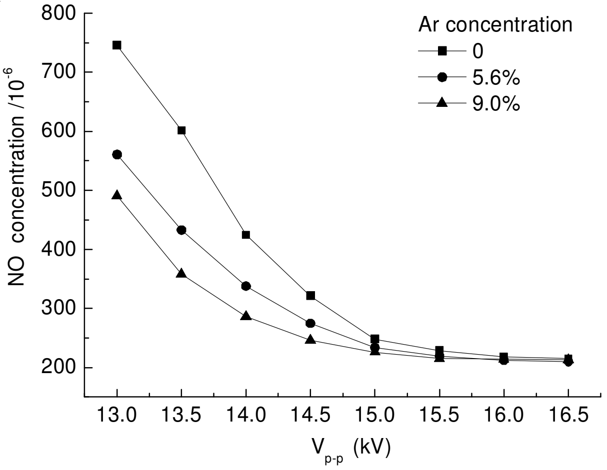


Fig. 2. NO concentration as a function of V_{p-p}

The O_3 concentration as a function of V_{p-p} for the different Ar concentrations is shown in Fig. 3. In Fig. 3, the O_3 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 O_3 concentration gradually decreases with the increasing of V_{p-p}. The O_3 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 O_3 with V_{p-p} above 14 kV. The higher Ar concentration is, the less O_3 molecules will be produced.

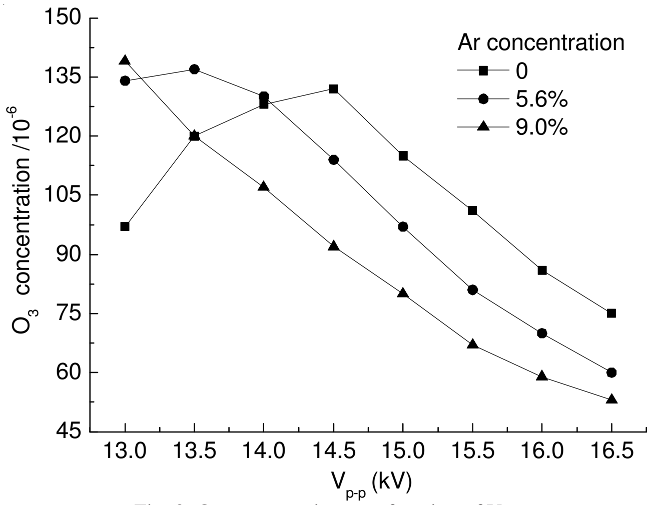


Fig. 3. O_3 concentration as a function of V_{p-p}

The NO_2 concentration as a function of V_{p-p} for different Ar concentration is shown in Fig. 4. It is obvious that the variation of NO_2 concentration is similar to that of O_3.

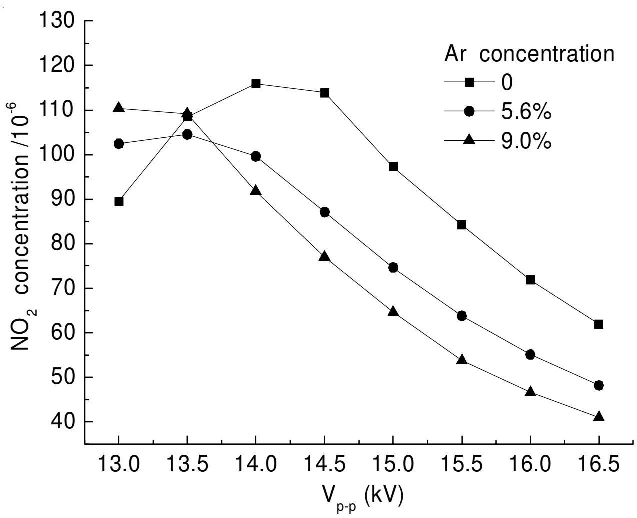


Fig.4. NO_2 concentration as a function of V_{p-p}

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 $NO/N_2/O_2/Ar$ plasma is shown in Fig. 5(a) and Fig. 5(b). The NO-γ band ($A^2\Sigma^+ \rightarrow X^2\Pi_r$) and N_2 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 N_2 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 N_2 second positive band increase with the increasing of Ar concentration and the growth rate of N_2 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 N_2 second positive band is enhanced. The larger version of N_2 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 N_2 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 broadening[8]. 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 equilibrium[9]. Therefore, adding Ar in the $NO/N_2/O_2$ mixture causes the increase in electron density of non-thermal plasma and then the number of the excited $N_2(C^3\Pi u)$ and metastable $N_2(A^3\Sigma u^+)$ particles rises, leading to simultaneously increase in spectral intensity of NO-γ band and N_2 second positive band (the emission spectrum of NO-γ band is excited by the collision of the N_2 metastable state). The rise in electron density is related to the reactions as follows[10]:

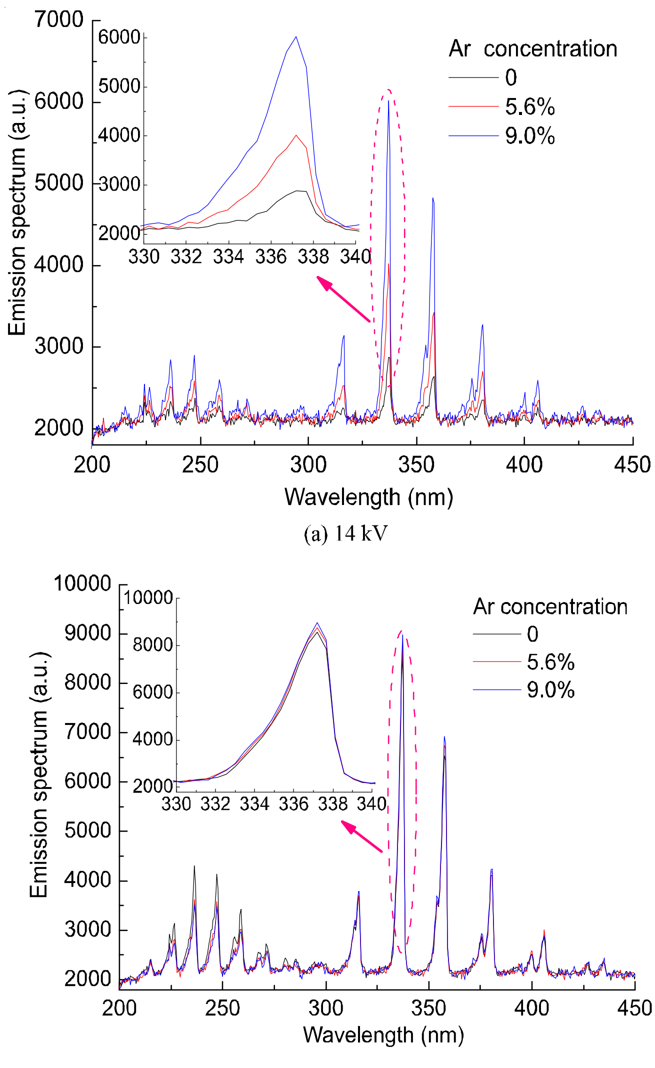
$$Ar + e \rightarrow Ar^+ + 2e \quad (1)$$

$$Ar^+ + e \rightarrow Ar \quad (2)$$

In addition, the metastable argon can also cause the change in $N_2(C^3\Pi u)$ population during the discharge of mixture. The excitation potential of $Ar_m4^3P_2$ and $Ar_m4^3P_0$ 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, $Ar_m4^3P_2$ and $Ar_m4^3P_0$ can transfer their energy to the ground state of N_2 easily, causing its excitation and the population of $N_2(C^3\Pi u)$ would be enlarged by the Penning effect when Ar was added in the $NO/N_2/O_2$ mixture. Consequently, the growth rate of the spectral intensity of N_2 second positive band is more obvious than that of NO-γ band. The related reaction mechanism is shown as follow:

$$N_2(X^1\Sigma g^+) + Ar_m^*(^3P_2, {}^3P_0) \rightarrow N_2(C^3\Pi u) + Ar \quad E > 11.05 \text{ eV} \quad (3)$$

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 N_2 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 $NO/N_2/O_2/Ar$ mixture is higher than that in $NO/N_2/O_2$ 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.



(a) 14 kV

(b) 15.5 kV

Fig. 5. Effect of Ar concentration on emission spectrum of $NO/N_2/O_2/Ar$ plasmas

Fig. 6 shows the emission spectra of argon in the pure Ar and $NO/N_2/O_2/Ar$ 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 $NO/N_2/O_2/Ar$ 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 process[11].

Reaction mechanism: The main chemical reactions of $NO/N_2/O_2/Ar$ mixture occurring in the discharge interval of DBD reactor can be drawn as follows[10,12-14]:

$$e + N_2 \rightarrow e + N(^4S) + N(^4S, {}^2D) \quad (4)$$

$$e + O_2 \rightarrow e + O(^3P) + O(^3P, {}^1D) \quad (5)$$

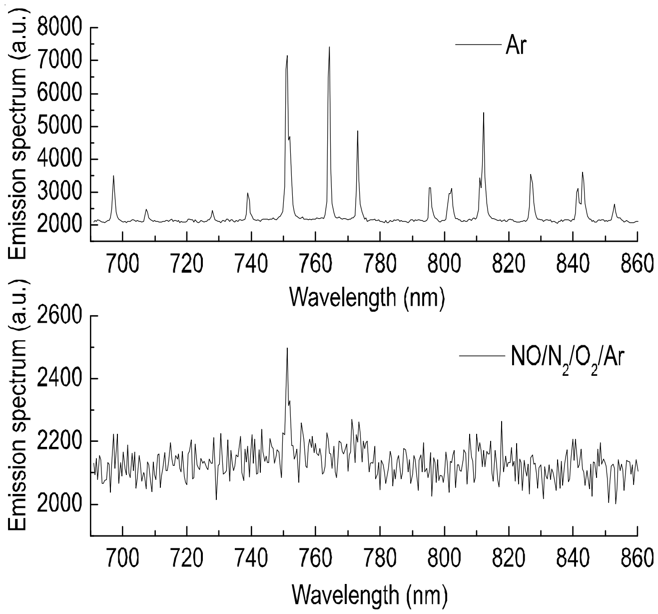


Fig. 6. Optical emission spectrum of Ar atom for various gas plasmas

$$N + NO \rightarrow N_2 + O \quad (6)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (7)$$

$$O_3 + NO \rightarrow O_2 + NO_2 \quad (8)$$

$$N + O_2 \rightarrow NO + O \quad (9)$$

$$N + NO_2 \rightarrow N_2O + O \quad (10)$$

$$e + O_3 \rightarrow e + O_2 + O \quad (11)$$

$$O + O_3 \rightarrow 2O_2 \quad (12)$$

$$Ar^+ + NO + e \rightarrow Ar + N + O \quad (13)$$

$$Ar_m + N_2 \rightarrow N + N + Ar \quad (14)$$

$$Ar_m + O_2 \rightarrow O + O + Ar \quad (15)$$

When breakdown of $NO/N_2/O_2$ mixture happens, the electrons in discharge space are accelerated with the action of external electric field and then impact N_2 molecules and O_2 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 N_2 and O_2 molecules rise and then an increasing number of NO molecules are reduced to N_2 or oxidized to NO_2 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. O_3 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 O_3 is suppressed when V_{p-p} is high. In addition, O_3 can also be decomposed according to reactions (11) and (12). Therefore, the O_3 concentration increases at first and then decreases with the increasing of V_{p-p}. Since NO_2 is mainly produced by the reaction of O_3 and NO, the variation of NO_2 is similar to that of O_3.

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, N_2, O_2 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 N_2, O_2 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 O_3 and more NO molecules are oxidized to NO_2. 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 mixture[13]. Consequently, O_3 and NO_2 concentration decrease with the increasing of Ar concentration when V_{p-p} is high.

Conclusions

The experimental system of NO conversion in $NO/N_2/O_2/Ar$ mixture by non-thermal plasma technology was carried out. The effects of V_{p-p} and Ar concentration on NO conversion efficiency, NO_2 and O_3 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 N_2 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 O_3 generation. O_3 concentration reduces with the increasing of Ar concentration and the variation of NO_2 concentration is similar to that of O_3 concentration.

ACKNOWLEDGEMENTS

This work was financially supported by the National Natural Science Foundation of China (51176067) and the Ph.D. Programs Foundation of Ministry of Education of China (20103227110014) and the Natural Science Foundation of Jiangsu Province (BK2010330) and a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

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