Journal of Environmental Sciences Vol.17, No.3, pp.445—447, 2005

ISSN 1001—0742
CN11—2629/X

Article ID: 1001-0742(2005)03-0445-03 **CLC number**: X1701 **Document code**: A

Mechanism of NO reduction with non-thermal plasma

YU Gang[1,2], YU Qi[3], JIANG Yan-long[2], ZENG Ke-si[2], GU Fan[1]

(1. Education Ministry Key Laboratory on Clean Coal Power Generation and Combustion Technology, Southeast University, Nanjing 210096, China. E-mail: gangyu@nuaa.edu.cn; 2. Department of Man-Machine and Environment Engineering, College of Aerospace Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China; 3. Department of Environmental and Chemical Engineering, Wuhan Institute of Science and Technology, Wuhan 430074, China)

Abstract: Non-thermal plasma has been proved to be an effective and competitive technology for removing NO in flue gas since 1970. In this paper, the NO reduction mechanism of the non-thermal plasma reaction in $NO/N_2/O_2$ system was investigated using the method of spectral analysis and quantum chemistry. By the establishment of NO reduction and gas discharge plasma emission spectrum measuring system, the NO reduction results, gas discharge emission spectra of $NO/N_2/O_2$ and pure N_2 were obtained, and then the model of molecular orbit of N_2 either in ground state or its excited state was worked out using the method of molecular orbit Ab initio in Self-Consistent Field(SCF). It was found that NO reduction in NO/N_2 gas discharge plasma was achieved mainly through a series of fast elementary reactions and the N(E6) at excited state was the base for NO reduction.

Keywords: NO reduction; plasma; mechanism; spectral analysis; quantum chemistry

Introduction

The removal of nitrogen oxides (NOx) has become an important issue because of stringent limits imposed on the allowable levels of NOx emissions. Some of the new methods being investigated for post-combustion removal of NO are based on non-thermal plasma (Galkimberti, 1988; Sun, 1996; Shimizu, 1999).

In non-thermal plasma, a majority of the electrical energy goes into the production of energetic electrons rather than into gas heating. The electrons undergo many collisions with the dominant background gas molecules and produce radicals through electron-impact dissociation and ionization. The radicals, in turn, reduce or oxidize the NO molecules.

Masuda (Masuda, 1987) and Vitello (Vitello, 1994) found that either positive or negative corona can remove NO. Some scholars think that the direct current partial voltage enhances the reaction between ions and molecules and then enhances the apparent removal rate (Masuda, 1987).

For $NO/N_2/O_2$ gas system, there is a critical issue in the practical implementation of non-thermal plasma processing of pollutants: electrical energy consumption. The electrical energy consumption in meeting the desired level of NO removal is of critical importance in practical situations. Due to the extreme complexity of plasma reacting system and the limitations of modern measurement means, it is much difficult to know exactly the actual reaction mechanism of NO removal. Therefore, the application of this technology is confined to some extent.

The atmospheric pressure discharge plasma process for NO removal, such as chemical reactions of active species, has not yet been fully understood. There are many investigations on the reaction kinetics simulation of NO removal using pulsed corona plasma (Lowke, 1995; Gentile, 1995; Orlandini, 2000). To lucubrate the NO removal mechanism through the plasma, the state of particles in plasma must be measured. Emission spectrum has been used to analyze the discharge plasma under various gas conditions or discharge conditions (Tochikubo, 2000). Wang (Wang, 1998; 1999) investigated only partially excited states of N_2 and NO, however, the results are not enough to explain the NO removal mechanism through plasma.

In non-thermal plasma, NO removal processes were observed through either oxidization or reduction. These reactions have been studied by many researchers (Shimizu, 2001). Reducing reactions in the atmospheric discharge could be enhanced by excited species or active species. Emission spectrometry in NO/N_2 plasma at atmospheric pressure has been applied to study the reaction mechanisms of active species (Shimizu, 2002). The N_2 second positive band (N_2 SPB), the N_2 first negative band (N_2 FNB) and the NO-γ band were investigated using a digital controlled spectrometer. N_2 SPB and N_2 FNB are excited by electron collisions and NO-γ band is energized by collisions of N_2 (A)-state molecules. But in these studies, the ultraviolet spectrum of gas mixture and the production process of the active species which plays an important role in NO reduction have not yet been obtained. Consequently, these studies cannot discover the essential steps of NO reduction and the experimental results are not enough to understand the reaction mechanisms of active species.

In this work, the NO reduction and emission spectra measuring system of $NO/N_2/O_2$ plasma were established and that the visible and ultraviolet spectra of $NO/N_2/O_2$ plasma were obtained. Based on the analysis of plasma emission spectral and relevant theory of molecular statistical physics, a study on the reduction mechanism of NO through $NO/N_2/O_2$ gas system plasma reaction was carried out.

1 Experimental setup

Fig. 1 shows the setup of the experiment for NO reduction and emission spectral measuring system which are made up of:

(1) Gas discharge plasma reacting device. It is a glass-tube type. Fig. 2 shows its structure. The inner diameter of inlet and outlet is 15 mm and the middle slim tube is 1 mm in internal diameter which can ensure that the gases flow fully in the plasma region.

(2) High frequency and high voltage transformer (model HB708). Its frequency output is 30 kHz, and the maximum voltage output is 15 kV.

(3) Experimental gases. The purity of N_2 is 99.99%. In this experiment, N_2 and NO are mixed in a proportion of

Foundation item: The National Basic Research Program (973) of China (No. G19990222909)

10:1 using a trifurcate mixer.

(4) Procedure monochromatic device(D500 HILGER). The focal length is 1 m, and the large area holographic surface glittering grating is 102 mm × 102 mm. The glittering value is 500 nm. The whole procedure grating control system scanning range is 200—500 nm.

(5) Spectral measuring system. It is of Vitatron HILGER Analytical SET LH ZERO.

(6) NO concentration analysis device. The gas analyzer (model SAE19, Germany) is used to measure the concentration of NO.

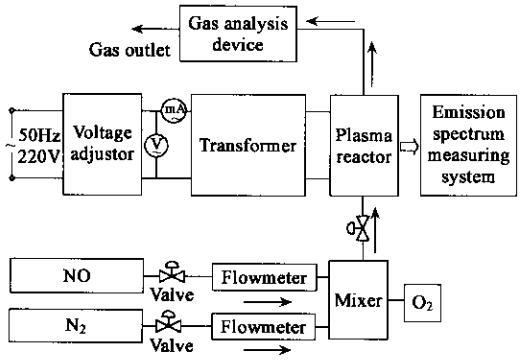

Fig.1 Schematic system for NO reduction and emission spectrum measuring

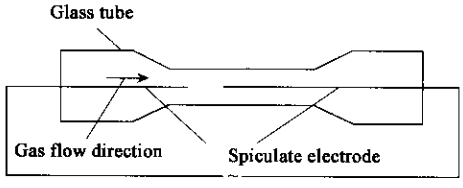

Fig.2 Schematic structure of glass-tube type gas discharge

The experiments were conducted on examining and recording NO reduction and gas discharge emission spectra.

2 Results and discussion

2.1 Discharge emission spectra of NO/N_2 and pure N_2 gas

D500 procedure monochromatic device is adopted to examine the gas discharge emission spectrum of NO/N_2 and pure N_2 in visible spectrum, results are showed in Fig.3 and Fig.4. Fig.5 shows the N_2 gas discharge emission spectrum in ultraviolet spectrum (0—200 nm) co-examined by the Plasma Research Institute of the Chinese Academy Sciences (CAS). Because no peaks oppeared in the range of 0—190 nm, the emission spectrum in this range is omitted (Fig.5).

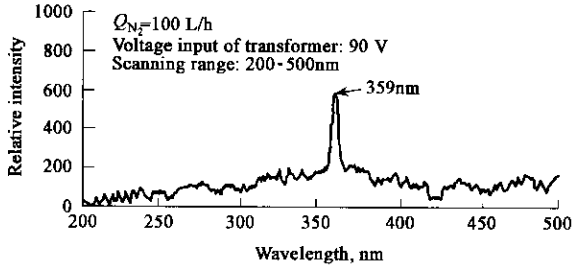

Fig.3 Emission spectrum of N_2 plasma

2.2 Analysis of N_2 ionization behavior

Fig.3 and Fig.4 are the gas discharge spectra in the range of 200—500 nm for pure N_2 and NO/N_2 respectively. It is quite clear that under the two discharge conditions, the two peak value locations are nearly the same, approaching to 359 nm, which indicate that the two corresponding activated states of gas molecular are the same. The two corresponding energy value can be deduced from the following two formulas: $h\nu = \Delta E$ and $\nu = \frac{C}{\lambda}$, when λ is replaced by 359 nm, the energy value of spectra in Fig.3 and Fig.4 is 3.46 eV.

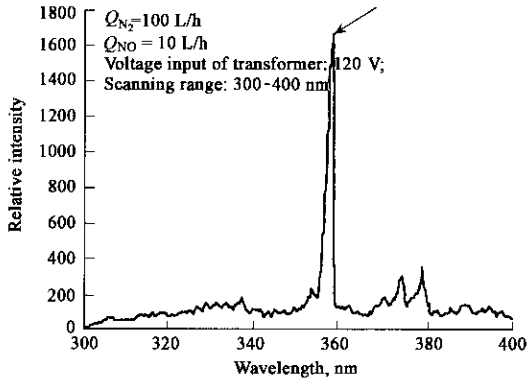

Fig.4 Emission spectrum of N_2/NO plasma

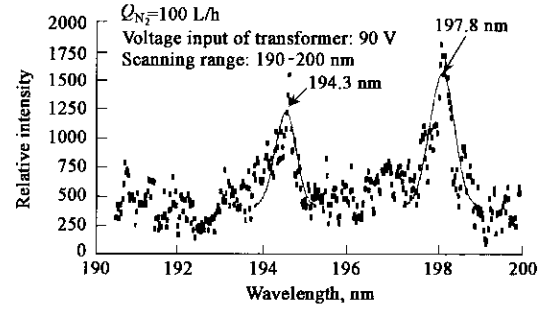

Fig.5 Emission spectrum of N_2 plasma co-examined by Plasma Research Institute of CAS

Fig.5 is the N_2 gas discharge emission spectra in the range of 0—200 nm. It can be deduced that the energy value of spectrum is 6.28 eV corresponds to the peak at 197.8 nm.

By using molecular orbit Ab initio method in Self-Consistent Field (SCF), the molecular of N_2 in its ground state and excited state can be worked out, as presented in Fig.6 and Fig.7.

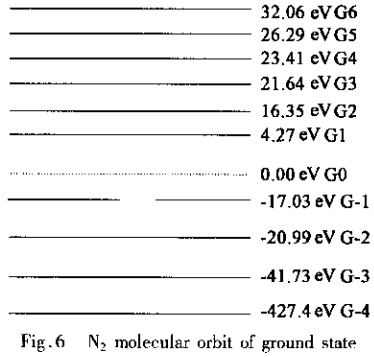

Fig.6 N_2 molecular orbit of ground state

From the former analysis on the results of gas discharge emission spectra, both pure N_2 and the mixture gas N_2/NO have a relatively high peak value near 359 nm, namely 3.46 eV. In addition, from the molecular obit of N_2, the energy level 31.60 eV-27.86 eV = 3.74 eV and the corresponding activating process is e + N_2 (E5) → 2N(E6) + e(Here, N

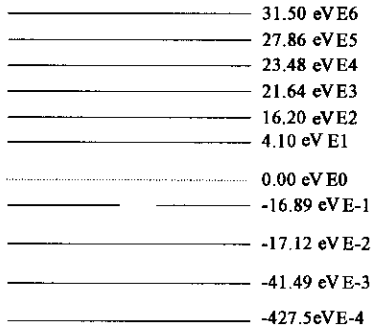

Fig.7 N_2 molecular orbit of excited state

(E6) stands for a certain excited state of N_2. Similarly, from 27.86 eV-21.64 eV = 6.22 eV, it can be worked out that 6.28 eV should correspond to the original activating process e + N_2(G3)→N_2(E5) + e. The statistical errors are resulted from the errors in measuring spectrum and calculating energy level of N_2, however, the errors are of little significance.

2.3 Effect of O_2 on NO reduction within gas discharge plasma of NO/N_2/O_2 mixture

Fig.8 is the results of the NO reduction in NO/N_2/O_2 plasma system.

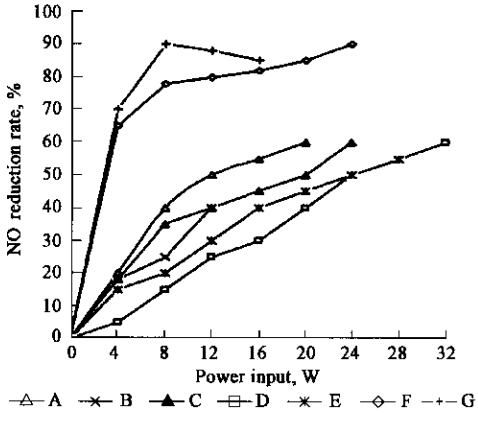

Fig.8 NO reduction rate versus input power

C represents the concentration, the rest is N_2; A: $C_{NO} = 125 \times 10^{-6}$, $C_{CO} = 0$, $C_{O_2} = 0$; B: $C_{NO} = 210 \times 10^{-6}$, $C_{CO} = 0$, $C_{O_2} = 0$; C: $C_{NO} = 170 \times 10^{-6}$, $C_{CO} = 0$, $C_{O_2} = 0$; D: $C_{NO} = 322 \times 10^{-6}$, $C_{CO} = 0$, $C_{O_2} = 12\%$; E: $C_{NO} = 240 \times 10^{-6}$, $C_{CO} = 0$, $C_{O_2} = 7\%$; F: $C_{NO} = 96 \times 10^{-6}$, $C_{CO} = 50 \times 10^{-6}$, $C_{O_2} = 0$; G: $C_{NO} = 94 \times 10^{-6}$, $C_{CO} = 58 \times 10^{-6}$, $C_{O_2} = 0$

Fig.8 indicates that the NO reduction rate will decrease when O_2 gets into the gases system. This phenomenon may be caused by the oxidation reaction: N + O_2→NO + O and there is NO in its products. Then, why is the general tendency of this system still that NO is reduced by N(E6)?

Table 1 shows the rates k of the following chemical reactions(T is the reaction temperature): N + NO→N_2 + O and N + O_2→NO + O(Baulch, 1994). It can be seen that the reaction N + NO→N_2 + O is much faster than N + O_2→NO + O, and the chemical reaction N + NO→N_2 + O, which is the key reaction of NO reduction, is prevailing.

Table 1 The rate of N atom reaction

N atom reaction	N + NO→N_2 + O	N + O→NO + O
Reaction rate k, $cm^3/(mol \cdot s)$	$7.1 \times 10^{-11} \times \exp(-790/T)$	$5 \times 10^{-14} T \times \exp(3270/T)$

Although in plasma reaction process NO can be oxidated by O_2, the general tendency of this system is that NO is reduced by N(E6) due to the low reaction speed of its oxidation reaction.

2.4 Mechanism of NO reduction in NO/N_2/O_2 gas discharge plasma

All these indicate that NO reduction in NO/N_2/O_2 gas discharge plasma is achieved mainly through the following three elementary reactions: e + N_2(G3)→N_2(E5) + e, e + N_2(E5)→2N(E6) + e and N(E6) + NO→N_2 + O. Therefore, one basic conclusion can be drawn that the N(E6) at excited state is the base for NO reduction and the effect of reducing NO is determined, to a large extent, by the concentration of N(E6) at excited state produced in the discharge process.

3 Conclusions

From what mentioned above, it can be seen the mechanism of NO reduction through plasma mainly includes the following elementary processes

$$e + N_2(G3) \rightarrow N_2(E5) + e, \quad (1)$$

$$e + N_2(E5) \rightarrow 2N(E6) + e, \quad (2)$$

$$N(E6) + NO \rightarrow N_2 + O. \quad (3)$$

The mechanism of NO reduction through plasma is to produce the N(E6) at excited state by Equation(1), (2), and (3), and then N(E6) react with NO to form a molecular N_2 and an atom of O through the fast reaction of Equation(3).

Although NO can be oxidated by O_2 in reaction process, the general tendency of this system is that N is to be reduced by NO because of the low speed of the oxidation reaction.

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(Received for review August 30, 2004. Accepted October 31, 2004)