Reaction mechanisms in $DeNO_x$ by activated ammonia generated by DBD

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Abstract— A unique SNCR system by activated ammonia injection using an intermittent dielectric barrier discharge (DBD) has been developed to remove NOx from an incinerator. However, the NOx reduction mechanisms are not elucidated so far. .In this paper, chemical species in the activated ammonia was investigated at the DBD reactor exit. Hydrogen was detected as main composition of the activated ammonia. The simulation gas of the activated ammonia (NH_3+H_2) was prepared to be clear the contribution of hydrogen, and the deNOx performance of the simulation gas was examined. It found that hydrogen has the role of enlargement of temperature window in deNOx reaction. DeNOx mechanisms were concerned using elementary reaction analysis based on Miller & Bowman mechanism. It was clear that formation of HNO and NH from hydrogen in the activated ammonia promoted deNOx reaction at low temperature region.

Keywords—Dielectric barrier discharge, nitrogen oxide, DeNOx, ammonia, hydrogen.

I. Introduction

Because an environmental problem came to attract attention, emission concentration regulation of NOx by local agreements came to be determined in smaller combustion facilities which was thus far left out of emission concentration regulation of NOx. A method to remove NOx is adopted generally by a combustion control and Selective Catalytic Reduction systems (SCR) in the combustion facilities of business use or the industrial use. But the practical use of a small and economical denitrification device is expected in smaller combustion facilities from a point of view such as a setting area and the driving cost.

However, DeNOx reaction temperature range for SNCR is very high temperature range from 850 ºC to 1175 ºC (hereinafter referred to as Temperature window) [1]. Since it is not possible to secure a sufficient reaction time at Temperature window, Decrease of NOx removal efficiency is a problem to smaller combustion facilities. It is necessary to technology to lower Temperature window in order to solve the problem.

The authors discovered that the Temperature window is 150-200 ºC extended to the low-temperature side to inject excited NH_3 gas by atmospheric pressure plasma into the combustion exhaust gas (hereinafter referred to as Radical Injection Method). We have studied experimentally the effect of various reaction parameters such as NH_3/NO molar ratio and input power on the NOx removal efficiency along the way [2] – [4]. However, it is not possible to elucidate the denitration reaction mechanism by radical injection method.

In order to clarify the denitration reaction mechanism of radical injection method, It is necessary to clarify quantitatively the product that excited NH_3 by atmospheric pressure plasma. In this paper, we quantified the composition of stable species (NH_3, H_2, and N_2) in excited ammonia by atmospheric pressure plasma and discussed the reaction mechanism of Radical Injection Method by comparing the denitrification property.

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II. Methodology

Figure 1 shows a schematic diagram of the ammonia radical injection De-NOx system test facility using the pulsed DBD. The facilities contains two gold furnaces with quartz tubes for controlling gas temperature, simulant gas ($NO/N_2/O_2$) supply system, Simultaneous NOx removal gas (NH_3/Ar) supply system, plasma reactor, high voltage pulsed power supply, three gas analyzer (NOx, N_2O and O_2), Micro GC and photo acoustic spectroscopy (PAS). Plasma reactor is double-tube structure cylinder made from SiO_2. Plasma reactor size is as below. Outside diameter of outside tube is 61 mm (thickness 2mm), outside diameter of inside tube is 54 mm (thickness 2mm), length is 490 mm and gap between outside tube and inside tube is 1.5 mm. High voltage electrode (SUS316) is placed in inside of inner-tube and punched metal (SUS316) is looped around outer-tube as ground electrode. Length of ground electrode is 360 mm. Electrical properties of the plasma reactor are described in past paper [2].

An NH_3/Ar mixture gas was supplied to gap section of plasma reactor. In the plasma reactor, NH_3 were excited by atmospheric pressure plasma generated by using a dielectric barrier discharge. Excited NH_3 was sampled at plasma reactor outlet. NH_3 concentration in the sample gas was measured by PAS, H_2 and N_2 concentrations were measured by Micro-GC.

On the other hand, simulated exhaust gas ($NO/O_2/N_2$) was supplied to pre-heating tube (Length 500mm) and pre-heated to 500 ºC. Simulated exhaust gas and excited NH_3 were mixed in mixing chamber, supplied to reaction tube (Length 600mm). NOx removal efficiency was calculated from outlet gas composition each of reaction temperature (500 ºC - 800 ºC). Gas composition of outlet gas is measured continuously by each gas analyzer.

Table 1 shows experimental conditions. We researched effect of NH_3/Ar flow rate and applied voltage for composition change of excited NH_3 and effect of applied voltage and reaction temperature for NOx removal efficiency.

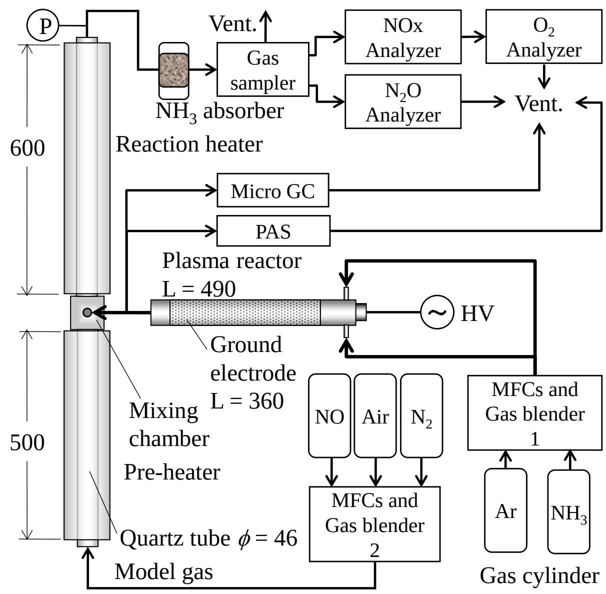

Fig.1 Schematic diagrams of experimental apparatus.

Table 1 Experimental conditions.

Measurements of chemical composition	
NH_3/Ar gas mixture	0.2, 0.4, 0.8 L/min*
Applied voltage	0−15 kV
Repetition rate	10 kHz
Initial NH_3 concentration	4840 ppm
DeNOx experiments	
NH_3/Ar gas mixture	0.8 L/min*
$NO/O_2/N_2$ gas mixture	2.2 L/min*
Initial NO concentration	500 ppm
Initial O_2 concentration	8.3 %
Temperature	500−800ºC

*Standard conditions (293 K and 0.1 MPa).

III. RESULTS & DISCUSSION

A. Chemical composition of excited NH_3

Figure 2 shows variation in NH_3 decomposition as functions of applied voltage and flow rate of NH_3/Ar gas. NH_3 decomposition is calculated according to the following equation.

$$D_{NH3} = ([NH_3]_I - [NH_3]_O) / [NH_3]_I \times 100. \quad (1)$$

Where $[NH_3]_I$ is initial concentration of NH_3 at plasma reactor inlet, $[NH_3]_O$ is concentration of NH_3 at plasma reactor outlet.

NH_3 decomposition increases with the increasing applied voltage and the decreasing flow rate of NH_3/Ar gas. The factor of NH_3 decomposition is considered that NH_3 get higher energy than bond enthalpy (450kJ·mol^{-1}) of NH_3 from electric energy of Ar plasma. The increasing of NH_3 decomposition is explained that electric energy to NH_3 increased by the increasing applied voltage and the decreasing NH_3/Ar gas flow rate. NH3 is decomposed completely at gas flow rate 0.2L/min and applied voltage 15kV.

Figure 3 shows chemical composition (H_2, N_2, and unreacted NH_3) in plasma reactor outlet gas at each applied voltage. NH_3 concentration decreases with the increasing applied voltage, but H_2 and N_2 concentrations increases. It was found that unknown substance is contained in excited NH_3 gas. The unknown substance is considered stable NmHn compound.

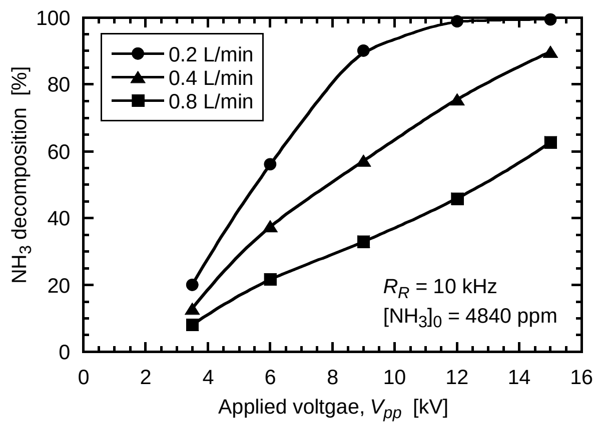

Fig.2 Variation in NH_3 decomposition as functions of applied voltage and flow rate of NH_3/Ar gas.

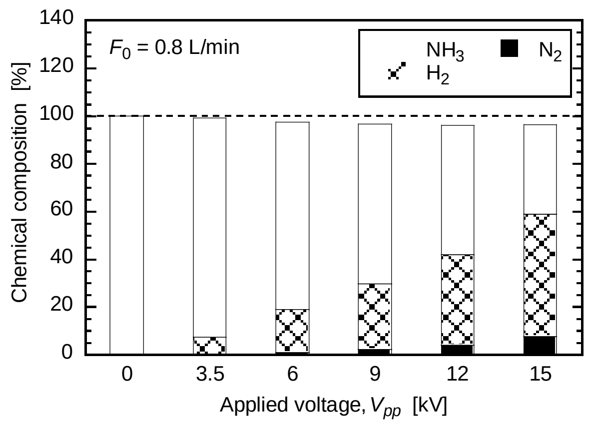

Fig.3 Gas composition of activated ammonia at the plasma reactor exit at NH_3/Ar flow rate of 0.8 L/min.

B. NOx removal characteristics by excited NH_3 gas

It was found that the components of excited NH_3 are H_2 and unreacted NH_3 mainly from Fig.3. Lyon et al. shows that Temperature window shifts about 150 ºC to lower temperature side [5]. Moreover, Muzio et al. shows that H_2/NO molar ratio to obtain maximum NOx removal varies according to reaction temperature and NH_3/NO molar ratio in addition to show similar findings to Lyon et al. [6]. In other words, it is highly possible that H_2 generated from the ammonia excited by atmospheric pressure plasma contribute to the expansion of Temperature window. Therefore, we prepares simulant excited NH_3 gas (NH_3 + H_2) according to Fig.3 and performs NOx removal experiments that injects simulant excited NH_3 gas to Mixing Chamber (Fig.1) directly. Figure 4 shows comparison of deNOx characteristics between excited NH_3 injection and its simulant gas injection in 600ºC and 700 ºC. When NH_3 only inject to reaction field, NOx removal reaction does not occur in this temperature range. However, when simulant gas (NH_3 + H_2) inject, NOx removal reaction occurs in this temperature range. That is, it is evident that H_2 contribute to the expansion of Temperature window.

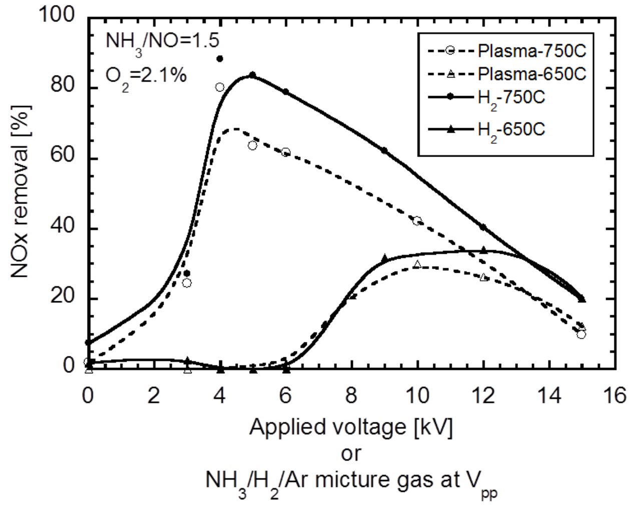

Fig.4 Comparison of deNOx characteristics between excited NH_3 injection and its simulant gas injection.

IV. Discussion

A. Inquest of NOx removal mechanism

We goes through NOx removal mechanism by excited NH_3 injection method with elementary process simulation because it has been found that chemical composition of excited NH_3 and contribution of H_2 to NOx removal. Elementary process simulation is simulated using Miller & Bowman mechanism [7] and CHEMKIN-PRO (chemical reaction mechanism analysis software). Plug flow reactor is assumed as the reactor model. Concentrations of Various chemical species (N_2, O_2, NH_3, and H_2) are set as an initial condition.

Figure 5 shows simulation result of the contribution of H_2 to NOx removal. As NH_3 coexists with H_2 in the reaction field, new reaction pathway(HNO → NH) occurs. It is suspected that NO reduction reaction by NH contributes to the expanding of Temperature window.

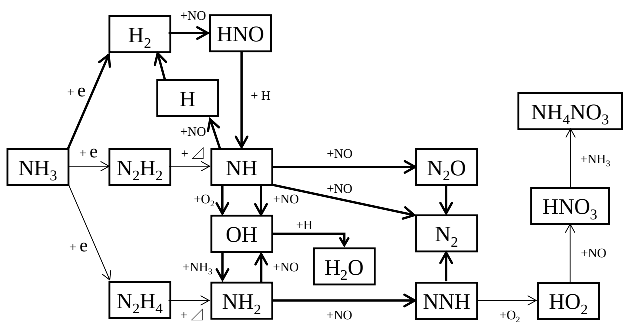

Fig.5 Comparison between elemental reaction analysis and experimental results.

V. Conclusion

It was shown that the Temperature window is 150-200 ºC extended to the low-temperature side to inject excited NH_3 gas by atmospheric pressure plasma into the combustion exhaust gas. Excited NH_3 gas contains H_2 and unreacted NH_3 as a major ingredient. It was found to expand Temperature window when NH_3 inject with H_2. In NOx removal reaction with excited NH_3, It was shown that H_2 contributes the expansion of Temperature window. It is suspected that NO reduction reaction by NH contributes to the expanding of Temperature window in deNOx reaction field.

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