307   Removal of NO$_x$ at Low Temperatures by Photochemical Reaction without Catalysis and Ammonia

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Abstract

Removal of nitrogen oxides (NO$_x$) from flue gas emitted from large-scale ships is desirable for environmental pollution control. Selective catalytic reduction (SCR), an efficient treatment technology, has been used worldwide for NOx removal in large-scale combustors such as coal fired power plants. However, a serious drawback of SCR systems in application to ships is that the traditional catalyst cannot use to the low temperature flue gas emitted from ships. The aim of the research was to develop an innovative method using effective chemical species for NO removal at low temperatures. Vacuum ultraviolet (VUV), wavelength of 172, 185, and 190 nm emitted from an excimer lamp, was employed as the excitation source for NO/O$_2$/N$_2$/NH$_3$ gas mixtures at a room temperature. The effects of NH$_3$/NO molar ratios (M_R), gas flow rate (gas residence time), and oxygen concentrations on NO removal were investigated. An approximate 98% NO$_x$ removal was attained with an M_R = 1.5, F = 1.0 L/min and 8.3% O$_2$.

Keywords: SNCR, Ammonia, NOx, Excimer Lamp, VUV

1   INTRODUCTION

Nitrogen oxides (NO$_x$) are emitted from various combustion processes. For environmental pollution control and public health, regulations of NO$_x$ emissions have been strengthening and expanding worldwide. Recently, NO$_x$ regulations to marine diesel engine exhaust gases has been become a hot topic, because it too difficult to protect the severe regulations using current techniques such as selective catalytic reduction (SCR). The conventional SCR is worked at around 400°C, therefore, it is not apply to marine diesel engine exhaust gases below the temperature of 180°C. And also, the exhaust gases contain a high concentration of sulfur oxides (SO$_2$), which poison the SCR catalyst. An advanced selective non-catalytic reduction (SNCR) working at low temperatures below 180°C have been desired.

The SNCR system has been used in some coal combustion processes. It is a simple device and low-cost system comparing with the SCR processes. However, reaction temperature range in the SNCR is the ranges from 850 to 1175°C [1]. Therefore, the current SNCR techniques are not applied to the marine diesel engine exhaust gases.

The detailed elemental reaction mechanisms in NO formation and reduction give important information for the development of the advanced SNCR working at the low temperatures. NO reduction mechanisms in an NO/NH$_3$/O$_2$ system have been demonstrated on a kinetic basis by several researchers [2,3]. The principal reaction sequence is as follows: ammonia first generates NH and NH$_2$ (NH$_i$) radicals by reacting with hydroxyl radicals (OH) above 850 °C; then, NO reduction takes place by reaction of NH$_i$ radicals with NO. NH$_i$ radicals are the most effective radicals for NO reduction; therefore, if amidogen radicals can be form at low temperatures below 180°C by something methods, NO$_x$ is removed.

Vacuum ultraviolet (VUV) is a promissed method to form radicals at low temperatures. Some chemcal species absorbs VUV, and then they are decomposed to radicals, ions, and different molecules. In particular, molecular ammonia (NH$_3$) has high absorption coeficient between 150 and 200 nm [4]. It is expected that NO$_x$ removal at low temperatures is possible by using VUV such as the wavelength of 172, 185/254, and 190 nm.

In this study, NO$_x$ removal experiments were carried out by direct irradiation of VUV. Effects of NH$_3$/NO molar ratios, gas flow rates, and wavelength on NO$_x$ removal were investigated.

2   EXPERIMENTAL

The experimental setup is shown in Fig. 1. The apparatus consists of the gas mixing and flow control systems, the photochemical reactor, and the gas analyzers. An NO/Air/N$_2$ gas mixture at room temperature was prepared using the mass-flow controllers and the gas blender, and fed into the photochemical reactor as the model flue gas. Ammonia gas diluted with nitrogen was used as the NO removal agent, which was mixed with the model gas by line blending, and then, the gas mixture fed into the photochemical reactor at room temperature. The gas composition of the output stream was continuously

measured by gas analyzers for NO_x (HORIBA VIA510), O_2 (SHIMAZU NOA-7000), and N_2O (HORIBA VIA510).

Fig.2 shows the details of the photochemical reactor. The photochemical reactor is a simple structure: the cylindrical excimer lamp generated ultraviolet (Ushio Inc., length in 100 mm, outer diameter of 40 mm) was placed to the center of the cylindrical reactor (inner diameter 80 mm). The excimer lamps were prepared three wavelength types of 172 nm, 185 nm, and 190 nm. The absorption coefficient of molecular ammonia is 59 $atm^{-1} \cdot cm^{-1}$ at 172 nm [4], implying that molecular ammonia is excited by photons emitted from the excimer lamp in the photochemical reactor, while nitrogen gas is inert.

NO and O_2 concentration in the model gas was fixed 600 ppm, and 8.3%, respectively. NH_3 concentrations (600 ppm−1200 ppm) and gas flow rates (1.0 L/min−3.0 L / min) were varied. The model gas mixture ($NO/O_2/N_2/NH_3$) was fed into the gap between the excimer lamp and the inside wall of the cylindrical chamber. The gap volume was 377 cm^3, the radiation power of the VUV ray was 26 mW/cm^2 on the quartz glass surface of the excimer lamp. When the excimer lamp turned on, NOx removal was occurred. The temperature inside photochemical reactor was about 150°C by the radiation heat of the excimer lamp, though the gas mixture was room temperature.
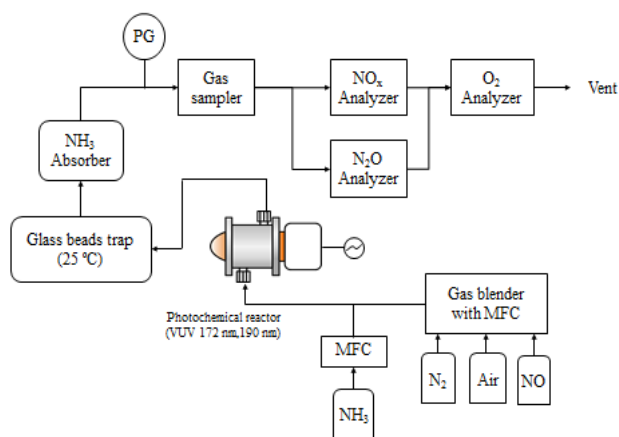

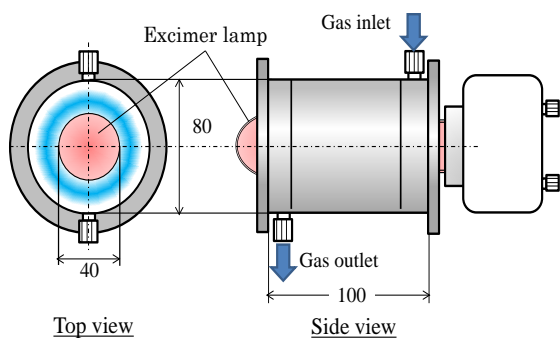Fig.1 A schematic diagram of experimental apparatus.

Fig.2 Details of the photochemical reactor.

3 RESULTS AND DISCUSSION

3.1 Characteristics of NO_x removal by VUV

Fig.3 shows the characteristics of the NO_x removal by photochemical reaction by the vacuum ultraviolet light. Parameters were the flow rates of the model gas mixture, wavelength (172 nm and 190 nm), and the molar ratios of NH_3/NO that was equal to the concentration ratios.

First, effect of the flow rates on the NO_x removal can easily understand as an influence of the residence time in the photochemical reactor. Number of photons irradiated to the NH_3 molecule during gas residence time is calculated by the following equation [5].

$$N = A \cdot P \cdot \theta \{1 - \exp(-\alpha \cdot P_{NH3} \cdot d)\}/hv \qquad (1)$$
$$v = c/\lambda \qquad (2)$$

where, A is surface area of the excimer lamp [cm^2], P is the power density of the excimer lamp [W/cm^2], θ is the gas residence time [s], α is the absorption coefficient of NH_3 [$atm^{-1}cm^{-1}$], P_{NH3} is the partial pressure of NH_3 [atm], d is the gap length [cm], h is Planck's constant [J s], v is frequency [1/s], c is velocity of light [m/s], λ is wavelength [m].

When the flow rates (F) is the lowest (θ is the highest), number of photons become maximum according to eq.1, because the other variables indicated in eq.1 are constant at the same wavelength. In this condition, the most of molecular NH_3 convert to NH_2 and NH radicals (eq.3). The produced NH radical rapidly reacts with NO, and NO is removed by conversion to N_2 (eq.4). Therefore, effect of the flow rates on NOx removal was proportional as shown in Fig. 3.

$$NH_3 + hv \rightarrow NH + H_2 \qquad (3)$$
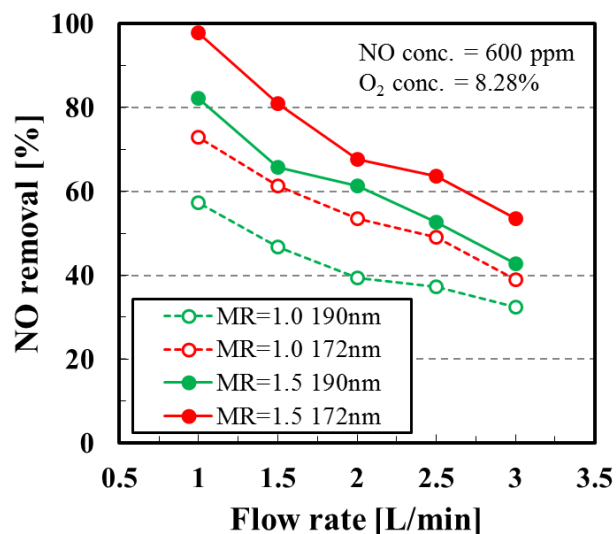$$NH + NO \rightarrow N_2 + OH \qquad (4)$$

Fig.3 Characteristics of NOx removal by VUV irradiation.

Second, effect of the molar ratios is considered. The number of molecular ammonia is increased with an increase of the molar ratio, so concentration of NH radical will be increased by reaction of eq.3, which will occur NO reduction of eq.4.

Effect of the wavelength will be described next section.

Maximum NO_x removal was 97.8% at $F = 1.0$ L/min, $M_R = 1.5$, and wavelength = 172 nm.

3.2 Effect of wavelength on NO_x removal

As the above mentioned, a controlled factor of NOx removal was concentration of NH radical generated by VUV irradiation. It seems that the concentration of NH radical is proportional to the fraction of NH_3 decomposition. Therefore, it is a good index for considerations of an influence of the wavelength to investigate variation in the fraction of NH_3, because NH radical cannot measure directly.

Fig.4 shows variation in NH_3 decomposition of each wavelength lamp with various photon numbers. The photon number was varied by adjustment of the gas residence time and characteristic of the power density of the each excimer lamp.

When the photons number was below 1.5×10^{20}, the highest NH_3 decomposition, 41%, was obtained by the 190 nm lamp. The absorption coefficient of molecular ammonia is approximately 700 $atm^{-1}\cdot cm^{-1}$ at 190 nm, that is higher than that of 172 nm. Therefore, the highest NH_3 decomposition was attained by the 190 nm lamp at the range below 1.5×10^{20}. However, the power density of the 185 nm lamp and the 190 nm lamp, P, was low levels by characteristic of the lamps. Therefore, the photon number was up to 0.5×10^{20} or 1.5×10^{20} for the 185 and 190 nm lamps.

The 172 nm lamp has strong power density (26 mW/cm^2); the photon number was up to 3.3×10^{20}. After all, the maxmum NH_3 decomposition was attained by the 172 lamp that can be obtained the maximum photon number.
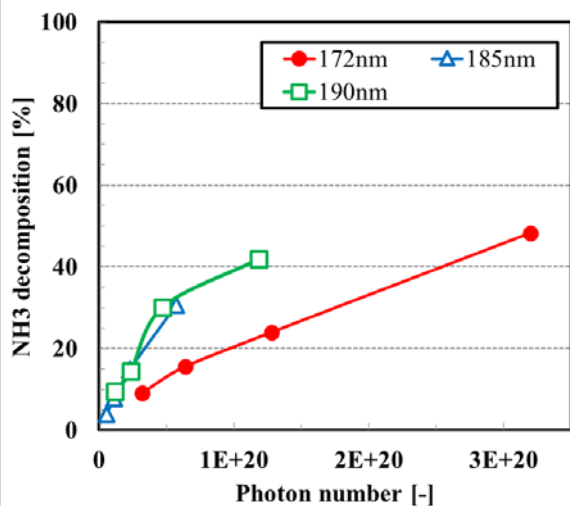

Fig.4 NH_3 decomposition by three different wavelength.

3.3 Co-products

Adhesion of white powders, co-products, was observed on the inner surface of the photochemical reactor after experiments. In $NO/O_2/N_2/NH_3$ system, it was easily estimated that the co-product was ammonium nitrate (NH_4NO_3). To be clear the chemical composition, differential thermogravimetric analysis was performed (SHIMADZU DTG-60/60H).

Fig. 4A and Fig. 4B shows the thermogravimetric curves from a literature and this analysis, respectively. It found that both curves indicated good agreement: the co-product was NH_4NO_3.

From this experimental results, the following reaction paths were considered in photochemical reactions in $NO/O_2/NH_3/N_2$ system.

$$O_2 + hv \rightarrow O + O \tag{5}$$
$$O_2 + O \rightarrow O_3 \tag{6}$$
$$NO + O_3 \rightarrow NO_2 + O_2 \tag{7}$$
$$O + H_2(\text{from } NH_3) \rightarrow OH + H \tag{8}$$
$$NO_2 + OH \rightarrow HNO_3 \tag{9}$$
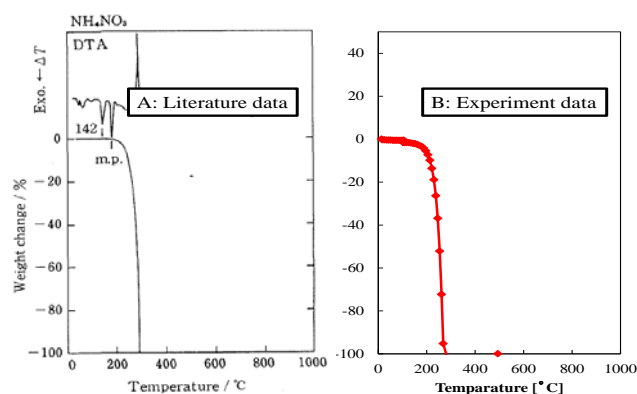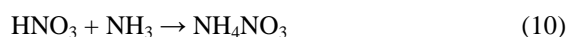$$HNO_3 + NH_3 \rightarrow NH_4NO_3 \tag{10}$$

Fig.5 Thermal analysis of residual products. A: Literature data, B: this study

3.4 Reaction mechanisms of NO_x removal

To consider NO_x removal mechanisms in the photochemical reactions, $NO/O_2/N_2$ system and NO/N_2 system without NH_3 was examined. Fig. 6 shows effect of flow rates, O_2 concentrations, and wavelength on NO decomposition.

It should be noted first that NO was removed (or decomposed) by photochemical reaction in the NO/N_2 system without O_2 and NH_3: there is a direct reaction pathway as follows:

$$NO + hv \rightarrow N + O \tag{11}$$
$$N + N \rightarrow N_2 \tag{12}$$

$$O + O \rightarrow O_2 \tag{13}$$

It should be noted second in Fig.6 that NO decomposition in the $NO/O_2/N_2$ system was lower than that in the NO/N_2 system. In this system, reactions (5)−(7) and (11)−(13) may be occurred. NO_2 is formed as the product by reactions (5)−(7), however, it does not contributes to NO decomposition. Consequantly, dominant reactions in the $NO/O_2/N_2$ system may be reactions (11)−(13).

Fig.6 NO decomposition in the $NO/O_2/N_2$ system and the NO/N_2 system (without NH_3).

4 CONCLUSIONS

This study are summarized as follows:

(1) In the $NO/O_2/N_2/NH_3$ system, an approximate 98% NO_x removal was attained with an $M_R = 1.5$, $F = 1.0$ L/min and 8.3% O_2.

(2) The 172 nm lamp was suitable for NOx removal among the wavelength of 172, 185, and 190 nm.

(3) The co-product in NOx removal by photochemical reaction was NH_4NO_3.

(4) There are a direct reaction pathway on NO_x decomposition: $NO + hv \rightarrow N + O$. About 40% contribution for NO_x decomposition were observed at $F = 1.0$ L/min without O_2.

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[5] S. Kambara, Y. Hayakawa, M. Masui, N. Hishinuma, K. Kumabe, H. Moritomi, "Removal of nitric oxide by activated ammonia generated by v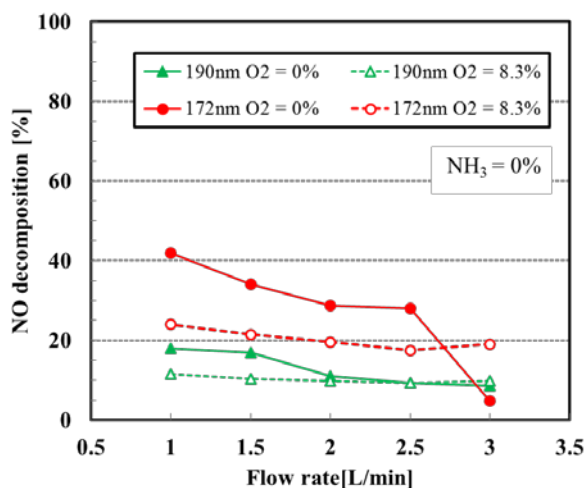acuum ultraviolet radiation", *Fuel*, 94, pp.274-279, 2012.