

NO_x removal by 172 nm VUV irradiation at room temperature

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ABSTRACT

An innovative selective non-catalytic reduction reacting at a low temperature has been desired for waste incinerators and ship exhausts to observe strict NO_x regulation. Photochemical NO_x removal by vacuum ultraviolet irradiation of a 172 nm wavelength is a promising technique. The dominant reactions in the photochemical reactions were investigated in detail by the small-scale photochemical reactor using a model gas such as NO, NO-O₂, NO-H₂O, and NO-H₂O-O₂ system. In NO, NO-O₂, and NO-H₂O system, NO concentration was gradually decreased, while NO₂ was formed by oxidation of a part of NO. Contrary, in NO-H₂O-O₂ system, NO concentration was rapidly decreased, and NO₂ concentration was low levels. The reaction mechanism was parallel reactions of three paths including HNO₃ generation from NO, NO₂ generation from NO, and HNO₃ generation from NO₂. The maximum amount of NO_x removal in NO-H₂O-O₂ gas system was examined for practical use by the large-scale photochemical reactor: it was 0.72 g-NO/h at 90% NO_x removal.

KEYWORDS

Vacuum ultraviolet, NO_x, HNO₃, deNO_x, SNCR

INTRODUCTION

Emission of nitrogen oxides (NO_x) from stationary combustors and ship diesel engines has been regulated for environmental pollution control and public health. In Japan, strict emission limits are in place for all stationary sources, including small-scale combustion plants such as waste incinerators. NO_x emission control from ship exhausts has launched in 2016 by International Maritime Organization (IMO).

Selective catalytic reduction (SCR), an efficient treatment technology, has been used world-wide for NO_x removal in large-scale combustors such as coal-fired power plants. In SCR systems, nitric oxide (NO) reacts with injected molecular ammonia in the presence of a catalyst and oxygen at a temperature of around 350 °C at which NO converts to molecular nitrogen and water [1]. A drawback of SCR systems in application to incinerators and ship diesel engines is that they are particularly costly because frequent replacement of the catalyst is required owing to catalyst poisoning by sulfur dioxide, plugging and erosion by ammonium bisulphate, and deposition of ash, amongst others.

Selective non-catalytic reduction (SNCR) is a conceptually simple process that involves the injection of molecular ammonia into a furnace without using a catalyst. SNCR systems offer a promising technology because of their cost-effectiveness, although critical issues regarding their application still exist. In SNCR systems, NO_x reduction occurs at a high temperature range of 850 °C–1175 °C. However, a sufficiently high efficiency of NO_x reduction cannot be obtained in combustors, because the gas residence time in the temperature window is very short for the deNO_x. [2]. On the other hand, SNCR is inappropriate for ship diesel engines, because the temperature of

ship exhausts is about 150 °C. Therefore, a novel deNO_x method reacting without catalysts at low temperature is desired.

We have been developed an original deNO_x reactor using vacuum ultraviolet (VUV) of 172 nm wavelength [3]. The advantages of the deNO_x system are no catalyst, ammonia free and low temperature reaction. The photochemical reactor using the VUV may be able to apply to waste incinerators and ship exhausts. In this study, reaction mechanisms of deNO_x by the VUV were investigated to find a rate-controlling reaction step.

EXPERIMENTAL APPARATUS AND METHOD

The experimental setup is shown in **Figure 1**. The apparatus consists of the gas supply system, the photochemical reactor with an excimer lamp, and the gas analyzers. The photochemical reactor had an inner diameter of 80 mm, and the length was 100 mm. An outer diameter of the excimer lamp was 40 mm, therefore, the gap length between the lamp and the inner wall of the reactor was 20 mm. The excimer lamp was continuously emitted a narrow wavelength distribution having a peak intensity at 172 nm. The power density was 27 mW/cm² at the lamp surface.

NO, NO₂, O₂, N₂, and saturated water vapor (H₂O) was prepared as model gas, which fed into the photochemical reactor at an atmospheric pressure. The model gas fed into the gap volume (377 cm³). The flow rate of the model gas was adjusted by the mass-flow controllers (MFC) at the ranges from 1.0 L/min to 5.0 L/min. The gas temperature was kept 60 °C to prevent dew condenses in the gas flow pipe. The pressure in the reactor was controlled to be slightly above atmospheric pressure using a gas sampler (SHIMAZU CFP-8000), which featured suction pumps, gas coolers, and flow meters. The composition of sample gas was continuously measured by gas analyzers for NO and NO₂ (HORIBA VIA510), O₂ (SHIMAZU NOA-7000), and N₂O (HORIBA VIA510).

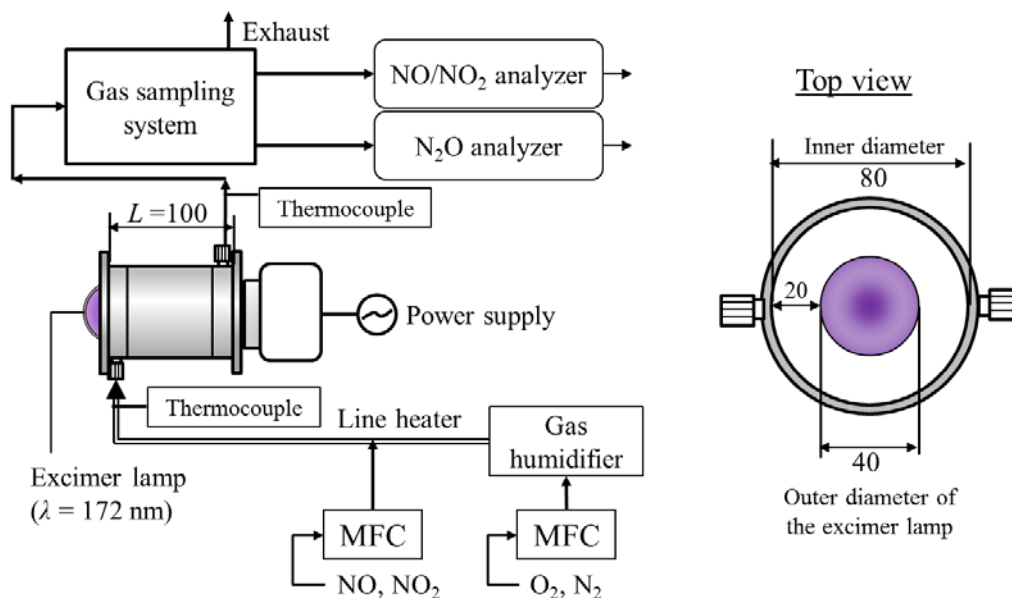


Figure 1. Experimental setup for fundamental studies of deNO_x. (Small-scale reactor).

To study reaction paths of deNO_x by irradiation of 172 nm VUV, fundamental experiments were carried out using the small-scale photochemical reactor shown in Fig. 1. The various model gas systems were used:

- | | |
|------------------------|---|
| 1. Single gas system | NO-N ₂ , O ₂ -N ₂ |
| 2. Two component gas | NO-O ₂ , NO-H ₂ O, O ₂ -H ₂ O |
| 3. Three component gas | NO-O ₂ -H ₂ O |

The gas concentrations of NO, NO₂, O₂, and H₂O were fixed at 600 ppm, 600 ppm, 8.0 %, and 7.0 %, respectively.

Figure 2 depicts the experimental setup for scale-up tests. The photochemical reactor was 1000 mm in the length and 43 mm in the inner diameter. The excimer lamp was 847 mm in the length and 20 mm in the outer diameter, which had the power density of 26 mW/cm². The gap volume was 964 cm³: the large-scale reactor is 2.6 times in scale-up comparing with the small-reactor.

To examine the performance of deNO_x by 172 nm VUV, the initial NO concentration and the flow rate of the simulation gas were varied in this tests. The gas concentrations of O₂ and H₂O were fixed at 8.3 %, and 6.6 %, respectively.

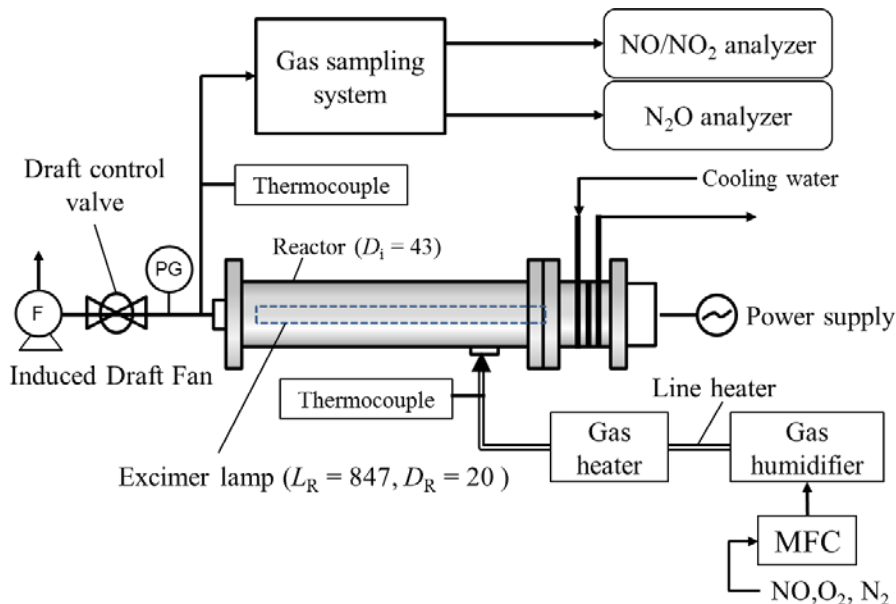


Figure 2. Experimental setup for scale-up tests. (Large-scale reactor)

RESULTS AND DISCUSSION

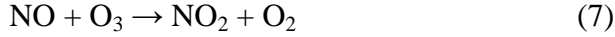
Reaction paths of 172 nm VUV irradiation

Fundamental deNO_x experiments using various gas components were examined as shown in **Figure 3**. In NO, NO-O₂, and NO-H₂O system (Fig.3 (a), (b), and (c)), NO concentrations were gradually decreased, while NO₂ were formed, and the NO₂ concentrations were increased with an increase in gas residence time, though each NO and NO₂ concentrations were different. N₂ is an inert gas in photochemical reactions, because molecular nitrogen does not absorb the wavelength of 172 nm. It is clear that NO₂ is generated by oxidation of NO during VUV irradiation. The photochemical reactions on NO₂ formation are supposed as follows:

Photochemical reactions:



Elemental reactions:



where, h [J·s] is Planck's constant, and ν [s⁻¹] is the frequency. The $h\nu$ is the photon energy [J]. NO, H₂O, and O₂ have a high absorption coefficient at 172 nm wavelength: they are decomposed by absorption of the photon energy [4].

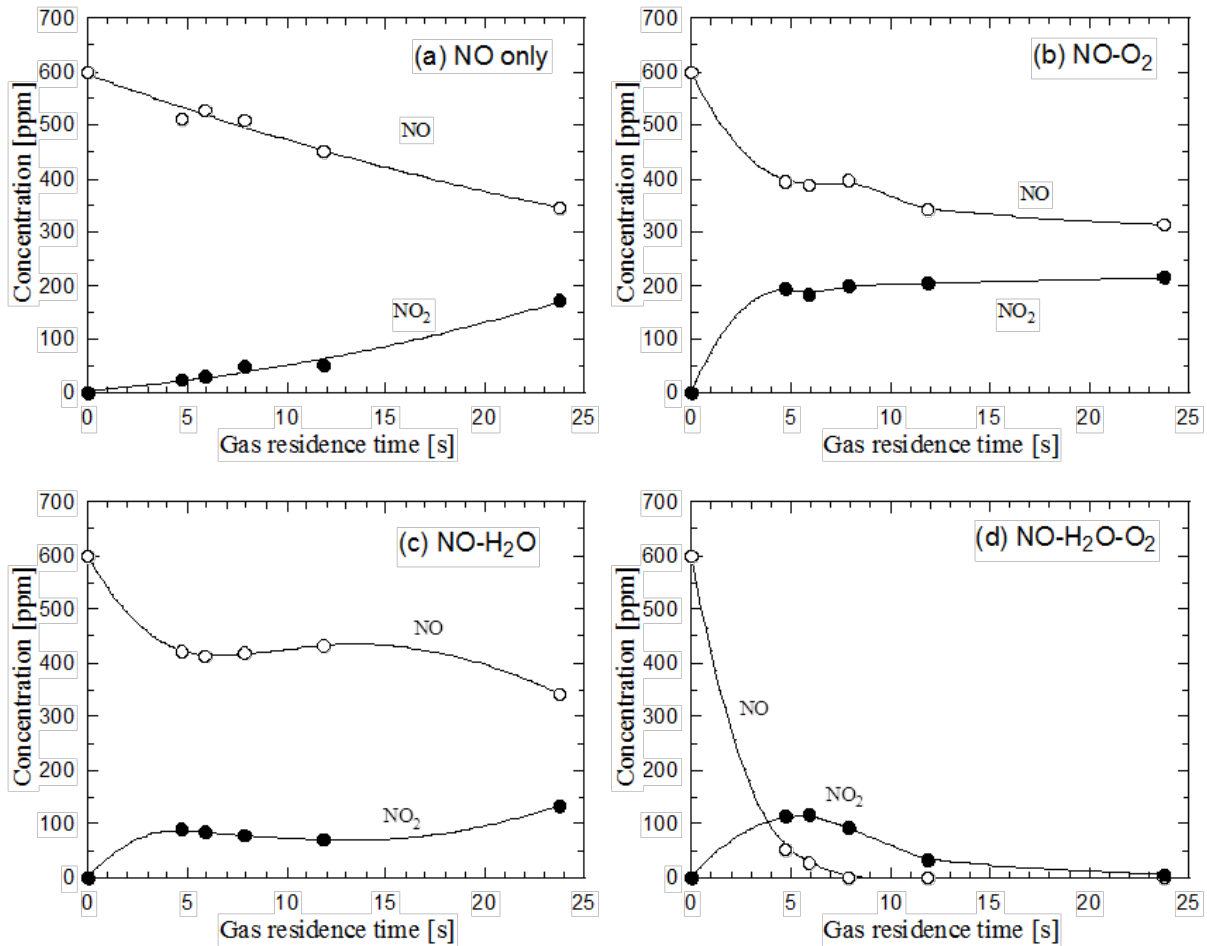


Figure 3. Fundamental studies of photochemical reactions using 172 nm VUV.

Figure 4 shows relation between $(\text{NO}_{\text{in}} - \text{NO}_{\text{out}})$ and NO_2 generations. NO_{in} and NO_{out} is NO concentration at the inlet and outlet of the reactor, respectively. NO_2 generation was directly proportional to an increase in $(\text{NO}_{\text{in}} - \text{NO}_{\text{out}})$. Therefore, it supposed that the reaction mechanism of NO_2 formation is same in the NO, NO- O_2 , and NO- H_2O system. However, NO_2 concentrations in the NO- O_2 system were higher than that in the NO and NO- H_2O system. This is because that ozone generated by reactions (2) and (6) contributes NO_2 generation by reaction (7): these reactions do not occur in the NO only and NO- H_2O system. Ozone formation characteristics show in **Figure 5** as a function of O₂ and H₂O concentration. At H₂O = 0%, a high concentration of O₃ was generated, therefore, NO_2 was rapidly formed by reactions (2), (6), and (7) in NO- O_2 system (Fig. 3(b)).

NO decrease and NO_2 generation in NO- H_2O - O_2 system shown in Figure 3 (d) was a different behaviour from the other system. NO was rapidly removed, while NO_2 was increased

below the short gas residence time of 6 s, after then, NO_2 was decreased. This result shows that high efficiency NO_x removal at low temperature is attained without catalysts and any reduction agents in the $\text{NO-H}_2\text{O-O}_2$ system.

In $\text{NO-H}_2\text{O-O}_2$ system, the final product by VUV irradiation is nitric acid (HNO_3) [3]. Therefore, the following reactions are applied.

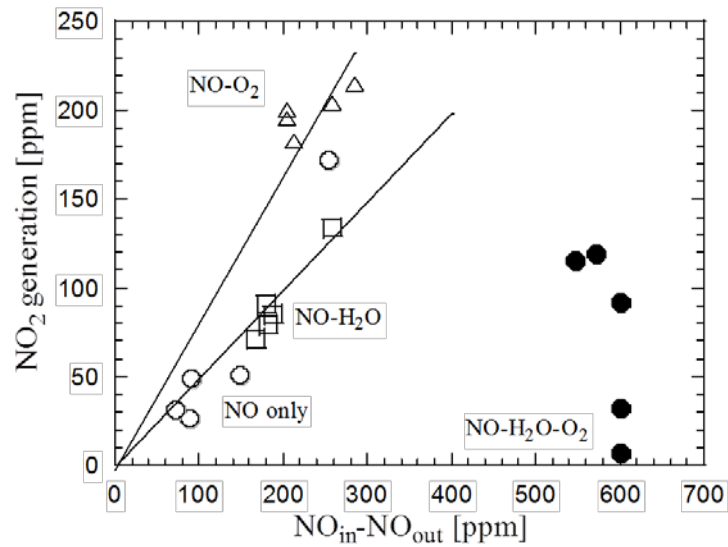
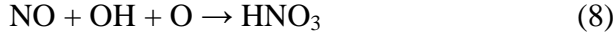


Figure 4 Relation between difference NO concentrations and NO_2 concentrations.

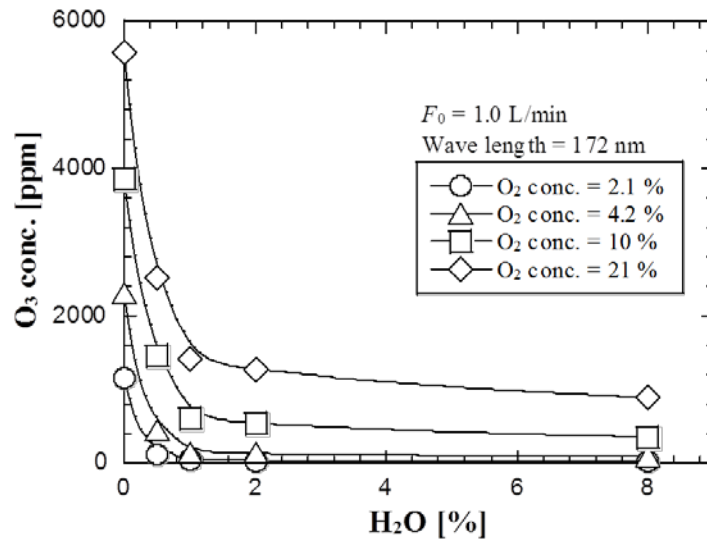


Figure 5. Ozone generation in $\text{O}_2\text{-H}_2\text{O}$ system.

The reaction paths in the $\text{NO-H}_2\text{O-O}_2$ system is parallel reactions as shown in **Figure 6**. In Figure 3(d), the NO concentration was suddenly decreased, however, the NO_2 formation rate was little comparing with the NO removal rate. Relation between concentrations of $(\text{NO}_{\text{in}} - \text{NO}_{\text{out}})$ and NO_2 generations in Figure 4 quantitatively indicates the slow rate of the NO_2 formation rate. Therefore, reaction (8) is fast comparing with reactions (1)–(7). The NO_2 oxidation rate by reaction (9) is the slowest, which understood from the NO_2 decrease behaviour at the gas residence time from 6 s to 24 s in Figure 3(d).

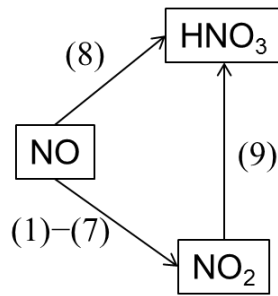


Figure 6. DeNO_x removal reaction paths in NO-H₂O-O₂ system.

Effect of H₂O concentration on NO removal

Figure 7 shows characteristics of NO removal at the gas residence time of 23.7 s in various H₂O concentrations. It found that high percentages of NO removal were obtained at more than H₂O concentration of about 4 %. Fortunately, flue gas from waste incinerators and ship exhausts contains enough H₂O concentration and O₂ concentration. The photochemical reactor may be able to apply to practical uses.

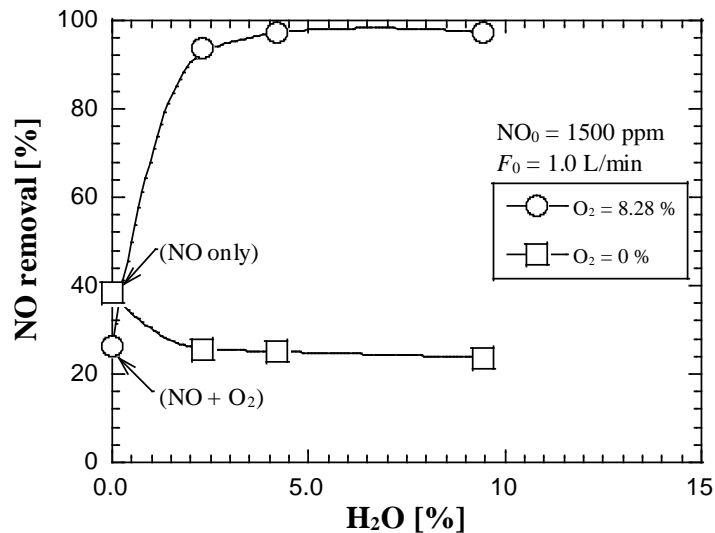


Figure 7. Effect of H₂O concentration on NO removal in NO-H₂O-O₂ system.

Effect of H₂O concentration on NO removal

To investigate the amount of the maximum NO_x removal by the 172 nm VUV irradiation, effect of initial NO concentration on NO_x removal was examined using the large-scale photochemical reactor shown in Figure 2. **Figure 8** shows variation in NO_x removal with an increase in initial NO concentration. The flow rate of the simulation gas (NO-H₂O-O₂), F , was varied at the ranges from 10 L/min to 20 L/min. About 90% NO_x removal was obtained at NO_{IN} = 500 ppm and F = 20 L/min. At the flow rate of 20 L/min, NO_x removal was gradually decreased above NO_{IN} = 500 ppm. The maximum NO_x removal at 90% NO_x removal in the large-scale photochemical reactor was 0.72 g-NO/h.

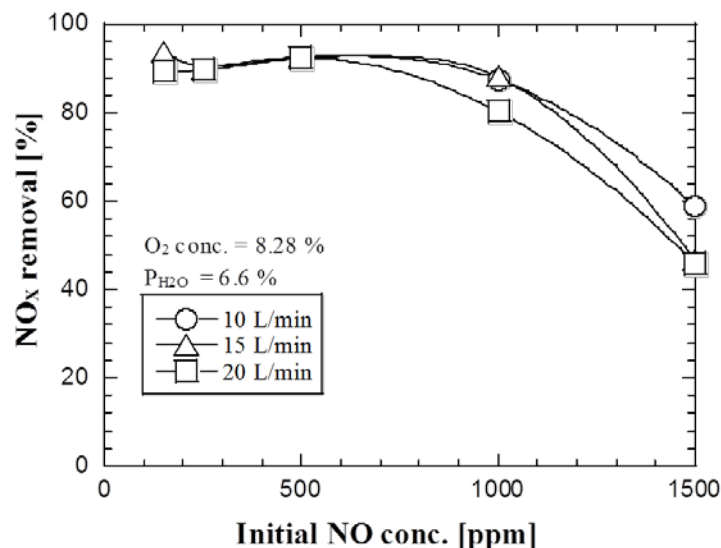


Figure 8. Characteristics of NO_x removal by large-scale photochemical reactor.

CONCLUSION

The reaction paths of NO_x removal by 172 nm VUV irradiation was investigated in detail using various model gases such as NO, O₂, NO-H₂O, NO-O₂, O₂-H₂O, and NO-H₂O-O₂.

In NO, NO-O₂, and NO-H₂O system, NO concentrations were gradually decreased, while NO₂ were formed. NO₂ concentrations were increased with an increase in gas residence time. Ozone was generated under O₂ existence. In NO-H₂O-O₂ system, NO was rapidly removed, and NO₂ concentration level was low. NO_x removal of 99% was obtained above H₂O = 4 %.

The reaction paths including three photochemical reactions and five elemental reactions were proposed: the reaction paths of NO_x removal by 172 nm VUV irradiation at a low temperature is parallel reactions containing NO, NO₂, and HNO₃.

The amount of the maximum NO_x removal was 0.72 g-NO/h, which was examined using the large-scale photochemical reactor.

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