Efficient Conversion of NO_2 into N_2 and O_2 in N_2 or into N_2O_5 in Air by 172-nm Xe_2 Excimer Lamp at Atmospheric Pressure

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Decomposition of NO_2 (200 ppm) in N_2 or air by 172-nm Xe_2 excimer lamp was studied at 1 atm. The NO_2 conversion in N_2 was 99%, and the formation ratios of N_2, O_2, NO, and N_2O were 47, 98, 0, and 2%, respectively, after 30 min irradiation. The NO_2 in air (5–20% O_2) could be completely converted to N_2O_5 and HNO_3 due to reactions by O_3 and H_2O after only 1.0–1.5 min irradiation. The present results give a new simple photochemical aftertreatment technique of NO_2 in air without using any catalysts.

We have recently initiated development of a photochemical method as a new promising removal method of NO*x* at atmospheric pressure without using expensive catalysts.[1–4] An advantage of photochemical method is that more selective decomposition is possible than electric discharge method, where energetic electrons are main energy carrier. We have recently studied decomposition of NO_2 into N_2 by using 193-nm ArF excimer laser in N_2 at atmospheric pressure.[2] Although more than 80% of NO_2 (200 ppm) could be converted into N_2, O_2, and NO in N_2 at atmospheric pressure, it was difficult to decompose NO_2 in air because after photolysis of NO_2 into NO + O (1a), such backward reaction (1b) occurs significantly.

$$NO_2 + h\nu\ (193\,\mathrm{nm}) \rightarrow NO + O \tag{1a}$$

$$NO + O + M \rightarrow NO_2 + M\ (M = N_2, O_2) \tag{1b}$$

When ArF excimer laser photolysis was applied to practical NO*x* removal process, there are a lot of severe problems. They are that excimer laser apparatus is expensive, running cost is high, and the apparatus is big and heavy including high power sources. In order to overcome these problems, we used here a low cost and compact ($\phi = 128$ mm, length = 330 mm) Xe_2 lamp as a new VUV right source. The absorption cross section of NO_2 ($1.4 \times 10^{-17}\,\mathrm{cm^2\,molecule^{-1}}$) at 172 nm is 20 times larger than that ($7.1 \times 10^{-19}\,\mathrm{cm^2\,molecule^{-1}}$) at 193 nm.[5] Therefore, more efficient photolysis of NO_2 is expected at 172 nm. We have found for the first time that NO_2 could be efficiently removed not only in N_2 atmosphere but also in air (5–20% O_2) at a low NO_2 concentration of 200 ppm.

NO_2 photolysis chamber used in this study was similar to that used for ArF laser photolysis[1] except for the VUV light source. Light from an unfocused 172-nm Xe_2 lamp (USHIO, UER20H172:50 mW/cm^2, 155–200 nm range) was used to decompose NO_2 at a room temperature. All experiments were carried out in a closed batch system. The total pressure was kept at atmospheric pressure, and the NO_2 concentration diluted in N_2 or N_2/O_2 mixtures was 200 ppm (v/v).

After 0.1–30 min photoirradiation, products were analyzed by using HORIBA gas analysis system (FG-100) equipped with an FTIR spectrometer and ANELVA gas analysis system (M-200GA-DTS) equipped with a quadrupole mass spectrometer. We determined the residual amount of NO_2, $[NO_2]/[NO_2]_0$, and the formation ratios of N_2, O_2, and NO*x*, defined as $[N_2]/[NO_2]_0$, $[O_2]/[NO_2]_0$, and $[NOx]/[NO_2]_0$, respectively, from gas analyses. Here, $[NO_2]_0$ is an initial concentration of NO_2. N_2 and O_2 cannot be detected by FTIR, because these diatomic molecules are inactive for IR light. If other NO*x* and O_3 are produced in the photolysis, all of them can be detected. Thus, the formation ratios of N_2 and O_2 in N_2 were determined from N and O balance before and after photolysis.

When NO_2 was decomposed by a 172-nm excimer lamp for 20 min, the main absorption band of NO_2 at 1600 cm^{-1} reduced its intensity, as shown in Figure S1 (Supporting Information).[8] Figure 1 shows the dependence of NO_2 conversion and the formation ratios of N_2, O_2, NO, and N_2O on the irradiation time of lamp. After 30 min photoirradiation, the residual amount of NO_2 decreases to 1%, while the formation ratios of N_2 and O_2 increase to 47 and 98%, respectively. The formation ratio of NO initially increases to 9% until 2 min then gradually decreases to 0% in the 9–30 min range. The formation ratio of N_2O can be kept as low as 3% in the all time range. On the basis of these results, NO_2 can be efficiently decomposed to N_2 and O_2 keeping NO and N_2O emissions at low levels under 172 nm irradia-

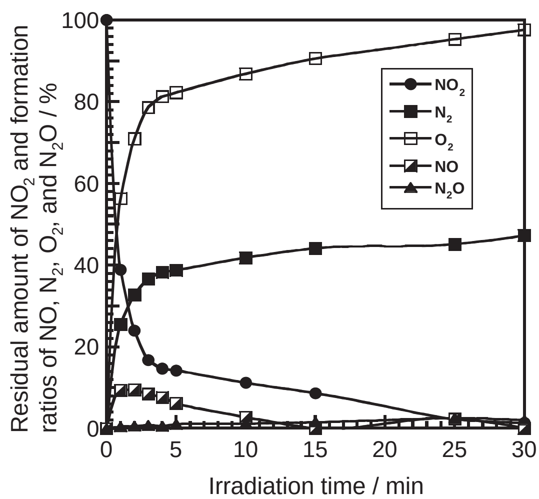

Figure 1. Dependence of residual amount of NO_2 and the formation ratios of products on the irradiation time of 172-nm excimer lamp at a NO_2 concentration of 200 ppm in N_2 at a total pressure of 1 atm.

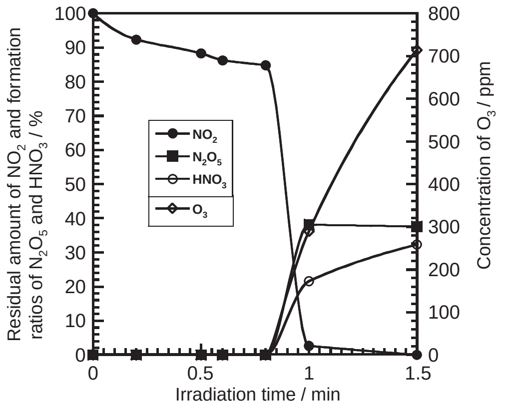

Figure 2. Dependence of residual amount of NO_2 and the formation ratios of products on the irradiation time of 172-nm excimer lamp at a NO_2 concentration of 200 ppm in air (5% O_2) at a total pressure of 1 atm.

tion, although it takes a long time to remove NO_2.

Since a small amount of O_2 (5–20%) is involved in N_2/O_2 mixtures in the practical combustion processes, removal technique of NO_2 must be developed in air. FTIR spectra observed before and after 172-nm photolysis of NO_2 were shown in Figure S2a–S2c.[8] Before photolysis, strong NO_2 peak is observed. After 0.5 min photoirradiation, only a small decrease (about 10%) in NO_2 peak intensity was observed. After 1.5 min photoirradiation, the spectrum changed significantly: NO_2 peak disappeared and N_2O_5, HNO_3, and O_3 peaks are observed.

Figure 2 shows the dependence of NO_2 conversion and the formation ratios of N_2O_5 and HNO_3 and concentration of O_3 on the irradiation time of lamp. The residual amount of NO_2 slowly decreases to 85% in the 0–0.8-min range, suddenly drops to 3% in the 0.8–1.0-min range, and becomes zero at 1.5 min. At about 0.8 min, the formation of N_2O_5, HNO_3, and O_3 starts, and their formation ratios increase in the 0.8–1.0-min range. At 1.5 min, the formation ratios of N_2O_5 and HNO_3 are 38 and 32%, respectively. The concentration of O_3 rapidly increases from 0.8 to 1.5 min and becomes 714 ppm at 1.5 min. These results indicate that NO_2 can be more efficiently converted to N_2O_5 and HNO_3 in air in the presence of O_2.

The reaction mechanisms of NO_2 in N_2 and air are briefly discussed from known photochemical and chemical reactions.[4–6] Rate constants shown below in parenthesis are given in $cm^3\ molecule^{-1}\ s^{-1}$ units. NO_2 is efficiently decomposed to N_2 and O_2 under 172-nm light in N_2. Detailed photolysis process of NO_2 at 172 nm has not been known to be best of our knowledge. In a similar 172-nm photolysis of NO, fast decomposition of NO to N_2 and O_2 in N_2 and conversion to NO_2 in air were observed.[7] Therefore, not only direct decomposition of NO_2 into N_2 and O_2 (1) but also multiple step decomposition via NO (2) probably takes part in the photolysis of NO_2 at 172 nm.

$$NO_2 + h\nu\ (172\,nm) \rightarrow N + O_2 \quad (1)$$

$$NO_2 + h\nu\ (172\,nm) \rightarrow NO + O(^3P, ^1D, ^1S) \quad (2a)$$

$$NO + h\nu\ (172\,nm) \rightarrow N + O \quad (2b)$$

N and O atoms produced in (2b) will be finally converted to N_2 and O_2 via subsequent reactions in N_2 and air.[1–6] It seems that the latter process is more significant, because direct formation of $N + O_2$ from NO_2 will be unfavorable channel.

In air, similar photolysis of NO_2 must occur until 0.8 min. The slower photolysis rate in the short range of 0–0.8 min can be attributed to absorption of 172-nm light by O_2 ($4.6 \times 10^{-19}\ cm^2\ molecule^{-1}$)[5] and fast backward reaction of $NO + O_3$:

$$NO + O_3 \rightarrow NO_2 + O_2\ (1.8 \times 10^{-14}) \quad (3)$$

Actually, the formation of O_3 by the following processes was observed from N_2/O_2 mixtures without addition of NO_2 after 172-nm irradiation (see Figure S3).[8]

$$O_2 + h\nu\ (172\,nm) \rightarrow O + O \quad (4a)$$

$$O + O_2 + N_2 \rightarrow O_3 + N_2\ (5.6 \times 10^{-34}[N_2]) \quad (4b)$$

The absence of O_3 in the 0–0.8 min range can be attributed to its fast removal via process (3).

After 0.8 min photoirradiation, the concentration of O_3 exceeds the concentration of NO. Then, the following oxidation reactions of NO_2 leading to N_2O_5 (5) take place:

$$NO_2 + O_3 \rightarrow NO_3 + O_2\ (3.5 \times 10^{-17}) \quad (5a)$$

$$NO_2 + NO_3 + N_2 \rightarrow N_2O_5 + N_2\ (3.6 \times 10^{-30}[N_2]) \quad (5b)$$

In the photolysis chamber, there is a small amount of residual H_2O (≈90 ppm), as observed OH peaks from residual H_2O in FTIR spectra. N_2O_5 has a high reactivity with H_2O leading to HNO_3:

$$N_2O_5 + H_2O \rightarrow 2HNO_3\ (2.5 \times 10^{-22}) \quad (6)$$

Thus, HNO_3 peaks arise from the result of reaction (6). Reaction (6) is an important reaction, because N_2O_5 can be easily removed as HNO_3 by the addition of H_2O.

The effects of O_2 concentration in N_2/O_2 mixtures were examined in the 5–20% range. With increasing the O_2 concentration from 5% to 10 and 20%, the formation of N_2O_5 starts at shorter time of 1 min.

In summary, NO_2 removal by 172-nm excimer lamp has been studied. It was found that NO_2 in air can efficiently be converted to N_2O_5 using O_3 generated from 172-nm photolysis of O_2. Since N_2O_5 can be easily converted to HNO_3 by the addition of H_2O, the present results are useful as a new simple and low cost photochemical aftertreatment technique of NO_2 in air without using any catalysts.

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