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# Effect of oxygen and water vapor on the removal of styrene and ammonia from nitrogen by non-pulse corona-discharge at elevated temperatures

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**Abstract**

The present work experimentally investigates the individual and combined effect of $O_2$ and $H_2O$ vapor on the separate and simultaneous removal of styrene and $NH_3$ from $N_2$ at elevated temperatures via corona-discharge reactions. Styrene and $NH_3$ are chosen to represent the trace components in crematory emission because they are chemically dissimilar. Since the crematory emission always contains some $O_2$ and $H_2O$ at elevated temperatures, their effects and the effect of elevated temperature are of practical interest. It is found that the presence of $O_2$ in $N_2$ always enhances the removal of styrene and/or $NH_3$ from $N_2$. The presence of $H_2O$ in $N_2$ generally enhances the removal of styrene and/or $NH_3$ but its presence retards that of $NH_3$ when $H_2O$ concentration is too high or the temperature is 300 °C. The combined effect of $O_2$ and $H_2O$ is found to substantially retard the removal of styrene and/or $NH_3$ compared to the sole effect of coexisting $O_2$. The general effect of elevated temperature is to decrease the removal efficiency of styrene and/or $NH_3$ compared to the case of room temperature.

*Keywords:* Styrene; Corona-discharge; Ammonia; Effect of oxygen; Effect of water vapour; Elevated temperature

## 1. Introduction

Recently, a considerable number of reports on the application of discharge technology to gas purification have appeared because the technique is deemed as a powerful method to remove dilute gaseous contaminants. There are several types of electrical discharge for gas purification such as dc corona-discharge [1,2], pulsed corona-discharge [3], surface discharge [4], and electron beam [5]. Among these methods, dc corona-discharge is considered to be superior in terms of low byproduct formation thanks to the low electron energy in the discharge region.

Nowadays air pollution in Thailand poses a serious environmental issue. There are numerous sources of air pollutants in big cities such as heavy concentration of vehicles and traffic congestion. One severe public nuisance is emission gas from the crematorium during cremation rites. There are nearly 23,000 temples nationwide, including approximately 300 temples with crematory furnaces in Bangkok Metropolitan Area alone. During cremation, various malodorous gases and particulate are often emitted without adequate treatment, causing frequent complaints from vicinal communities. A few rich temples have installed furnaces with effective after-burning systems but an overwhelming majority of the temples have inadequate systems. For this reason it is worthwhile to develop an alternative gas treatment method that achieves high efficiency at relatively low energy consumption. This similar issue may affect some other developing and even developed countries, where cremation is widely practiced.

In potential applications of corona-discharge reactors, it is important to know the influence of temperature, especially the high temperature range. For example, the exhaust gas temperature from a cremating furnace may be as high as 300 °C. In spite of this practical condition, a limited number of reports on temperature effects on discharge-assisted gas purification have appeared since the reported removal of methanol and trichloroethylene from air by dielectric barrier and pulsed corona-discharges under 300 °C [6]. The present

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**Nomenclature**

| | |
|---|---|
| $A$ | cross-sectional area ($m^2$) |
| $C$ | concentration (ppm) |
| $E$ | electric field strength (V/m) |
| $N$ | gas density ($mol/m^3$) |
| SV | space velocity ($h^{-1}$) |
| $t_r$ | ratio of residence times in the corona-discharge zone |
| $V$ | effective volume of the corona-discharge reactor ($m^3$) |

*Greek letters*

| | |
|---|---|
| $\theta$ | mean residence time (s) |
| $\langle \upsilon \rangle$ | superficial velocity (m/s) |
| $\psi$ | removal efficiency |
| $\psi'$ | removal efficiency per unit residence time |
| $\psi_{elec}$ | electron-based efficiency |
| $\psi_{ener}$ | energy-based efficiency (mol gas/J) |

*Subscripts*

| | |
|---|---|
| in | inlet of reactor |
| out, 0 mA | outlet of reactor at zero discharge current |
| out, any mA | outlet of reactor at non-zero current |

work applies non-pulse corona-discharge to the removal of styrene and $NH_3$, two dissimilar components chosen to represent crematory emission [7,8]. Since, in addition to $N_2$, the crematory emission contains $H_2O$ vapor and residual $O_2$ at elevated temperatures, their effects on the separate and simultaneous removal of styrene and $NH_3$ are investigated experimentally.

## 2. Experimental

Fig. 1 shows a schematic diagram of the experimental set-up which consists of a non-pulse corona-discharge reactor, a test gas mixing system, a high-voltage dc generator and a temperature controller. The reactor consists of a SUS tube, 3.7 cm inner diameter and 80 cm length, as the anode. The cathode is a 0.5 mm stainless-steel wire suspended from a silicone plug at the top of the reactor and straightened along the central axis of the vertical anode by a small weight. A high-voltage dc generator (Matsusada, HAR-30N5) whose maximum allowable voltage is 50 kV is utilized to supply a steady stream of low-energy electrons to the corona-discharge reactor. A slim pyrex glass tube is used to sheath either end of the cathode in order to limit the corona-discharge zone to an effective length of 10 cm in the middle section of the reactor and to expose the zone to an essentially flat axial temperature distribution. A type-K thermocouple is inserted into the reactor to measure the gas temperature in the discharge zone. To control the reactor temperature, six infrared heating lamps (700 W each) are installed lengthwise around the outside perimeter of the reactor. The temperature control unit consists of a temperature controller and a thyrister power regulator.

The desired concentrations of styrene, $NH_3$, and/or coexisting $O_2$ are adjusted by diluting standard gases with pure $N_2$ carrier gas. Water vapor is mixed into the carrier gas by bubbling it through liquid water whose temperature is suitably controlled at 34–50 °C. The inlet concentrations of styrene and $NH_3$ are either 500 or 40 ppm, and either 400, 250, or 200 ppm, respectively. Similarly, the concentrations of coexisting $O_2$ and $H_2O$ are varied from 0–25% and 0–23,000 ppm, respectively. Concentrations of styrene are analyzed using a gas chromatograph (Shimadzu Corp., GC

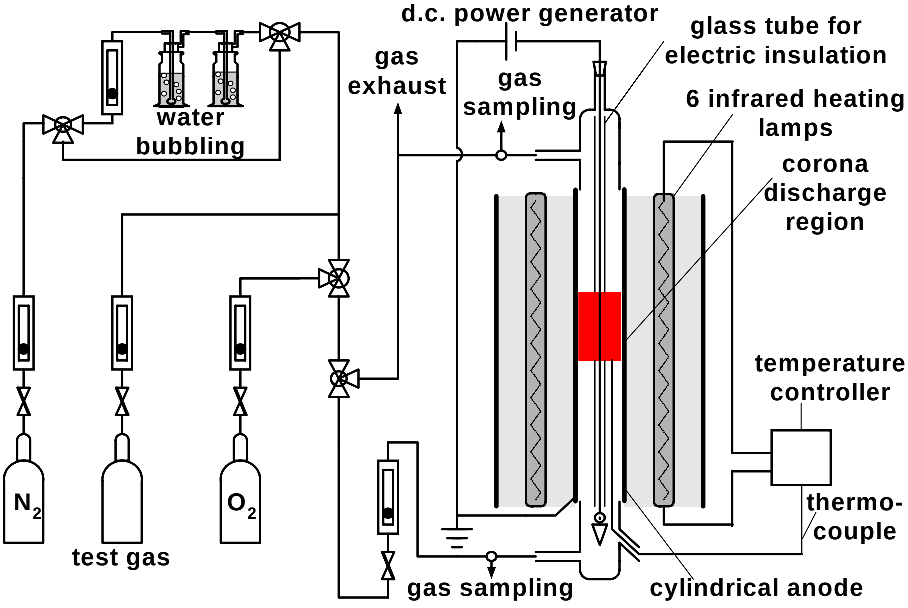

Fig. 1. Experimental apparatus.

9A) equipped with a flame ionization detector (FID). Concentrations of $NH_3$ are analyzed using another gas chromatograph (Shimadzu Corp., GC 14A) equipped with a thermal conductivity detector (TCD). The concentrations of byproduct $O_3$ and/or $NO_x$ can separately be detected with appropriate gas detector tubes (GASTEC Co., Ltd. and Kitagawa Co., Ltd.). $NH_3$ can also be detected or double-checked by detector tubes. Compared to the GC method, the detecor-tube measurements were found to differ by less than 12%.

The inlet concentrations of styrene and $NH_3$ are deliberately set higher than their reported values in crematory emission for two reasons. First, our present and previous investigations have conclusively shown that, as the inlet concentration of a gaseous impurity rises, its removal efficiency always drops because the ratio of the number of gas molecules to the number of discharged electrons decreases. Thus, the experimental results yield conservative values. Second, if the gas concentration is too low (a few ppm order or less), there may be significant uncertainty in the measurement values obtained by the gas chromatographs.

In our case, the voltages required to generate 0.05 mA in the removal of either 500 ppm styrene or 400 ppm $NH_3$ from $N_2$–$O_2$ (20%) mixture are, respectively, 10.1 and 10.5 kV at room temperature, and these voltages decrease to 6.4 and 5.9 kV, respectively, as temperature rises to 300 °C. The voltages in the removal from pure $N_2$ are significantly lower but become unstable at the same 0.05 mA. Therefore, a higher current is used. Even when the current is increased 10-folds to 0.5 mA, the required voltage increases less than 10% for styrene and even decreases about 45% for $NH_3$. As the discharge current increases, ion wind [9] becomes stronger, causing the suspended wire cathode to sway. This effect imposes a maximum stable current, which is found to be around 0.5 mA, in our condition.

## 3. Results and discussion

### 3.1. Definition of removal efficiency

Generally the removal efficiency is obtained by comparing the inlet and outlet gas concentrations. At high temperatures, significant thermal decomposition of styrene and ammonia in $N_2$ might occur, which also depends on the type and concentration of the coexisting gas. For example, 23–33% of the influent styrene but less than 1.5% of the $NH_3$ were found to decompose at 200–300 °C in pure $N_2$. When $H_2O$ coexists at 20,000–23,000 ppm, the decomposition of styrene and $NH_3$ become ca. 31 and 16–20%, respectively. This means that only ammonia decomposition is accelerated by the presence of $H_2O$. On the contrary, the decomposition of styrene in the presence of 20% $O_2$ and $NH_3$ in the presence of 5% $O_2$ become ca. 38–40 and 1.5%, respectively This means that only styrene decomposition is accelerated by $O_2$. To show the sole effect of corona-discharge and excludes the effect of high-temperature thermal decomposition inside the reactor, the removal efficiency $\psi$ in this work is defined by Eq. (1)

$$\psi = \frac{C_{\text{out, 0 mA}} - C_{\text{out, any mA}}}{C_{\text{out, 0 mA}}} \tag{1}$$

Here, $C_{\text{out, 0 mA}}$ (ppm) and $C_{\text{out, any mA}}$ (ppm) are the outlet concentrations of the impurity gas without and with discharge current, respectively. At steady state, the equation of continuity requires that $\rho_1\langle\upsilon_1\rangle A_1 = \rho_2\langle\upsilon_2\rangle A_2$. Since $A_1 = A_2$ and $\rho$ is a function of the gas temperature, the gas velocity at an elevated temperature $T_2$ will be faster than its velocity at room temperature $T_1$. Thus, the mean residence time $\theta_2 = V/\langle\upsilon_2\rangle A$ of this gas at $T_2$ is shorter than $\theta_1 = V/\langle\upsilon_1\rangle A$ at room temperature. Here, $V$ is the effective volume of the corona-discharge reactor. The removal efficiency per unit residence time, $\psi'$, in Eq. (2) takes into consideration the shorter residence time of the hot gas in the reactor even when the inlet gas flow rate (mole basis) remains unchanged before and after the reactor temperature is elevated. Strictly speaking, this definition is scientifically correct only in the initial reaction stage where the yield is proportional to the residence time. Nevertheless, it is adopted here as a handy indicator that reasonably offsets the effect of reduced residence time.

$$\psi' = \frac{\psi \times \text{residence time at } 25\,^{\circ}\text{C}}{\text{residence time at } T\,^{\circ}\text{C}} \tag{2}$$

It is a common practice to obtain reaction rate constants based on some proposed reaction system in order to elucidate detailed reaction kinetics. In the purification of $N_2$ contaminated with several individual sulfur compounds and $CH_3CHO$ in a corona-discharge reactor, a mathematical model based on the first-order reaction of electron attachment and the fitted ion-diffusivity is shown to correlate well with experimental results [1,10]. However, this model is not applicable to this study in which its “electron efficiency”, the number of gas molecules removed per electron, is greater than unity. The experimental electron efficiencies obtained here range from 0.9 at 300 °C in the case of pure $N_2$ to 36.6 at room temperature in the case of 20% $O_2$. The large values indicate that not only electron attachment but other reaction paths such as radical reaction and dissociation by electron impact also play an important role. The mathematical modeling of such a highly complex reaction system is beyond the scope of the present study. To qualitatively compare the apparent “intrinsic” reaction rate of removal, the values of $\psi'$ are handy and practical. It is reasonable to think that the overall reaction rate is higher when $\psi'$ is higher.

### 3.2. Influence of temperature on removal mechanism

As mentioned in Section 2, the voltage required for a corona-discharge current of 0.5 mA decreased with the elevated temperature. This voltage drop causes the decreaed acceleration of electrons in the discaharge zone. In spite of this factor, the temperature elevation causes the gas to expand and its density to decrease, resulting in lower collision frequency of drifting electrons with gas molecules. It is also important to note that the electron energy depends on the electric field strength divided by the gas density, $E/N$. To approximate $E/N$, the electric field strength described as Eq. (3) is used.

$$E = \frac{V}{r\ln(D_1/D_0)} \tag{3}$$

where $V$, $r$, $D_1$, $D_0$ are the applied voltage, radial distance from the cylindrical axis, inner diameter of the cylindrical anode, and diameter of the wire cathode, respectively. Thus, the mean $E/N$ is approximated by Eq. (4).

$$\left\langle \frac{E}{N} \right\rangle = \frac{\int_{D_0/2}^{D_1/2}(2\pi r)(E/N)\,\mathrm{d}r}{\pi((D_1/2)^2-(D_0/2)^2)} = \frac{4V}{N(D_1+D_0)\ln(D_1/D_0)} \tag{4}$$

$N$ is calculated as $p/\{R(273+T)\}$, where $p$, $R$, $T$ are total pressure, gas constant, and gas temperature, respectively. From this correlation, the average $\langle E/N\rangle$ in our case is 6.2 and 7.2 kV m$^2$/mol at room temperature and 300 °C, respectively. Since the electric field strength increases only slightly when the temperature is elevated, the electron energy at 300 °C turns out to be approximately 13% higher than at room temperature. Generally, the electron energy level should affect the reaction mechanism. For example, electron attachment tends to occur when electron energy is relatively low [18,19,28], while formation of radicals may take place when electron energy is very high.

Rigorously speaking, the relevant reactions contributing to the removal of styrene and $NH_3$ are affected not only by the change in electron energy level but also by other effects of the elevated temperature. To consider the reaction mechanism, one must take byproduct formation into account. As for the gaseous byproducts, $O_3$ and $NO_x$ were, respectively, detected mainly in the low and high temperature ranges. In fact, our measurements of $O_3$ concentration during the removal of toluene from $N_2$–$O_2$ mixture reveal that $O_3$ is produced up to 1370 ppm at room temperature but it rapidly drops down to 430 ppm at 100 °C. When $T$ is further increased above 300 °C, $O_3$ concentration becomes negligible [11]. This is because $O_3$ is unstable at high temperature [12,13]. Therefore, oxidation by $O_3$ should play a negligible role in the high temperature range.

Contrary to $O_3$ formation, it is known that production of $NO_x$ by the discharge process is favored at high temperature. This is also confirmed in our experiments. While the outlet concentration of $NO_x$ was negligible at room temperature, its concentration gradually increased with temperature and reached 300 ppm at 400 °C. Since $NO_x$ formation can be attributed to the reaction of discharge-induced N radicals with $O_2$ [14,15], N radicals should also contribute to the removal of styrene and/or $NH_3$ from both $N_2$ and air at high temperatures. In addition, in the removal from air, there should be the extra effect of O radicals produced by electron impact to $O_2$ and by $O_3$ decomposition [12,16,17]. Therefore, the removal efficiency from air at high temperatures should be enhanced by O radicals, though $O_3$ oxidation is not effective. In fact Peyrous et al. [12] simulated the concentrations of $O_3$ and O radicals in pulsed corona-discharge in the presence of $O_2$, and showed that temperature elevation brings about higher O radical concentration and lower $O_3$.

When $H_2O$ is present in the gas stream, $H^-$, $OH^-$ and a few $O^-$ anions are expected to be produced by dissociative electron attachment to $H_2O$ molecules at low temperature [18,19]. The selectivity for these ionic products should depend on the gas temperature and electron energy. At high temperature, electron detachment would become significant so that radicals of O, H, and OH may play a more important role than their anionic counterparts. These radicals are also expected to contribute to the removal of the target gases. More specifically, OH is believed to dissociate $NH_3$ to produce an aminogen radical ($NH_2$) and $H_2O$ [20].

In non-thermal corona-discharge in the air at room temperature, electrons are sometimes captured by $O_2$ to form negative ions, $O^-$, $O_2{}^-$, $O_3{}^-$, and clusters via electron attachment. The reversed electron detachment process, however, becomes significant at high temperature, causing ion clusters to become unstable [21]. Our previous articles indicate that the corona-discharge reactor plays host to electron attachment reactions and relevant ion cluster formation at room temperature [10,22]. However, because of high temperature effects such as electron detachment and radical formation, electron attachment and ion clustering would be less and less important as the temperature rises.

The removed styrene was converted to non-volatile deposit, which was observed inside the reactor and in the gas line after the reactor. The observed conversion to non-volatile deposit is consistent with our previous report on the removal of certain aromatic compounds, benzene and *p*-dichlorobenzene, from $N_2$ and $N_2$–$O_2$ mixture at room temperature [23]. There it was discussed that negative ions induced by dissociative electron attachment initiated chain polycondensation reactions to form the deposit. The present reaction mechanism for the removal of styrene at room temperature may be considered to be analogous to the chain polycondensation found in the removal of benzene and *p*-dichlorobenzene because of the similar aromatic structure of these molecules. Since the terminating reaction for styrene chain polycondensation at room temperature is considered to be effected by the reactions of electron-attachment-induced ions with styrene molecules, we may likewise consider that, in the high temperature range, radical reactions involving N and O radicals and electron impact to styrene molecules, instead of ionic reactions, could initiate the chain polycondensation reaction required to form non-volatile deposit. It should be emphasized that the proposed mechanism is clearly different from the removal of methanol and trichloroethylene reported by Hsiao et al. [6], in which they are converted to $CO_x$ by decomposition. The temperature dependency of this chain polycondensation reaction might have a role in determining the removal efficiency at various temperatures.

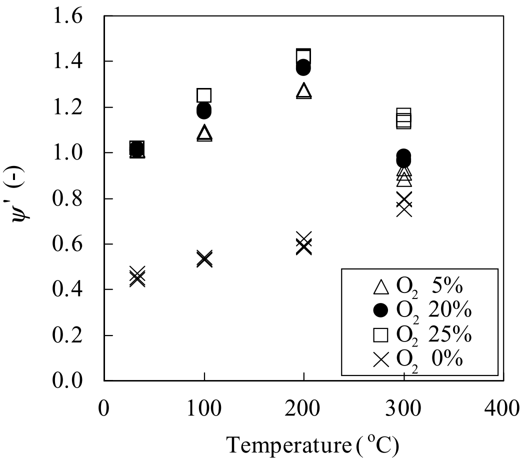

Fig. 2. Effect of coexisting $O_2$ on the removal efficiency $\psi'$ of styrene from $N_2$; [styrene] = 500 ppm, SV = 55.8 $h^{-1}$ at room temperature, $I = 0.05$ mA (except $I = 0.5$ mA in the absence of $O_2$).

In the case of $NH_3$ removal, the removed $NH_3$ was converted to needle-like bright crystal, which was observed inside the reactor and the gas line after it. It is reported [24] that $NH_3$ does not react with $O_3$ to directly form $NH_4NO_3$. Instead the following consecutive reactions are mentioned: $2NH_3+4O_3 = NH_4NO_2+H_2O_2+4O_2$; $NH_4NO_2+H_2O_2 = NH_4NO_3+H_2O$. Our result is also consistent with published reports that $NH_4NO_3$ solid is produced by corona treatment of humid air containing $NH_3$ [20,25,26]. The mechanism for $NH_4NO_3$ formation in the high temperature range is not clear but it may be considered that $NH_3$, $H_2O$ and $NO_x$ as well as N and H radicals could react to form $NH_4NO_3$.

Since our blank tests show negligible change in the concentrations of styrene and $NH_3$ when they are fed together to the reactor at various temperatures and no extraneous peaks are detected in the gas chromatograms, it may be considered that styrene does not react with $NH_3$ in the presence of air.

### 3.3. *Effect of coexisting $O_2$ on removal of styrene from $N_2$*

Fig. 2 shows the removal efficiency $\psi'$ of styrene from $N_2$ versus temperature when the styrene inlet concentration is 500 ppm. Partly because of the above-mentioned swaying effect of the ion wind [9], there is a maximum fluctuation of around +6% at some of the experimental points. It is obvious that the presence of $O_2$ in $N_2$ greatly enhances the styrene removal efficiency despite the fact that the discharge current in the $N_2$–$O_2$ case has been reduced 10-folds to 0.05 mA compared to the case of pure $N_2$. As explained in Section 3.2, this may be attributed to the fact that $O_3$ is produced from $O_2$ by the corona-discharge reaction and is quite stable at room temperature. At room to moderate temperatures, electron attachment reactions contribute to, and relevant ion cluster formation enhances, the removal of numerous electro-negative compounds [10,22]. Considered to be applicable to the removal of styrene, this mechanism is consistent with the observation that the biggest effect of coexisting $O_2$ is found at the highest concentration of 25% $O_2$.

As mentioned in Section 3.2, the removed styrene was converted to non-volatile deposit, which is consistent with our previous report [23]. In addition, the reaction mechanism in the removal of styrene at room temperature may be considered to be chain polycondensation of styrene, whereas the terminating reaction is considered to be effected by the reactions of electron-attachment-induced ions with styrene molecules. In the high temperature range, radical reactions involving N and O radicals and electron impact to styrene molecules, instead of ionic reactions, could initiate the chain polycondensation reaction required to form the observed non-volatile deposit.

As the gas temperature increases, there was a gradual reduction in the removal efficiency $\psi$ omitted here. Above 200 °C, $O_3$ is unstable and not detected. Instead O radicals are produced [12,17,18] and so are N radicals, which might be more reactive than O radicals because N≡N bonding energy at 225 kcal/mol is much higher than that of O=O at 118 kcal/mol. Since the increased production of $NO_x$ at higher temperatures consumes N radicals, the styrene removal efficiency tends to decrease. Coupled with the negative effect of reduced residence time, this explains why the value of the omitted $\psi$ decreases monotonically in the high temperature range. When the effect of residence time is considered, the value of $\psi'$ in Fig. 2 increases up to 200 °C before subsequently decreasing. In the low to moderate temperature range, the combined effect of both $O_3$ and N radicals results in an efficiency increase despite the reduced residence time. In the high temperature, the positive effect of diminishing N radicals turns out to be negated by the much reduced residence time.

Generally, two other types of removal efficiency are reported for a corona-discharge system. The electron-based efficiency $\psi_{\mathrm{elec}}$ is defined as the number of gas molecules removed by one discharged electron, and the energy-based efficiency $\psi_{\mathrm{ener}}$ (mol gas/J) is defined as the mole of gas removed per energy consumption (J). At 306, 373, 473 and 573 K, the experimental values of $\psi_{\mathrm{elec}}$ and $\psi_{\mathrm{ener}}$ are as follows:

Pure $N_2$ ($I = 0.5$ mA): $\psi_{\mathrm{elec}} = 1.6, 1.7, 1.2$ and $0.9$; $\psi_{\mathrm{ener}} \times 10^{-9} = 1.66, 1.94, 1.45$ and $1.21$.

$N_2$–20% $O_2$ ($I = 0.05$ mA): $\psi_{\mathrm{elec}} = 36.6, 28.4, 21.8$ and $10.6$; $\psi_{\mathrm{ener}} \times 10^{-9} = 186, 160, 149$ and $86.2$

In the absence of $O_2$, $\psi_{\mathrm{elec}}$ ranges from 1.7 at 373 K to 0.9 at 573 K while $\psi_{\mathrm{ener}}$ ranges from $1.7 \times 10^{-9}$ to $0.9 \times 10^{-9}$. In the presence of 20% $O_2$, $\psi_{\mathrm{elec}}$ and $\psi_{\mathrm{ener}}$ increases 22.9–11.8-fold and 112–71.2-fold, respectively, despite a 10-fold reduction in the discharge current compared to the case of pure $N_2$. The remarkable enhancement effect of $O_2$ can be attributed to the effect of $O_3$ and $O^-$ anion at low temperatures and N and O radicals at high temperatures. Generally, $\psi_{\mathrm{elec}}$ and $\psi_{\mathrm{ener}}$ tend to decrease as the gas temperature increases. This trend may be ascribed to the combined effect of reduced residence time and the shift in

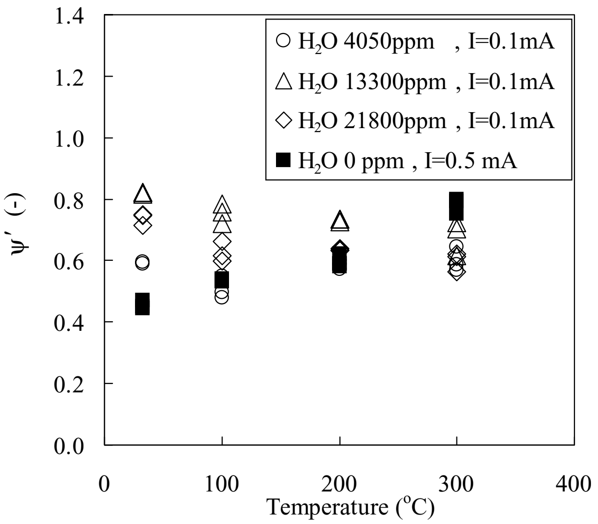

Fig. 3. Influence of water vapor on the removal efficiency $\psi'$ of styrene from $N_2$; [styrene] = 500 ppm, SV = 55.8 $h^{-1}$ at room temperature.

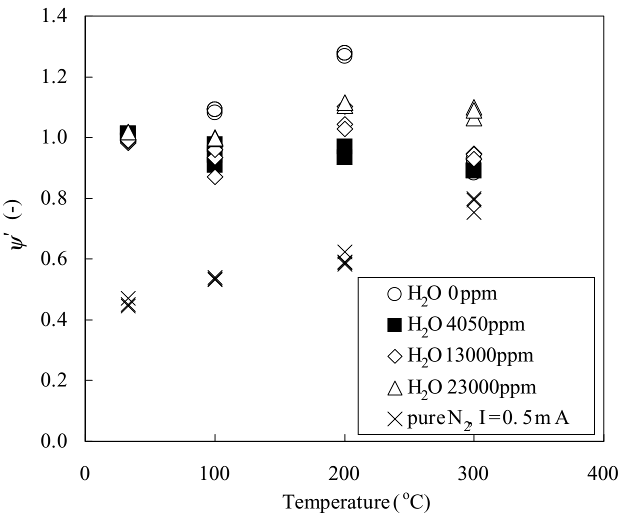

Fig. 4. Combined effect of oxygen and water vapor on the removal efficiency $\psi'$ of styrene from $N_2$ at 5% $O_2$; [styrene] = 500 ppm, $I = 0.05$ mA, SV = 55.8 $h^{-1}$ at room temperature.

removal mechanism. Interestingly, in the case of pure $N_2$, $\psi_{elec}$ and $\psi_{ener}$ at 373 K become higher than at room temperature, thus indicating the possible existence of an optimal temperature.

### 3.4. Effect of water vapor on removal of styrene from $N_2$

Fig. 3 shows the styrene removal efficiency from $N_2$ $\psi'$ versus temperature at various concentrations of water vapor. Regarding the general influence of $H_2O$, its presence significantly raises the removal efficiency despite a five-fold reduction in the discharge current, compared to the case of pure $N_2$. As mentioned in Section 3.2, $H^-$, $OH^-$ and a few $O^-$ anions are expected to be produced by dissociative electron attachment to $H_2O$ molecules at low temperature [18,19]. To gain some insight into the electron affinity of styrene and $H_2O$ molecules, electron affinities of $H_2O$ molecule and styrene molecule were obtained by subtracting the total energies of neutral molecules from their anionic counterparts. These calculations were carried out by Density Functional Theory at B3LYP/6-31G(d) level using Gaussian 98W program [27], resulting in 88 and 403 kJ/mol for styrene and $H_2O$, respectively. This means that the $H_2O$ anion is much more difficult to form than the styrene anion. The difficulty of forming $H_2O$ anions is also confirmed by drift tube experiment [28]. As a result it may be considered that electron attachment to $H_2O$ is dissociative. Similarly, it is reasonable to assume that electron attachment reactions to other gaseous species such as styrene and $NH_3$, are also dissociative. Therefore, it should be more meaningful to consider electron affinity of constituent atoms in these gas species. The values of Mulliken-scale electron negativity of O, N, and H atoms, which constitutes $O_2$, $O_3$, $H_2O$, $NH_3$ and styrene, are, respectively, 3.5, 3.0 and 2.1 eV. These values mean that $O^-$ anion is easier to produce from $O_2$, $O_3$, and $H_2O$ than $N^-$ and $H^-$ from $NH_3$ and $H^-$ from styrene. This explains why styrene removal efficiency is significantly enhanced by the presence of $H_2O$.

At high temperature, electron detachment becomes significant and as a result, radicals of O, H, and OH as well as N radicals are produced. As the gas temperature increases, the omitted styrene removal efficiency $\psi$ decreases monotonically from room temperature to 300 °C mainly because of the reduction in residence time. Fig. 3 reveals that, even when the effect of reduced residence time is taken into consideration, the value of $\psi'$ in the presence of $H_2O$ still decreases slightly with temperature. This trend is completely different from the removal efficiency in the absence of $H_2O$. As mentioned in Section 3.2, $NO_x$ formation can be attributed to the reaction of discharge-induced N radicals with $O_2$ [14,15], and N radicals are considered to contribute to the removal of styrene from both $N_2$ and air at high temperatures. Since N radicals are consumed by their reaction with $H_2O$ at high temperatures, the styrene removal efficiency at high temperatures decreases in the presence of $H_2O$. In contrast, in the absence of $O_2$ and $H_2O$, N radicals are not consumed and this results in a slight increase in $\psi'$ in Fig. 3.

### 3.5. Effect of coexisting $O_2$ and water vapor on removal of styrene from $N_2$

A number of experiments were carried out to observe the combined effect of $O_2$ and $H_2O$ on the removal of styrene from $N_2$. The $O_2$ concentrations investigated were 5, 10 and 20%. Because of space limitation, only the case of 5% $O_2$ is introduced here. Fig. 4 shows the observed removal efficiency $\psi'$ of styrene from $N_2$ at elevated temperatures. Again note that the discharge current in the case of pure $N_2$ is 10 times the case of $N_2$–$O_2$ mixture. As the gas temperature

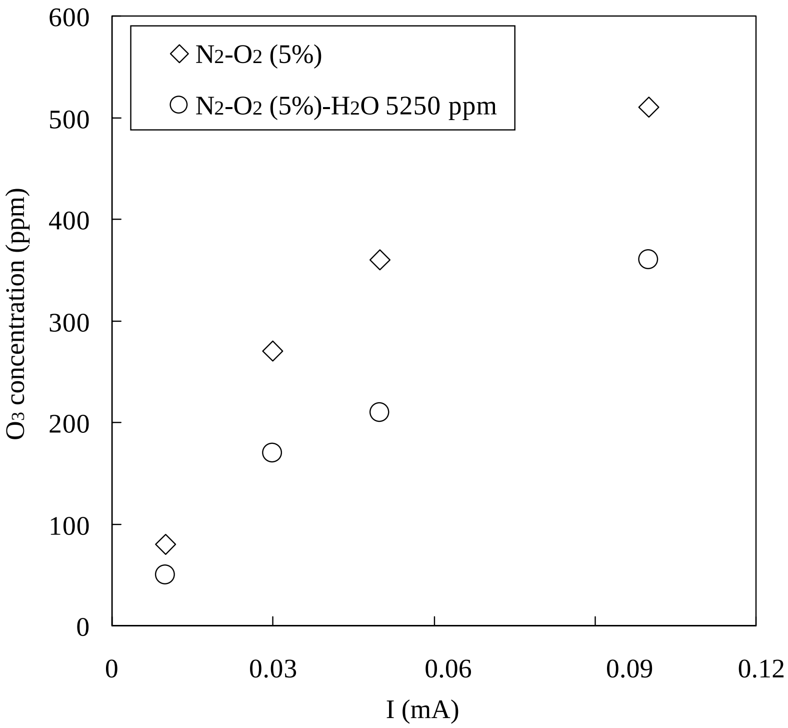

Fig. 5. Effect of water vapor on $O_3$ generation from 5% $O_2$ in $N_2$; SV = 55.8 $h^{-1}$ at room temperature.

increases, the omitted $\psi$ substantially decreases mainly because of the effect of reduced residence time. In Fig. 4, the presence of $H_2O$ (4050, 12,900 and 23,000 ppm) have no discernable effect on the removal efficiency $\psi'$ at room temperature because complete removal of styrene is obtained at all $H_2O$ concentrations. In the intermediate temperature range, the calculated value of $\psi'$ becomes significantly higher than unity in the absence of $H_2O$ because electron attachment reactions and $O_3$ cluster formation enhance the removal efficiency [10,22] but $O_3$ formation is not retarded in the absence of $H_2O$. Fig. 5 confirms the retarding effect of water vapor on ozone generation at room temperature. At 300 °C, O, OH and H radicals should be produced from $O_2$ and/or $H_2O$, thus enhancing the removal efficiency, though $O_3$ is hardly observed at 300 °C.

### 3.6. Effect of coexisting $O_2$ on removal of $NH_3$ from $N_2$

Fig. 6 shows the removal efficiency $\psi'$ of $NH_3$ from $N_2$ at various concentrations of co-existing $O_2$ when the $NH_3$ inlet concentration is 400 ppm. As in the case of styrene, the presence of $O_2$ in $N_2$ greatly enhances the $NH_3$ removal efficiency despite the fact that the discharge current has been reduced six-folds to 0.05 mA, compared to the case of pure $N_2$ in the same figure. As mentioned in Section 3.2, this may be attributed to the facts that $O_3$ is produced from $O_2$ by the corona-discharge reaction in the low to moderate temperature range, where electron attachment reactions and relevant ion cluster formation contribute to the removal of $NH_3$, and that the removed $NH_3$ is converted to non-volatile deposit, which was observed inside the reactor and the gas line after it. At room temperature $NH_3$ may react $O_3$ with to form $NH_4NO_3$ [24] via the following consecutive reactions: $2NH_3+4O_3 = NH_4NO_2+H_2O_2+4O_2$; $NH_4NO_2+H_2O_2 = NH_4NO_3 + H_2O$. This is consistent with the observation that the biggest effect of coexisting $O_2$ on $\psi$ is found at the highest concentration of 25% $O_2$.

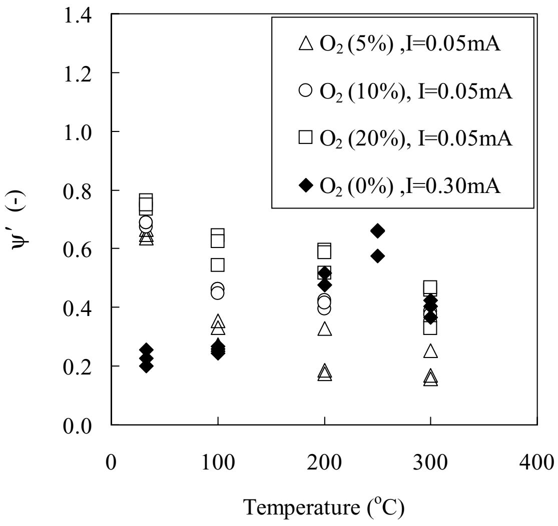

Fig. 6. Effect of coexisting $O_2$ on the removal efficiency $\psi'$ of ammonia from $N_2$; [ammonia] = 400 ppm, SV = 55.8 $h^{-1}$ at room temperature.

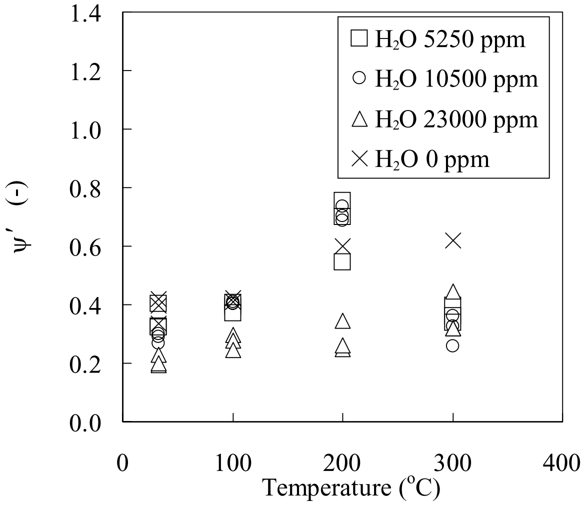

Fig. 7. Influence of water vapor on the removal efficiency $\psi'$ of ammonia from $N_2$; [ammonia] = 250 ppm, $I = 0.3$ mA, SV = 55.8 $h^{-1}$ at room temperature.

As the temperature increases, the omitted ammonia removal efficiency $\psi$ in the presence of $O_2$ drops monotonically starting from room temperature to 300 °C because $O_3$ is unstable and not detected above 200 °C. Instead O and N radicals are produced and contribute to $NH_3$ removal [12,14,17]. Since more N radicals are consumed to form $NO_x$ as the temperature increases, the $NH_3$ removal efficiency significantly decreases. Coupled with the negative effect of reduced residence time, the value of $\psi$ decreases drastically in the high temperature range. Even when the effect of residence time is considered, the value of $\psi'$ in Fig. 6 still decreases monotonically with temperature, albeit less drastically.

### 3.7. *Influence of $H_2O$ on removal of $NH_3$ from $N_2$*

Fig. 7 shows the removal efficiency $\psi'$ of $NH_3$ from $N_2$ at various concentrations of coexisting water vapor. Note that the discharge current is all 0.3 mA here compared to 0.05 mA in the case of dry $N_2$–$O_2$ mixture. The effect of elevated temperature on $\psi'$ and the omitted $\psi$ is not straightforward but appears to depend on the $H_2O$ concentration. When the $H_2O$ concentration is highest at 23,000 ppm, both $\psi$ and $\psi'$ are retarded compared to the absence of $H_2O$, while the effect of elevated temperature is slight. In contrast, the retarding effect at two lower $H_2O$ concentrations (5250 and 10,500 ppm) is relatively small up to 100 °C. Both $\psi$ and $\psi'$ become enhanced at 200 °C but become retarded again at 300 °C compared to the absence of $H_2O$. As mentioned in Section 3.2, $H^-$, $OH^-$ and a few $O^-$ anions are produced by dissociative electron attachment to $H_2O$ molecules at low temperature [18,19]. At room temperature the required voltages for corona-discharge are 8.1, 8.7, 8.3, and 8.7 kV, respectively, for $H_2O = 0$, 5250, 10,500 and 23,000 ppm. At 100, 200 and 300 °C, the corresponding sets of voltage values are (6.9, 7.2, 6.8 and 6.6 kV), (5.1, 5.1, 5.1 and 5.2 kV), and (3.5, 3.6, 3.7 and 4.1 kV), respectively. The decrease in required kV against increasing $H_2O$ concentration at room temperature means that the rate of ozone and radicals formation become lower. This explains the observed retardation effect of $H_2O$ at low temperatures.

At 200 °C or more, electron detachment produces radicals of O, H, and OH from their anions. More specifically, OH radical is believed to dissociate $NH_3$ to produce an aminogen radical ($NH_2$) and $H_2O$ [20]. This reversible reaction is, however, retarded by a big excess of the reaction product $H_2O$. Similarly, N and H radicals are produced from $NH_3$, especially at 300 °C. Since N and H radicals are considered to contribute more to the formation of $NH_4NO_3$, the high consumption of N radicals at 300 °C to form $NO_x$ leads to the observed retardation effect. At 200 °C fewer N radicals are consumed to form $NO_x$ and, without excessive $H_2O$, the combined effect of N, H and OH radicals lead to the observed efficiency enhancement.

### 3.8. *Influence of coexisting $O_2$ and $H_2O$ on removal of $NH_3$ from $N_2$*

Experiments were carried out to observe the combined influence of $H_2O$ and $O_2$ on the removal of $NH_3$ from $N_2$. Fig. 8 shows the experimental results when $O_2$ concentration is 5%. In the absence of $H_2O$ and $O_2$, the removal efficiency $\psi'$ and the omitted $\psi$ are not high even at $I = 0.3$ mA because the electro-negativity of $NH_3$ is not so high. As explained in Section 3.4, the presence of 5% $O_2$ without water vapor greatly enhances $\psi$ and $\psi'$ because of the generation of $O_3$ and $O^-$ anions at low temperatures, and O radicals at high temperatures. The combined effect of $O_2$ and 5250 ppm $H_2O$ slightly retard $\psi$ and $\psi'$ compared to the case of pure $N_2$. However, at 10,500 ppm $H_2O$ the combined effect of $O_2$

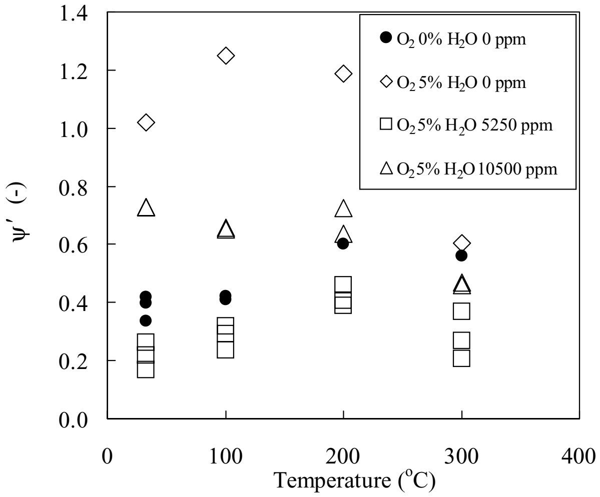

Fig. 8. Combined effect of $O_2$ and $H_2O$ on the removal efficiency $\psi'$ of ammonia from $N_2$ ($O_2 = 5\%$); [ammonia] = 250 ppm, $I = 0.3$ mA, SV = 55.8 $h^{-1}$ at room temperature.

and $H_2O$ becomes positive at low temperatures compared to pure $N_2$. As mentioned in Section 3.2, $H^-$, $OH^-$ and a few $O^-$ anions are produced by dissociative electron attachment to $H_2O$ molecules at low temperature [18,19]. At room temperature the required voltages for corona-discharge are 13.1, 8.2 and 12.9 kV, respectively, for $H_2O = 0$, 5250 and 10,500 ppm. At 100, 200 and 300 °C, the corresponding sets of voltage values are (11.8, 6.7 and 9.0 kV) and (8.3, 5.0 and 6.8 kV) and (5.4, 3.7 and 5.3 kV), respectively. At room temperature the U shape in the required kV against increasing $H_2O$ concentration means that the average electron energy decreases and then increases, thus little $O_3$ and few O radicals are produced from $O_2$ at 5250 ppm. Combined with the reduced formation of N radicals, this explains the retardation effect at $H_2O = 5250$ ppm compared to the case of pure $N_2$. At $H_2O = 10,500$ ppm, the much higher energy level leads to significant formation of O and N radicals, thus enhancing the removal of $NH_3$. The U shape in the required kV versus $H_2O$ concentration is observed at elevated temperatures, and a similar explanation is applicable up to 200 °C. When $H_2O = 10,500$ ppm, the electron energy level at 300 °C becomes so low that the reactions of O and N radicals may be reduced.

### 3.9. *Effect of coexisting $O_2$ on the simultaneous removal of styrene and $NH_3$ from $N_2$*

No significant reduction in the outlet concentrations of styrene and $NH_3$ was observed that might indicate their spontaneous reaction at high temperature without corona-discharge in the presence of nitrogen. In addition no extraneous peaks were observed in the gas chromatograms of the effluent stream. Therefore it may be considered that styrene and ammonia did not react to generate new pollutants. In fact they were observed together in the exhaust gas from the crematory furnace.

Figs. 9 and 10 show the effect of $O_2$ on the simultaneous removal efficiency of styrene and $NH_3$ from $N_2$, respectively. The inlet concentrations of styrene and $NH_3$ are 40 and 200 ppm, respectively, while the current is rather high at 0.3 mA. Obviously, the presence of $O_2$ has a significant enhancement effect on the simultaneous styrene removal efficiency $\psi$ in Fig. 9. As the temperature increases, the styrene removal efficiency remains essentially at 100% from room temperature to 300 °C, except at 5% $O_2$ and 300 °C. As expected, the presence of $O_2$ also has a significant effect on the simultaneous $NH_3$ removal efficiency in Fig. 10. As the temperature increases, the $NH_3$ removal efficiency $\psi$ above 200 °C tends to significantly decrease. In either figure, the removal efficiency enhancement is found to depend on the concentration of coexisting $O_2$. As mentioned previously, the improved removal efficiency for both styrene and $NH_3$ can be attributed to effect of $O_3$ and $O^-$ anion at low temperatures and various radicals at high temperatures.

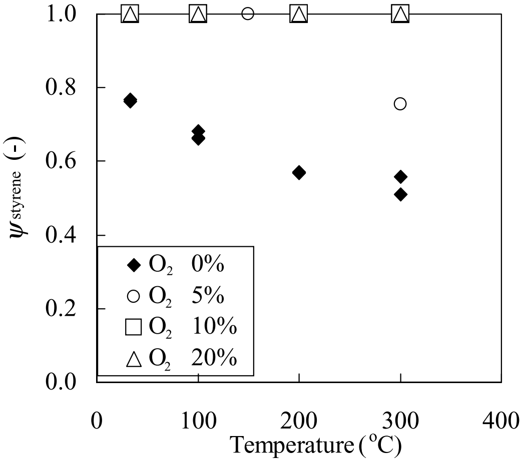

Fig. 9. Effect of $O_2$ on simultaneous removal of styrene and ammonia from $N_2$ (removal efficiency of styrene); [ammonia] = 200 ppm, [styrene] = 40 ppm, $I = 0.3$ mA, SV = 55.8 $h^{-1}$ at room temperature.

### 3.10. *Effect of coexisting $O_2$ and $H_2O$ on the simultaneous removal of styrene and $NH_3$ from $N_2$*

Figs. 11 and 12 show the combined effect of $O_2$ and $H_2O$ on the simultaneous removal efficiency $\psi$ of styrene and $NH_3$ from $N_2$. Compared to the case of only coexisting $O_2$, the simultaneous removal efficiency of both styrene and $NH_3$ is retarded by the presence of $H_2O$. In Fig. 11, the presence of $H_2O$ significantly decreases the simultaneous removal efficiency of styrene only above 200 °C. In Fig. 12, however, the presence of $H_2O$ significantly decreases the simultaneous removal efficiency of $NH_3$ from 100 °C upward. As explained above, an increase in the gas temperature leads to a significant drop in the importance of electron

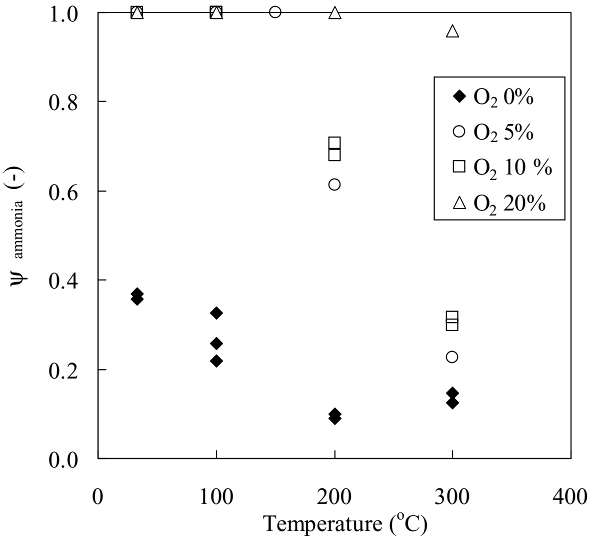

Fig. 10. Effect of $O_2$ on simultaneous removal of styrene and ammonia from $N_2$ (removal efficiency of ammonia); [ammonia] = 200 ppm, [styrene] = 40 ppm, $I = 0.3$ mA, SV = 55.8 $h^{-1}$ at room temperature.

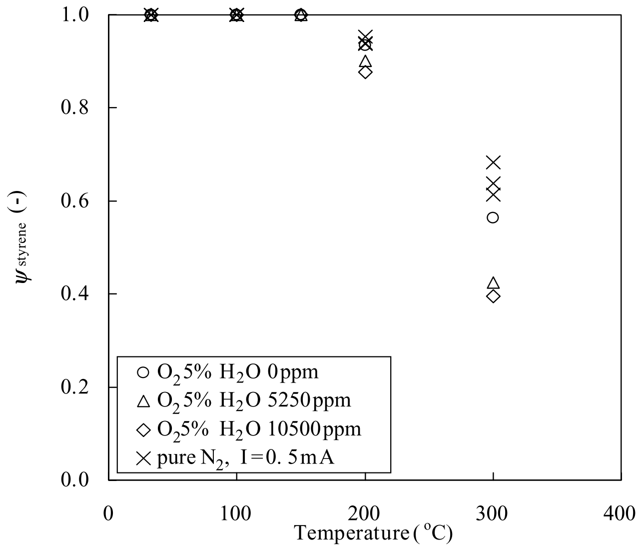

Fig. 11. Combined effect of $O_2$ and $H_2O$ on simultaneous removal of styrene and ammonia from $N_2$ at 5% $O_2$; removal efficiency of styrene; [ammonia] = 200 ppm, [styrene] = 40 ppm, $I = 0.10$ mA, SV = 55.8 $h^{-1}$ at room temperature.

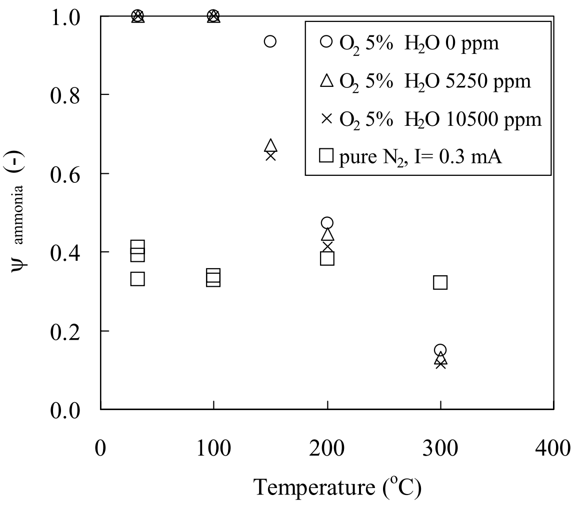

Fig. 12. Combined effect of $O_2$ and $H_2O$ on simultaneous removal of styrene and ammonia from $N_2$ at 5% $O_2$; removal efficiency of ammonia; [ammonia] = 200 ppm, [styrene] = 40 ppm, $I = 0.10$ mA, SV = 55.8 $h^{-1}$ at room temperature.

attachment reaction, while various radicals become important. N radicals produced at elevated temperature are consumed to form $NO_x$, thus causing a drop in the $NH_3$ removal efficiency.

## 4. Conclusion

Generally, the apparent removal efficiency of styrene and/or $NH_3$ from $N_2$ tends to drop with the elevated temperature because of the reduced gas residence time, while the removal efficiency per unit residence time can increase with temperature. The presence of $O_2$ substantially enhances the removal efficiency of styrene and/or $NH_3$ because of the effect of $O_3$ and $O^-$ anion at low temperatures and N and other radicals at high temperatures. The presence of $H_2O$ in nitrogen generally enhances the removal efficiency of styrene and/or $NH_3$ but the presence of $H_2O$ retards that of $NH_3$ when $H_2O$ concentration is too high or the temperature is 300 °C. The combined effect of $O_2$ and $H_2O$ is found to significantly retard the removal efficiency of styrene and/or $NH_3$ compared to the sole effect of coexisting $O_2$.

There are still a number of points on the complex removal mechanism left for further investigation. Though negligible gaseous byproducts besides $O_3$ and $NO_x$ were detected in the gas chromatograms, more detailed investigation should be also carried out.

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