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Conversion of dilute nitrous oxide (N₂O) in N₂ and N₂–O₂ mixtures by plasma and plasma-catalytic processes†

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A coaxial dielectric barrier discharge (DBD) reactor has been developed for plasma and plasma-catalytic conversion of dilute N₂O in N₂ and N₂–O₂ mixtures at both room and high temperature (300 °C). The effects of catalyst introduction, O₂ content and inlet N₂O concentration on N₂O conversion and the mechanism involved in the conversion of N₂O have been investigated. The results show that N₂O in N₂ could be effectively decomposed to N₂ and O₂ by plasma and plasma-catalytic processes at both room and high temperature, with much higher decomposition efficiency at 300 °C than at room temperature for the same discharge power. Under an N₂–O₂ atmosphere, however, N₂O could be removed only at high temperature, producing not only N₂ and O₂ but also NO and NO₂. Production and conversion of N₂O occur simultaneously during the plasma and plasma-catalytic processing of N₂O in a N₂–O₂ mixture, with production and conversion being the dominant processes at room and high temperature, respectively. N₂O conversion increases with the increase of discharge power and decreases with the increase of O₂ content. Increasing the inlet N₂O concentration from 100 to 400 ppm decreases the conversion of N₂O under an N₂ atmosphere but increases that under an N₂–O₂ atmosphere. Concentrating N₂O in the N₂–O₂ mixture could alleviate the negative influence of O₂ by increasing the involvement of plasma reactive species (e.g., N₂(A³Σ_u⁺) and O(¹D)) in N₂O conversion. Packing the discharge zone with a RuO₂/Al₂O₃ catalyst significantly enhances the conversion of N₂O and improves the selectivity of N₂O decomposition under an N₂–O₂ atmosphere, revealing the synergy of plasma and catalyst in promoting N₂O conversion, especially its decomposition to N₂ and O₂.

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1. Introduction

Nitrous oxide (N₂O) emitted from various human activities including agriculture (soil cultivation and the use of nitrogen-fertilizers), biomass burning, fossil fuel combustion, industrial processes (production of adipic and nitric acids), and wastewater treatment is the third most significant anthropogenic greenhouse gas and the largest stratospheric-ozone-depleting substance.^{1–3} Limiting the formation of N₂O is the best solution to reduce N₂O emissions from the agricultural sector and uncontrolled biomass burning taking into account the diffuse character of these emissions, while employment of after-treatment technologies is important for control of N₂O emissions from combustion and industrial sources.³

Technologies developed and adopted so far for abatement of N₂O are mainly based on catalysis, including non-selective

catalytic reduction (NSCR), selective catalytic reduction (SCR), and direct catalytic decomposition.^{1,3–8} Among these technologies, the direct catalytic decomposition of N₂O to N₂ and O₂ has received great attention due to simplicity and high efficiency and significant research efforts have been focused on development of novel catalytic materials with satisfactory activity at relatively low temperatures.^{1,3,5–8} As a promising alternative to develop new catalysts, combination of catalysts with non-thermal plasma has been widely investigated in recent years for treatment of a variety of air contaminants such as volatile organic compounds (VOCs) and nitrogen oxides (NO_x).^{9–16} The synergetic effects between plasma and catalysis include initiating chemical reactions at low temperature and improving products selectivity.^{9–16} In fact, plasma and plasma-catalysis systems have also been investigated for decomposition of N₂O, with nitrogen or argon as the background gas in most cases.^{17–22} These oxygen-free systems proved to be effective in decomposing N₂O even at room temperature.^{17–22} In real exhaust gases, however, O₂ always coexists with N₂O and N₂ and it is therefore of great significance to investigate the N₂O conversion behavior under N₂–O₂ atmosphere.³

In a recent study by Jo *et al.*,²³ O₂ in N₂–O₂–N₂O mixture was verified to have obviously adverse effects on the plasma-catalytic

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decomposition of N_2O . Besides the negative influence of O_2 on the catalytic decomposition of N_2O , the intrinsic formation of N_2O by discharge in $\text{N}_2\text{--O}_2$ should have also contributed to the decreasing N_2O conversion with increasing O_2 content, which however was not taken into account in that study.²³ From our perspective, a better understanding of both N_2O production and conversion processes in the presence of O_2 is essential for optimizing the plasma-catalytic decomposition of N_2O . On the other hand, Jo *et al.*²³ inferred from the thermodynamic calculations that N_2O was mainly decomposed into N_2 and O_2 in the presence of O_2 . However, Krawczyk *et al.*^{24,25} found that N_2O in mixtures with O_2 or air was both oxidized to NO and decomposed to N_2 and O_2 by gliding arc discharge, combined with or without a catalytic bed. Oxidation of N_2O into NO and reusing NO for production of nitric acid is a profitable method for reducing concentrated N_2O emissions, *e.g.*, in adipic acid plants.²⁴ For removal of dilute N_2O from sources such as nitric acid production and fluidized bed combustion, however, decomposition of N_2O into N_2 and O_2 would be more desired.³

The aim of this study is to investigate the conversion behavior and mechanism of dilute N_2O in plasma and plasma-catalytic processes, in both the presence and absence of O_2 and at both room and high temperature (300 °C). For this purpose, a coaxial dielectric barrier discharge (DBD) reactor was constructed, to generate plasma and to combine plasma with catalysts. $\text{RuO}_2/\text{Al}_2\text{O}_3$ was chosen as the catalyst besides Al_2O_3 for plasma-catalytic conversion of N_2O due to its reported good performance for catalytic N_2O decomposition.²⁶ The effects of catalyst (Al_2O_3 or $\text{RuO}_2/\text{Al}_2\text{O}_3$) introduction, O_2 content (0–20%, volumetric) and inlet N_2O concentration (100–400 ppm, volumetric) on the conversion of N_2O were systematically examined. In order to elucidate the mechanism of N_2O conversion, the production of N_2O by discharge in $\text{N}_2\text{--O}_2$ mixture with and without catalyst was also investigated and products/byproducts generated in these processes were analyzed in detail.

2. Experimental

2.1 Experimental set-up

A schematic diagram of the experimental system is shown in Fig. 1. It consists of reaction gas supply, a DBD reactor with an

alternating current (AC) high voltage power supply (0–100 kV, 50–500 Hz, sinusoidal wave), and analytical instrumentation. The reaction gas which was fed into the reactor at a total flow rate of 1 L min^{−1} at ambient temperature and pressure (around 20 °C, 100 kPa) throughout this work was prepared by mixing pure N_2 , O_2 , and N_2O in N_2 (Beijing HaiRui Tongda Gas Technology Co., Ltd., China) whose flow rates were controlled by a set of mass flow controllers (MFC, D07-7, Beijing Sevenstar Electronics Co., Ltd., China). O_2 content in the feed gas was adjusted to 0%, 5%, 10% or 20% while inlet concentration of N_2O ranged from 0 to 400 ppm.

A quartz glass tube reactor (length: 600 mm; inner diameter: 29 mm; thickness: 1.5 mm) was used with a concentric tungsten wire (diameter: 1.4 mm) acting as the discharge electrode and an aluminum foil (50 mm in length) wrapping around the glass tube as the ground electrode. For the plasma-catalytic process, Al_2O_3 or $\text{RuO}_2/\text{Al}_2\text{O}_3$ catalyst pellets (20 g, 3–5 mm in diameter) were packed in the space between the discharge electrode and the tube at near maximum packing density, with an apparent volume of *ca.* 27 mL. The plasma/plasma-catalytic reactor was installed in normal indoor environments or in a temperature-controlled tube furnace to obtain room temperature and high temperature (300 °C) reaction conditions, respectively.

2.2 Experimental methods

2.2.1 Preparation and characterization of catalyst.

Commercial $\gamma\text{-Al}_2\text{O}_3$ pellets (Brunauer–Emmett–Teller (BET) specific surface area 226 m² g^{−1}, specific pore capacity 0.48 mL g^{−1}, Tianjin Fuchen Chemical Reagents Factory, China) were used as the catalyst as well as the support of $\text{RuO}_2/\text{Al}_2\text{O}_3$ catalyst. For the preparation of $\text{RuO}_2/\text{Al}_2\text{O}_3$, a given amount of $\gamma\text{-Al}_2\text{O}_3$ pellets were impregnated with an aqueous solution of RuCl_3 (99% purity, J&K Scientific). After the impregnation, drying overnight at 110 °C and calcining at 550 °C for 6 h in air atmosphere were performed. The nominal loading amount of Ru over Al_2O_3 was 2.4 wt% and the BET specific surface area of the prepared $\text{RuO}_2/\text{Al}_2\text{O}_3$ catalyst was 194 m² g^{−1}, measured by N_2 adsorption at −196 °C on a surface area and pore size analyzer (Micromeritics Gemini V, USA).

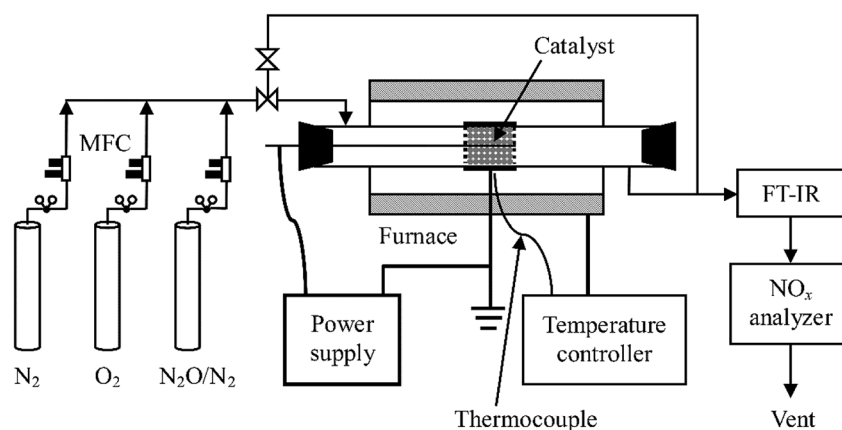


Fig. 1 Schematic diagram of the experimental set-up.



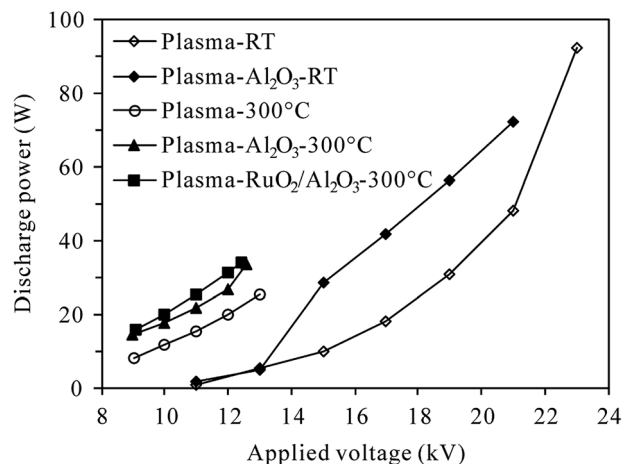


Fig. 2 Dependence of discharge power on the applied voltage at room temperature (RT) and 300 °C (inlet N₂O: 0 ppm; O₂ content: 5%).

In addition, X-ray diffraction (XRD) patterns of Al₂O₃ and RuO₂/Al₂O₃ catalysts before and after use in plasma-catalytic conversion of N₂O were obtained using a Bruker D8 Discover diffractometer (Co K α radiation, 35 kV, 30 mA).

2.2.2 Measurement of discharge characteristics. The DBD reactor was energized at 200 Hz in the range of 9–23 kV (root-mean-square (RMS) value) in this study. The applied voltage and discharge current was measured using a 1000:1 high voltage probe (P6015A, Tektronix, USA) and a current monitor (UT61D, UNI-T, China), respectively. The discharge power delivered to the reactor was calculated by multiplying the time-dependent voltage and current. Fig. 2 presents typical discharge power values of plasma and plasma-catalytic reactors at room temperature and 300 °C as functions of applied voltage. It is worth pointing out that although higher discharge power could be delivered to the reactors under higher reaction temperature (300 °C) for a given applied voltage, the breakdown voltage and maximum applicable discharge power were much lower at 300 °C than those at room temperature.

2.2.3 Analysis of gas components and calculation of N₂O conversion. The reactor outlet gas stream was analyzed using an on-line Fourier transform infrared (FT-IR) spectrometer (Nicolet iS10, Thermo-Scientific, USA) equipped with a heated gas cell (optical path length: 2.4 m; volume: 300 mL; temperature: 100 °C) and a deuterated triglycine sulfate (DTGS) KBr detector. Spectra were recorded automatically every 35 s (average of 16 scans from 4000 to 650 cm⁻¹ with a resolution of 4 cm⁻¹) from the start to the end of each experiment, with the background spectra being recorded under dry N₂ before the experiment. For quantification of N₂O, NO and NO₂, the FT-IR spectrometer was calibrated using standard gases of these components, with measurement uncertainty of ± 1 ppm. Besides, NO and NO₂ concentrations were also measured by a NO_x analyzer (42i-HL, Thermo-Scientific, USA, uncertainty $\pm 1\%$). Considering the relative low infrared absorption of NO and potential interference by H₂O, concentration of NO was mainly determined by the NO_x analyzer in this work while that of NO₂ by the FT-IR spectrometer.

The conversion of N₂O is calculated based on its inlet ($C_{\text{N}_2\text{O},\text{in}}$, ppm) and outlet concentrations ($C_{\text{N}_2\text{O},\text{out}}$, ppm), as shown in eqn (1).

$$\text{Conversion of N}_2\text{O} = \frac{C_{\text{N}_2\text{O},\text{in}} - C_{\text{N}_2\text{O},\text{out}}}{C_{\text{N}_2\text{O},\text{in}}} \times 100\% \quad (1)$$

The selectivity of NO, NO₂ and NO_x (NO + NO₂) produced from N₂O conversion is calculated based on the N-balance as follows:

$$\text{Selectivity of NO} = \frac{C_{\text{NO},\text{with N}_2\text{O}} - C_{\text{NO},\text{w/o N}_2\text{O}}}{2 \times (C_{\text{N}_2\text{O},\text{in}} - C_{\text{N}_2\text{O},\text{out}})} \times 100\% \quad (2)$$

$$\text{Selectivity of NO}_2 = \frac{C_{\text{NO}_2,\text{with N}_2\text{O}} - C_{\text{NO}_2,\text{w/o N}_2\text{O}}}{2 \times (C_{\text{N}_2\text{O},\text{in}} - C_{\text{N}_2\text{O},\text{out}})} \times 100\% \quad (3)$$

$$\text{Selectivity of NO}_x = \text{selectivity of NO} + \text{selectivity of NO}_2 \quad (4)$$

where $C_{\text{NO},\text{with N}_2\text{O}}$, $C_{\text{NO},\text{w/o N}_2\text{O}}$ and $C_{\text{NO}_2,\text{with N}_2\text{O}}$, $C_{\text{NO}_2,\text{w/o N}_2\text{O}}$ indicate the outlet concentrations of NO and NO₂ (ppm) detected with and without N₂O in the inlet gas, respectively; 2 is the number ratio of nitrogen atoms of N₂O and NO/NO₂.

3. Results and discussion

3.1 Conversion of N₂O at room temperature

3.1.1 Conversion of N₂O under N₂ atmosphere. Fig. 3 shows the conversion of 100 ppm-N₂O in N₂ as functions of discharge power in plasma and plasma-Al₂O₃ reactors at room temperature. It can be seen that without O₂ in the reaction gas, N₂O can be effectively decomposed by both plasma and plasma-Al₂O₃ processes. The N₂O conversion increased with the increase of discharge power, which can be easily ascribed to the

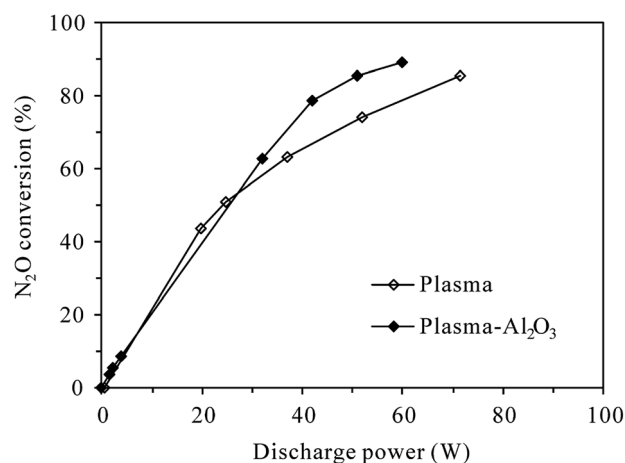
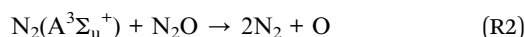
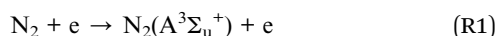


Fig. 3 Dependence of N₂O conversion on the discharge power in plasma and plasma-Al₂O₃ reactors at room temperature (inlet N₂O: 100 ppm; O₂ content: 0%).



increment of active species for N_2O decomposition at higher discharge power. In an intensive study of N_2O conversion by pulsed corona discharge in N_2 , Zhao *et al.*¹⁸ confirmed that among the active species, the first excited state of molecular nitrogen, *i.e.*, $\text{N}_2(\text{A}^3\Sigma_u^+)$ produced by electron impact excitation of nitrogen molecules (reaction (R1)²⁷), appeared to be mainly involved in the decomposition of N_2O through reaction (R2). Reaction (R2) was also concluded to be responsible for the conversion of N_2O in N_2 DBD plasma by Trinh *et al.*²⁰ With the increase of discharge power, more $\text{N}_2(\text{A}^3\Sigma_u^+)$ would be produced for N_2O decomposition due to the increase of energetic electrons. As shown in Fig. 3, the highest N_2O conversion was 85.7% and 89.4% observed at the highest discharge power of 71.6 W and 59.8 W tested for plasma and plasma- Al_2O_3 process, respectively. Packing with Al_2O_3 catalyst slightly facilitated the decomposition of N_2O in N_2 , probably by enhancing the electric fields around the contact points of dielectric Al_2O_3 pellets.¹⁹



3.1.2 Conversion and production of N_2O under N_2 - O_2 atmosphere. Once O_2 (5%, 10% or 20%) was added into the reaction gas, N_2O could not be decomposed anymore at room temperature, no matter in the presence or absence of Al_2O_3 catalyst. In fact, N_2O concentration increased due to additional production of N_2O , which was widely accepted to proceed mainly by the reaction of $\text{N}_2(\text{A}^3\Sigma_u^+)$ with oxygen, as shown in (R3).^{27–29} Obviously, $\text{N}_2(\text{A}^3\Sigma_u^+)$ plays an important role in both production and decomposition of N_2O *via* (R3) and (R2), respectively.

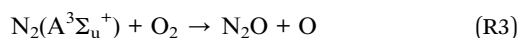


Fig. 4 compares the increased concentration of N_2O ($C_{\text{N}_2\text{O},\text{out}} - C_{\text{N}_2\text{O},\text{in}}$) under different O_2 contents with and without 100 ppm- N_2O in the N_2 - O_2 mixture. As can be seen from Fig. 4(a), no matter with or without N_2O in the inlet gas, the increased concentration of N_2O in the plasma reactor first increased and then decreased with the increase of discharge power, attaining a maximum at *ca.* 35 W. The reason for this may be that the increase of discharge power promotes not only the formation of N_2O *via* (R3), but also N_2O loss by (R2) and/or (R4)–(R6).^{27,29–31} Higher discharge power means that more energy could be used to excite/dissociate N_2 and O_2 molecules, producing more reactive species such as $\text{N}_2(\text{A}^3\Sigma_u^+)$ and $\text{O}(\text{D})$. At relatively low discharge power, the concentration of N_2O increased with increasing discharge power due to the enhanced production of $\text{N}_2(\text{A}^3\Sigma_u^+)$ species for N_2O formation (R3). With the increase of N_2O concentration and increasing production of reactive species ($\text{N}_2(\text{A}^3\Sigma_u^+)$ and $\text{O}(\text{D})$), the probability of N_2O loss reactions ((R2), (R5) and (R6)) raised, explaining the observed decrease of N_2O concentration at higher discharge power. In the whole discharge power range tested, however, the production of N_2O surpassed the loss since the increased concentration of N_2O was always positive.

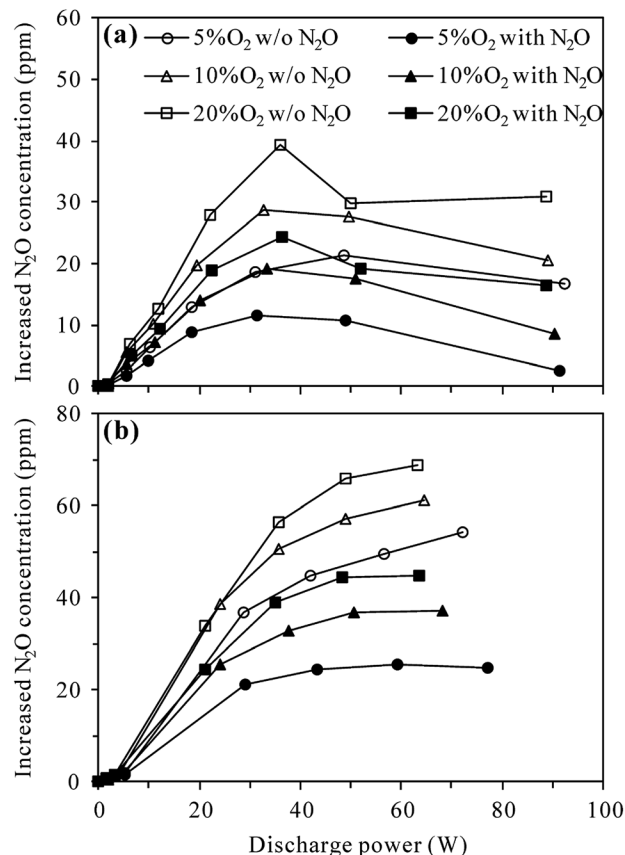


Fig. 4 Effects of N_2O presence in N_2 - O_2 mixture on the production of N_2O by discharge in (a) plasma and (b) plasma- Al_2O_3 reactors at room temperature (inlet N_2O : 0 or 100 ppm; O_2 content: 5%, 10% or 20%).

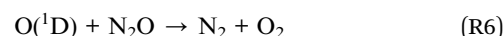
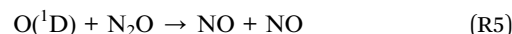
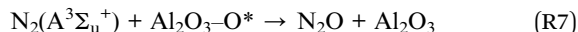


Fig. 4(a) also shows that in both the presence and absence of N_2O in the inlet gas, more N_2O was produced in the plasma reactor under higher O_2 contents for a given discharge power, indicating the important role of O_2 in N_2O production.^{27,29} Compared with the case without N_2O in the inlet gas, introduction of 100 ppm- N_2O significantly reduced the production of N_2O under all O_2 contents. In the presence of initial N_2O , more $\text{N}_2(\text{A}^3\Sigma_u^+)$ species would be consumed in N_2O decomposition (reaction (R2)), reducing the amount of $\text{N}_2(\text{A}^3\Sigma_u^+)$ species for N_2O production (reaction (R3)) as a result.

Compared to plasma alone, more N_2O was produced in the plasma- Al_2O_3 reactor (Fig. 4(b)) under otherwise similar conditions, indicating the promotion effects of Al_2O_3 catalyst on N_2O formation by discharge. In a study focusing on N_2O formation by DBD in N_2 - O_2 mixtures, Tang *et al.* also reported similar increase of N_2O production by packing Al_2O_3 in the discharge zone and surface oxygen species ($\text{Al}_2\text{O}_3\text{-O}^*$) brought by Al_2O_3



into the plasma chemical process (reaction (R7)) was considered as the main reason.²⁹



where * represents an active site on the catalyst and O* represents atomic oxygen bound to the site.²⁹

In the presence of Al_2O_3 catalyst (Fig. 4(b)), the increased concentration of N_2O first increased and then tended to reach equilibrium values with the increase of discharge power, demonstrating that N_2O production was counterbalanced by N_2O loss at high discharge power, especially when N_2O was introduced into the inlet gas. As in the plasma case, introduction of 100 ppm- N_2O into the $\text{N}_2\text{-O}_2$ mixture also resulted in less production of N_2O in the plasma- Al_2O_3 reactor (Fig. 4(b)).

In addition, it is worth mentioning that although the presence of 100 ppm- N_2O in the $\text{N}_2\text{-O}_2$ mixture significantly affected the production of N_2O by discharge, it did not induce significant changes to the formation behavior of NO and NO_2 in both plasma (Fig. S1†) and plasma- Al_2O_3 reactors (Fig. S2†) at room temperature.

3.2 Conversion of N_2O at high temperature

In order to decompose N_2O in the O_2 -containing atmosphere, the reaction temperature was raised to 300 °C in this section and $\text{RuO}_2/\text{Al}_2\text{O}_3$ was also investigated besides Al_2O_3 for plasma-catalytic decomposition of N_2O .

3.2.1 Effects of catalyst introduction. Fig. 5 presents the conversion of N_2O in plasma and plasma-catalytic reactors as functions of discharge power at 300 °C. The concentrations of N_2O and O_2 in the inlet gas were 400 ppm and 5%, respectively. In the absence of plasma (at discharge power of 0 W), a small conversion of N_2O (1.8%) was observed in the plasma- $\text{RuO}_2/\text{Al}_2\text{O}_3$ reactor while no N_2O was converted in the plasma or plasma- Al_2O_3 reactors. This indicated that N_2O was stable in the gas phase and over the Al_2O_3 catalyst at as high as 300 °C, but

$\text{RuO}_2/\text{Al}_2\text{O}_3$ catalyst did show low activity for N_2O decomposition. The conversion of N_2O increased with the increase of discharge power no matter the catalyst was introduced or not, demonstrating that N_2O in $\text{N}_2\text{-O}_2$ mixture could indeed be removed by plasma and plasma-catalytic processes at high temperature. When no catalyst was packed in the discharge zone, however, the N_2O conversion was very low, reaching only 3.8% at the highest discharge power tested (21.8 W). Introducing catalyst, especially $\text{RuO}_2/\text{Al}_2\text{O}_3$ into the discharge zone greatly improved the conversion of N_2O . Considering that Al_2O_3 and $\text{RuO}_2/\text{Al}_2\text{O}_3$ catalysts alone showed no or very low activity for N_2O decomposition at 300 °C, the enhanced conversion of N_2O in the plasma-catalytic process could only be attributed to the synergy of plasma and catalyst in N_2O conversion.^{23,24} The highest conversion of N_2O , however, was only 31.2% observed in the plasma- $\text{RuO}_2/\text{Al}_2\text{O}_3$ reactor. As stated in Section 2.2.2, the maximum applicable discharge power was limited at 300 °C due to easy breakdown of the reactor wall material (quartz glass). Further increase of the discharge power and N_2O conversion may be achieved by using reactors with higher resistance to breakdown, such as alumina ceramic tube reactor.²³

On the other hand, Fig. 6 shows the production of N_2O in the plasma and plasma-catalytic processes at 300 °C without N_2O in the inlet gas (inlet gas composition: 5% $\text{O}_2 + \text{N}_2$). It can be seen that for both plasma and plasma-catalytic processes, N_2O concentration increased almost linearly with discharge power in the range tested. Packing catalyst in the discharge zone greatly enhanced the production of N_2O , but no significant difference was observed in N_2O production between the plasma- Al_2O_3 and plasma- $\text{RuO}_2/\text{Al}_2\text{O}_3$ systems. Compared to the room-temperature case (Fig. 4), much less N_2O was produced at 300 °C for the same O_2 content (5%) and discharge power. Considering the low conversion of N_2O obtained, especially in the plasma and plasma- Al_2O_3 processes (Fig. 5), the observed less production of N_2O (Fig. 6) should be mainly due to the low effectiveness of N_2O formation reactions (e.g., (R3)) at high temperature. In other words, high reaction temperature is

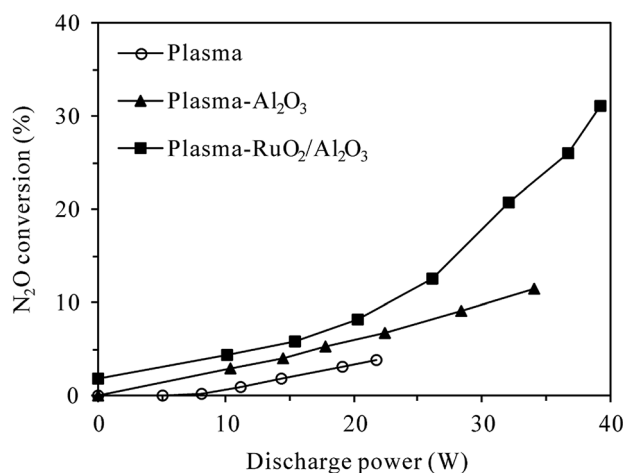


Fig. 5 Dependence of N_2O conversion on the discharge power in plasma and plasma-catalytic reactors at 300 °C (inlet N_2O : 400 ppm; O_2 content: 5%).

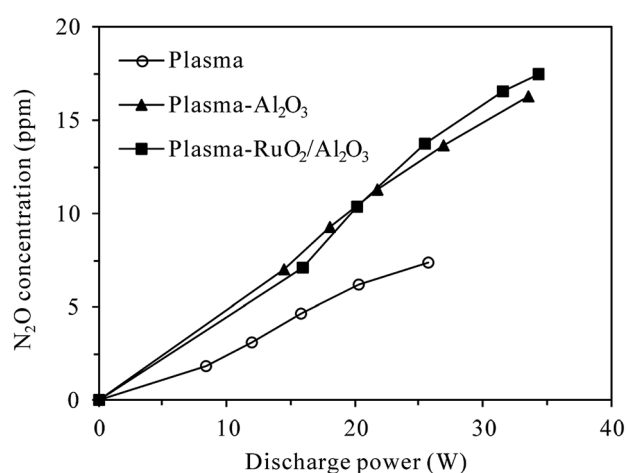


Fig. 6 Dependence of N_2O production on the discharge power in plasma and plasma-catalytic reactors at 300 °C (inlet N_2O : 0 ppm; O_2 content: 5%).



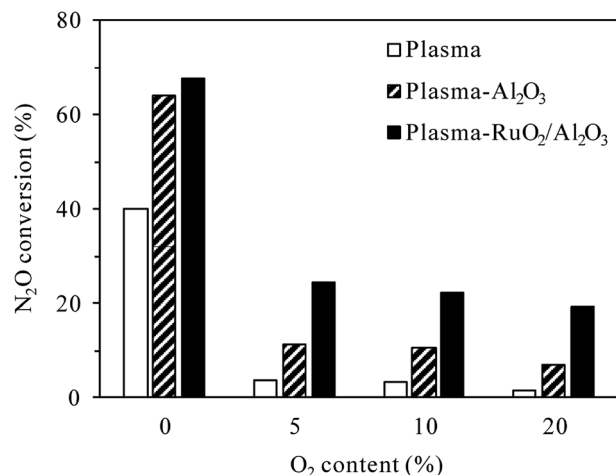
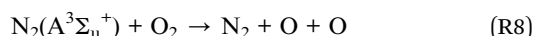


Fig. 7 Effects of O₂ content on N₂O conversion in plasma and plasma-catalytic reactors at 300 °C (inlet N₂O: 400 ppm; discharge power: 22 W for the plasma process and 34 W for the plasma-catalytic process).

favorable not only for conversion of N₂O but also for reduction of N₂O formation by discharge in N₂-O₂ mixture. At high temperature (300 °C), introducing catalyst, especially RuO₂/Al₂O₃ into the discharge zone significantly enhances the conversion of N₂O, overbalancing its promoting effects on N₂O production, which finally results in effective removal of N₂O from the N₂-O₂ mixture (Fig. 5).

3.2.2 Effects of O₂ content. O₂ content can largely influence the plasma/plasma-catalytic conversion of N₂O due to the intrinsic formation of N₂O in N₂-O₂ plasma. Fig. 7 shows the effects of O₂ content on N₂O conversion (inlet N₂O 400 ppm) in plasma and plasma-catalytic processes at 300 °C. In both the presence and absence of catalyst, the conversion of N₂O drastically decreased when the O₂ content was changed from 0 to 5%, revealing that O₂ inhibited the plasma and plasma-catalytic decomposition of N₂O significantly. Jo *et al.*²³ attributed the negative influence of O₂ on catalytic and plasma-catalytic decomposition of N₂O to the competitive adsorption of O₂ onto the active sites over RuO₂/Al₂O₃ catalyst. Besides this, O₂ could significantly decrease the electron density and the formation rate of N₂(A³Σ_u⁺) species in plasma due to its electronegative characteristics.^{32–35} In addition to directly react with N₂(A³Σ_u⁺) species to produce additional N₂O (reaction (R3)), O₂ could also reduce the amount of N₂(A³Σ_u⁺) species by dissociative quenching (reaction (R8)) due to its low dissociation energy (5.2 eV per molecule).^{32,36} The decrease of N₂(A³Σ_u⁺) species for N₂O decomposition, additional production of N₂O as well as the competitive adsorption of O₂ over the catalyst sites should all contribute to the dramatic decrease of N₂O conversion in the presence of O₂.



As also shown in Fig. 7, for the same discharge power of 34 W, N₂O conversion in the plasma-Al₂O₃ process decreased from 64.3% for 0% O₂ content to 11.4% for 5% O₂ content,

while that in the plasma-RuO₂/Al₂O₃ process decreased from 67.9% to 24.4%. The superiority of RuO₂/Al₂O₃ over Al₂O₃ was more pronounced in the O₂-containing cases. Further increase of the O₂ content from 5% to 10% and 20% caused further decrease of the N₂O conversion, but the extent of decrease was less prominent.

3.2.3 Effects of inlet N₂O concentration. The inlet concentration of N₂O can also be an important factor influencing the plasma and plasma-catalytic decomposition processes. The effects of inlet N₂O concentration on N₂O conversion at 300 °C with 0% and 5% O₂ in the reaction gas are presented in Fig. 8. For the plasma process (Fig. 8(a)), at a given discharge power of 22 W, the conversion of N₂O without O₂ significantly decreased from 71.6% to 40.0% while that with 5% O₂ slightly increased from 1.2% to 3.8% when the inlet N₂O concentration was increased from 100 to 400 ppm. It is obvious that higher inlet concentration leads to lower conversion of N₂O in N₂ plasma due to the competitive consumption of reactive species for N₂O decomposition (N₂(A³Σ_u⁺)) by increasing N₂O molecules. In the presence of 5% O₂, however, the conversion of N₂O was enhanced by injecting more N₂O into the reaction gas. The reason for this may be that more N₂(A³Σ_u⁺) species would be consumed in the decomposition of higher-concentration N₂O

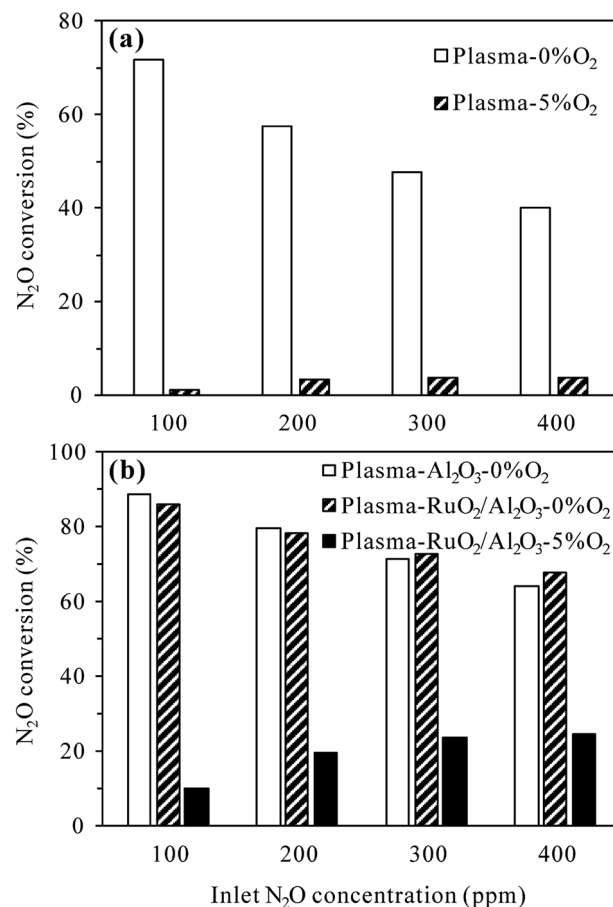


Fig. 8 Effects of inlet N₂O concentration on N₂O conversion in (a) plasma and (b) plasma-catalytic reactors at 300 °C (O₂ content: 0% or 5%; discharge power: 22 W for the plasma process and 34 W for the plasma-catalytic process).



(reaction (R2)), reducing the amount of $N_2(A^3\Sigma_u^+)$ species for N_2O formation (reaction (R3)).

For the plasma-catalytic process (Fig. 8(b)), at a given discharge power of 34 W, the conversion of N_2O without O_2 also decreased with increasing inlet N_2O concentration, but the decrease was less significant compared to that in the plasma process, proving the higher capacity of plasma-catalytic process in decomposing N_2O . Besides, it was noticed that the difference in the N_2O conversion between the plasma- Al_2O_3 and plasma- RuO_2/Al_2O_3 processes was insignificant in the absence of O_2 , indicating the minor role of RuO_2 in promoting N_2O decomposition under N_2 atmosphere although RuO_2 greatly improved the N_2O conversion under N_2-O_2 atmosphere (Fig. 5 and 7).

As in the plasma process (Fig. 8(a)), the conversion of N_2O in the plasma- RuO_2/Al_2O_3 process also increased with the increase of inlet N_2O concentration in the presence of 5% O_2 , especially from 100 to 200 and 300 ppm (Fig. 8(b)). Further increasing the inlet N_2O concentration, e.g., to 400 ppm, showed limited effects in enhancing the N_2O conversion, probably due to the limited amount of reactive species ($N_2(A^3\Sigma_u^+)$ and $O(^1D)$) produced under a given discharge power for N_2O conversion. From the point of fully utilizing the generated reactive species and reducing the negative influence of O_2 on N_2O conversion, dilute N_2O in N_2-O_2 mixture should be concentrated, e.g., by adsorption-desorption process before being converted by the plasma-catalytic process.²⁰

In addition, it is noteworthy that for the same inlet N_2O concentration of 100 ppm and background gas of N_2 , N_2O conversion in the plasma process increased from 47.1% at room temperature (Fig. 3) to 71.6% at 300 °C (Fig. 8(a)) for the same discharge power of 22 W. Similarly, N_2O conversion in the plasma- Al_2O_3 process increased from 66.2% at room temperature (Fig. 3) to 88.7% at 300 °C (Fig. 8(b)) for the same discharge power of 34 W. These results suggest that N_2O in N_2 could be decomposed more efficiently by plasma and plasma-catalytic processes at higher reaction temperature.

3.3 Mechanism of N_2O conversion

3.3.1 N_2O conversion pathways. On-line FT-IR (Fig. S3†) and NO_x measurement results show that under N_2 atmosphere, no other nitrogen oxide species were produced during the plasma and plasma-catalytic decomposition of N_2O regardless of the reaction temperature. O radicals generated in (R2) should have recombined and/or reacted with N_2O ((R6)) to give out O_2 as the final product instead of being consumed for NO/NO_2 production. In other words, N_2O was degraded to N_2 and O_2 by discharge in N_2 in both the presence and absence of catalyst and at both room and high temperature. Trinh *et al.*²⁰ proposed similar mechanism for direct decomposition of N_2O in N_2 DBD plasma.

On the other hand, as stated in Section 3.2, N_2O in N_2-O_2 mixture could be removed by plasma and plasma-catalytic processes only at high temperature. Fig. S4† shows typical FT-IR spectra of the effluents of plasma and plasma-catalytic reactors with and without 400 ppm- N_2O in the inlet gas (O_2 content 5%) and before and after discharge at 300 °C. Clearly,

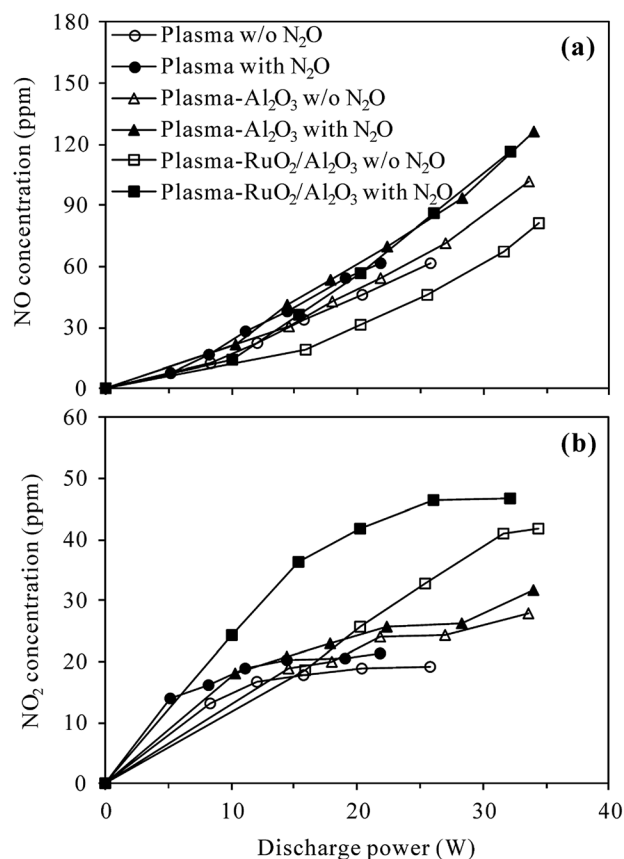


Fig. 9 Concentrations of (a) NO and (b) NO_2 formed with and without 400 ppm N_2O in the inlet gas of plasma and plasma-catalytic reactors at 300 °C (O_2 content: 5%).

discharge in N_2-O_2 mixture at 300 °C produced N_2O , NO and NO_2 as byproducts no matter the catalyst was present or not. When N_2O was introduced into the N_2-O_2 mixture, NO and NO_2 were also detected besides the residual N_2O . In order to clarify whether N_2O was converted to NO and NO_2 under N_2-O_2 atmosphere, the outlet concentrations of NO and NO_2 detected with and without 400 ppm- N_2O in the inlet gas were compared in Fig. 9.

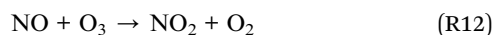
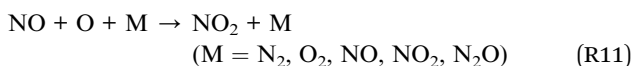
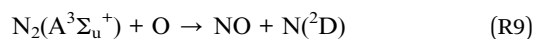
Overall, NO and NO_2 concentrations increased with the increase of discharge power and the presence of 400 ppm- N_2O in the N_2-O_2 mixture did not obviously change the variation trends of NO or NO_2 concentrations. For a given discharge power, however, higher concentrations of NO and NO_2 were always detected when N_2O was introduced, especially in the plasma- RuO_2/Al_2O_3 process. This result revealed that N_2O was partially transformed into NO and NO_2 during the O_2 -containing conversion processes, being in agreement with the observations of Krawczyk *et al.*^{24,25} Table 1 lists the selectivity of NO, NO_2 and NO_x ($NO + NO_2$) at typical discharge power in the plasma and plasma-catalytic processes. As seen, the selectivity of NO_x ranged from 28.7% of the plasma- Al_2O_3 process at 34.0 W to 79.5% of the plasma process at 14.4 W. Other removed N_2O should have been degraded to benign N_2 and O_2 since no N-containing byproducts other than NO and NO_2 were observed.



Table 1 Selectivity of NO, NO₂ and NO_x (NO + NO₂) at typical discharge power in plasma and plasma-catalytic processes (inlet N₂O: 400 ppm; O₂ content: 5%; reaction temperature: 300 °C)

Process	Discharge power (W)	Selectivity of NO (%)	Selectivity of NO ₂ (%)	Selectivity of NO _x (%)
Plasma	14.4	59.2	20.3	79.5
	21.8	37.1	7.6	44.7
Plasma-Al ₂ O ₃	14.4	34.0	6.5	40.5
	34.0	24.7	4.0	28.7
Plasma-RuO ₂ /Al ₂ O ₃	15.4	36.9	38.7	75.6
	32.1	28.4	3.4	31.8

Table 1 also shows that compared to the plasma process, the selectivity of NO_x was relatively low in the plasma-catalytic process, indicating that catalyst packed in the discharge zone promoted N₂O decomposition to N₂ and O₂ to a larger extent than oxidation to NO and NO₂. For all processes, the selectivity of NO and NO₂ decreased with the increase of discharge power, probably due to the substantial increase of NO and NO₂ formation from plasma-induced reactions between N₂ and O₂ which competitively consumed oxidative species, as shown in reactions (R9)–(R12).^{27,29,32,37} Besides, the selectivity of NO was much higher than that of NO₂ except at low discharge power of the plasma-RuO₂/Al₂O₃ process. This can be easily ascribed to the step-wise oxidation of N₂O (first (R5) and then (R11) and (R12)) under oxidative plasma atmosphere.^{27,32,37}



Compared to Al₂O₃ catalyst, RuO₂/Al₂O₃ catalyst significantly enhanced the selectivity of NO₂ at low discharge power. At higher discharge power, however, the difference in the selectivity of NO and NO₂ between the two plasma-catalytic processes became insignificant. At the relatively high discharge power tested, more than 40% and *ca.* 30% of the removed nitrogen in N₂O was transformed into NO_x in the plasma and plasma-catalytic process, respectively.

3.3.2 Synergy mechanism of plasma and catalyst for N₂O conversion under N₂–O₂ atmosphere. From the above-mentioned analysis, it can be concluded that introducing catalyst, especially RuO₂/Al₂O₃ into the discharge zone significantly enhanced the conversion of N₂O and promoted N₂O decomposition to N₂ and O₂ under N₂–O₂ atmosphere. Fig. 10 shows the XRD patterns of Al₂O₃ and RuO₂/Al₂O₃ catalysts before and after use in plasma-catalytic conversion of N₂O at 300 °C. From the XRD analysis, cubic Al₂O₃ was observed for all catalyst samples and tetragonal RuO₂ was formed over the RuO₂/Al₂O₃ catalyst. For both Al₂O₃ and RuO₂/Al₂O₃ catalysts, the XRD patterns were almost unchanged after use, indicating

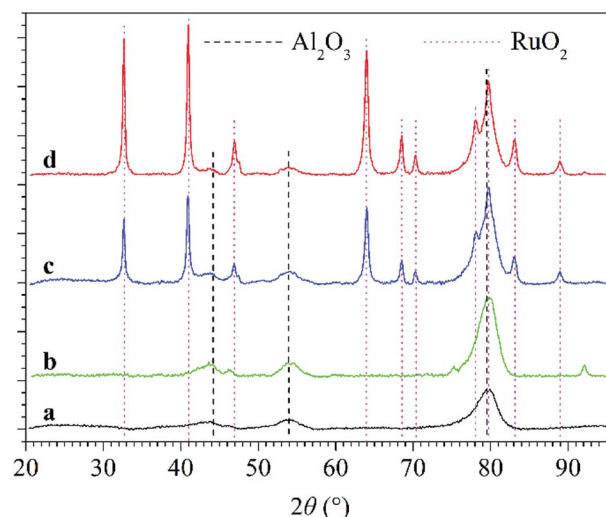


Fig. 10 XRD patterns of Al₂O₃ and RuO₂/Al₂O₃ catalysts: (line a) fresh Al₂O₃ catalyst; (line b) Al₂O₃ catalyst after use in plasma-catalytic conversion of N₂O at 300 °C; (line c) fresh RuO₂/Al₂O₃ catalyst; (line d) RuO₂/Al₂O₃ catalyst after use in plasma-catalytic conversion of N₂O at 300 °C.

that neither plasma nor the N₂O conversion reactions changed the phase composition of the catalysts.

According to literatures, the decomposition of N₂O over metal oxide catalysts can be expressed as a Langmuir–Hinshelwood mechanism:



where * stands for an active site of the catalyst.^{3,23} In this mechanism, the adsorbed surface oxygen (O*) migrates from one active site to another to form O₂ by recombination, which is known to be the rate-determining step.^{3,23} Applying DBD plasma in the RuO₂/Al₂O₃ catalyst bed could not only initiate gas-phase conversion of N₂O ((R2), (R5) and (R6)), but also accelerate the catalytic conversion of N₂O by speeding up the consumption of adsorbed surface oxygen (O*), *e.g.*, via reaction (R15) to regenerate the active sites.²³ In fact, the scavenging of O* by O radicals (reaction (R15)) also explained the decreased selectivity of NO_x



(increased selectivity of N₂ and O₂) in the presence of catalyst (Table 1), revealing the synergy of plasma and catalyst in promoting N₂O decomposition.



4. Conclusions

In the present work, conversion of dilute N₂O in N₂ and N₂–O₂ mixtures by plasma and plasma-catalytic processes was investigated at both room and high temperature (300 °C). It is found that N₂O in N₂ can be effectively decomposed to N₂ and O₂ by plasma and plasma-catalytic processes at both room and high temperature, with much higher decomposition efficiency at 300 °C than at room temperature for the same discharge power. However, N₂O in N₂–O₂ mixture can be removed only at high temperature, producing not only N₂ and O₂ but also NO and NO₂. Production and conversion of N₂O occur simultaneously during the plasma and plasma-catalytic processing of N₂O in N₂–O₂ mixture, with production and conversion being the dominant process at room and high temperature, respectively.

N₂O conversion increases with the increase of discharge power and decreases with the increase of O₂ content. The negative influence of O₂ on N₂O conversion could be suppressed to some extent by concentrating N₂O in N₂–O₂ mixture which increases the involvement of plasma reactive species (e.g., N₂(A³Σ_u⁺) and O(¹D)) in N₂O conversion. Introducing catalyst, especially RuO₂/Al₂O₃ into the discharge zone significantly enhances the conversion of N₂O and improves the selectivity of N₂O decomposition under N₂–O₂ atmosphere, revealing the synergy of plasma and catalyst in promoting N₂O conversion, especially its decomposition to N₂ and O₂. The combined plasma-catalytic processing may be an efficient way for reducing N₂O emissions from combustion and industrial sources.

Conflicts of interest

There are no conflicts to declare.

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