




Cite this: *RSC Adv.*, 2018, 8, 26998

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

Xing Fan, *^a Sijing Kang,^a Jian Li^a and Tianle Zhu^b

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.

Received 1st July 2018
 Accepted 21st July 2018

DOI: 10.1039/c8ra05607b

rsc.li/rsc-advances

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

^aKey Laboratory of Beijing on Regional Air Pollution Control, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China. E-mail: fanxing@bjut.edu.cn

^bSchool of Space and Environment, Beihang University, Beijing 100191, China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8ra05607b



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 $\text{m}^2 \text{g}^{-1}$, 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 $\text{m}^2 \text{g}^{-1}$, measured by N_2 adsorption at –196 °C on a surface area and pore size analyzer (Micromeritics Gemini V, USA).

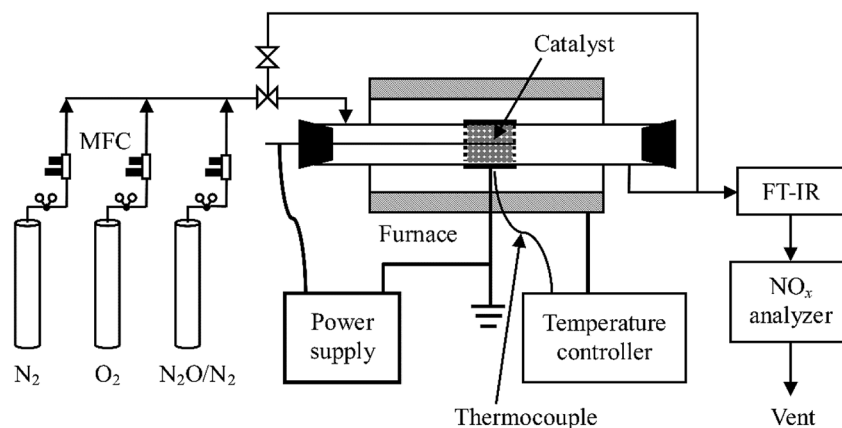


Fig. 1 Schematic diagram of the experimental set-up.



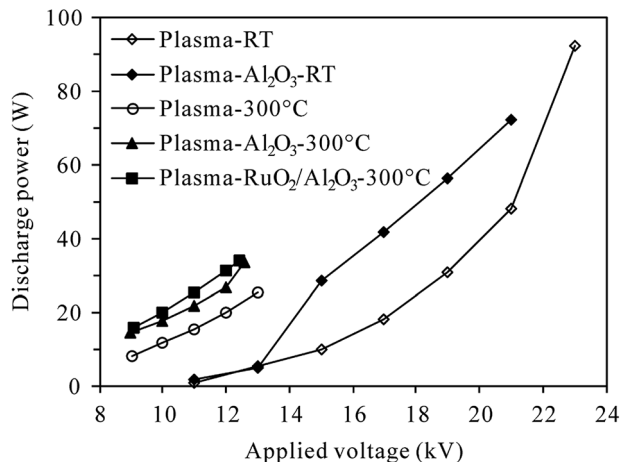


Fig. 2 Dependence of discharge power on the applied voltage at room temperature (RT) and 300 °C (inlet N₂O: 0 ppm; O₂ content: 5%).

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_{N₂O,in}, ppm) and outlet concentrations (C_{N₂O,out}, ppm), as shown in eqn (1).

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

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

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

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

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

where C_{NO,with N₂O}, C_{NO,w/o N₂O} and C_{NO₂,with N₂O}, C_{NO₂,w/o N₂O} 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

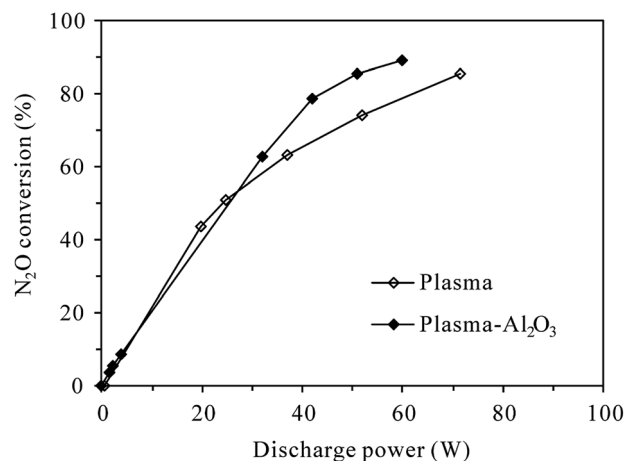
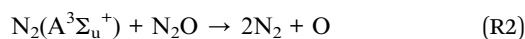
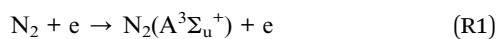


Fig. 3 Dependence of N₂O conversion on the discharge power in plasma and plasma-Al₂O₃ reactors at room temperature (inlet N₂O: 100 ppm; O₂ content: 0%).



increment of active species for N₂O decomposition at higher discharge power. In an intensive study of N₂O conversion by pulsed corona discharge in N₂, Zhao *et al.*¹⁸ confirmed that among the active species, the first excited state of molecular nitrogen, *i.e.*, N₂(A³Σ_u⁺) produced by electron impact excitation of nitrogen molecules (reaction (R1)²⁷), appeared to be mainly involved in the decomposition of N₂O through reaction (R2). Reaction (R2) was also concluded to be responsible for the conversion of N₂O in N₂ DBD plasma by Trinh *et al.*²⁰ With the increase of discharge power, more N₂(A³Σ_u⁺) would be produced for N₂O decomposition due to the increase of energetic electrons. As shown in Fig. 3, the highest N₂O 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-Al₂O₃ process, respectively. Packing with Al₂O₃ catalyst slightly facilitated the decomposition of N₂O in N₂, probably by enhancing the electric fields around the contact points of dielectric Al₂O₃ pellets.¹⁹



3.1.2 Conversion and production of N₂O under N₂-O₂ atmosphere. Once O₂ (5%, 10% or 20%) was added into the reaction gas, N₂O could not be decomposed anymore at room temperature, no matter in the presence or absence of Al₂O₃ catalyst. In fact, N₂O concentration increased due to additional production of N₂O, which was widely accepted to proceed mainly by the reaction of N₂(A³Σ_u⁺) with oxygen, as shown in (R3).²⁷⁻²⁹ Obviously, N₂(A³Σ_u⁺) plays an important role in both production and decomposition of N₂O *via* (R3) and (R2), respectively.

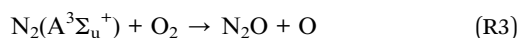


Fig. 4 compares the increased concentration of N₂O ($C_{\text{N}_2\text{O},\text{out}} - C_{\text{N}_2\text{O},\text{in}}$) under different O₂ contents with and without 100 ppm-N₂O in the N₂-O₂ mixture. As can be seen from Fig. 4(a), no matter with or without N₂O in the inlet gas, the increased concentration of N₂O 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 N₂O *via* (R3), but also N₂O loss by (R2) and/or (R4)–(R6).^{27,29-31} Higher discharge power means that more energy could be used to excite/dissociate N₂ and O₂ molecules, producing more reactive species such as N₂(A³Σ_u⁺) and O(¹D). At relatively low discharge power, the concentration of N₂O increased with increasing discharge power due to the enhanced production of N₂(A³Σ_u⁺) species for N₂O formation (R3). With the increase of N₂O concentration and increasing production of reactive species (N₂(A³Σ_u⁺) and O(¹D)), the probability of N₂O loss reactions ((R2), (R5) and (R6)) raised, explaining the observed decrease of N₂O concentration at higher discharge power. In the whole discharge power range tested, however, the production of N₂O surpassed the loss since the increased concentration of N₂O was always positive.

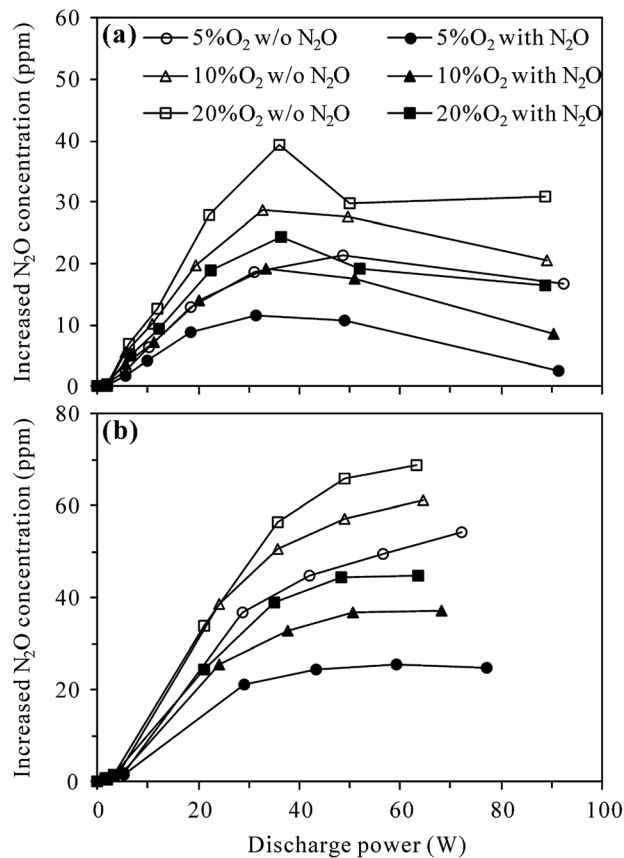


Fig. 4 Effects of N₂O presence in N₂-O₂ mixture on the production of N₂O by discharge in (a) plasma and (b) plasma-Al₂O₃ reactors at room temperature (inlet N₂O: 0 or 100 ppm; O₂ content: 5%, 10% or 20%).

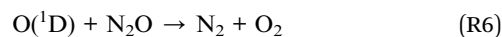
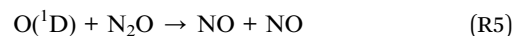
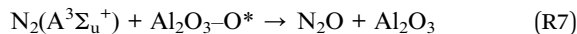


Fig. 4(a) also shows that in both the presence and absence of N₂O in the inlet gas, more N₂O was produced in the plasma reactor under higher O₂ contents for a given discharge power, indicating the important role of O₂ in N₂O production.^{27,29} Compared with the case without N₂O in the inlet gas, introduction of 100 ppm-N₂O significantly reduced the production of N₂O under all O₂ contents. In the presence of initial N₂O, more N₂(A³Σ_u⁺) species would be consumed in N₂O decomposition (reaction (R2)), reducing the amount of N₂(A³Σ_u⁺) species for N₂O production (reaction (R3)) as a result.

Compared to plasma alone, more N₂O was produced in the plasma-Al₂O₃ reactor (Fig. 4(b)) under otherwise similar conditions, indicating the promotion effects of Al₂O₃ catalyst on N₂O formation by discharge. In a study focusing on N₂O formation by DBD in N₂-O₂ mixtures, Tang *et al.* also reported similar increase of N₂O production by packing Al₂O₃ in the discharge zone and surface oxygen species (Al₂O₃-O*) brought by Al₂O₃



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 Al₂O₃ catalyst (Fig. 4(b)), the increased concentration of N₂O first increased and then tended to reach equilibrium values with the increase of discharge power, demonstrating that N₂O production was counterbalanced by N₂O loss at high discharge power, especially when N₂O was introduced into the inlet gas. As in the plasma case, introduction of 100 ppm-N₂O into the N₂-O₂ mixture also resulted in less production of N₂O in the plasma-Al₂O₃ reactor (Fig. 4(b)).

In addition, it is worth mentioning that although the presence of 100 ppm-N₂O in the N₂-O₂ mixture significantly affected the production of N₂O by discharge, it did not induce significant changes to the formation behavior of NO and NO₂ in both plasma (Fig. S1†) and plasma-Al₂O₃ reactors (Fig. S2†) at room temperature.

3.2 Conversion of N₂O at high temperature

In order to decompose N₂O in the O₂-containing atmosphere, the reaction temperature was raised to 300 °C in this section and RuO₂/Al₂O₃ was also investigated besides Al₂O₃ for plasma-catalytic decomposition of N₂O.

3.2.1 Effects of catalyst introduction. Fig. 5 presents the conversion of N₂O in plasma and plasma-catalytic reactors as functions of discharge power at 300 °C. The concentrations of N₂O and O₂ 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 N₂O (1.8%) was observed in the plasma-RuO₂/Al₂O₃ reactor while no N₂O was converted in the plasma or plasma-Al₂O₃ reactors. This indicated that N₂O was stable in the gas phase and over the Al₂O₃ catalyst at as high as 300 °C, but

RuO₂/Al₂O₃ catalyst did show low activity for N₂O decomposition. The conversion of N₂O increased with the increase of discharge power no matter the catalyst was introduced or not, demonstrating that N₂O in N₂-O₂ 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 N₂O conversion was very low, reaching only 3.8% at the highest discharge power tested (21.8 W). Introducing catalyst, especially RuO₂/Al₂O₃ into the discharge zone greatly improved the conversion of N₂O. Considering that Al₂O₃ and RuO₂/Al₂O₃ catalysts alone showed no or very low activity for N₂O decomposition at 300 °C, the enhanced conversion of N₂O in the plasma-catalytic process could only be attributed to the synergy of plasma and catalyst in N₂O conversion.^{23,24} The highest conversion of N₂O, however, was only 31.2% observed in the plasma-RuO₂/Al₂O₃ 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 N₂O 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 N₂O in the plasma and plasma-catalytic processes at 300 °C without N₂O in the inlet gas (inlet gas composition: 5% O₂ + N₂). It can be seen that for both plasma and plasma-catalytic processes, N₂O concentration increased almost linearly with discharge power in the range tested. Packing catalyst in the discharge zone greatly enhanced the production of N₂O, but no significant difference was observed in N₂O production between the plasma-Al₂O₃ and plasma-RuO₂/Al₂O₃ systems. Compared to the room-temperature case (Fig. 4), much less N₂O was produced at 300 °C for the same O₂ content (5%) and discharge power. Considering the low conversion of N₂O obtained, especially in the plasma and plasma-Al₂O₃ processes (Fig. 5), the observed less production of N₂O (Fig. 6) should be mainly due to the low effectiveness of N₂O formation reactions (e.g., (R3)) at high temperature. In other words, high reaction temperature is

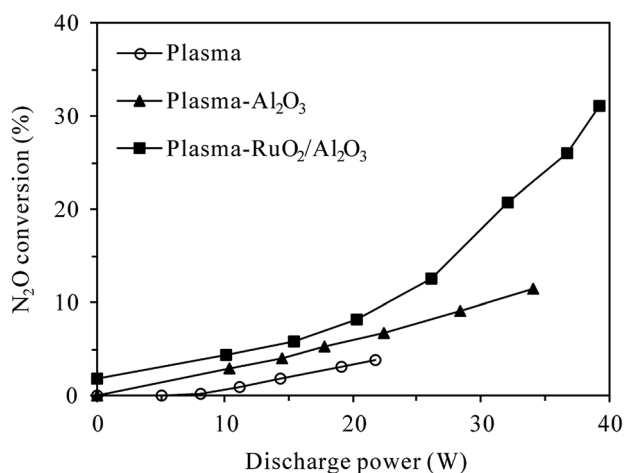


Fig. 5 Dependence of N₂O conversion on the discharge power in plasma and plasma-catalytic reactors at 300 °C (inlet N₂O: 400 ppm; O₂ content: 5%).

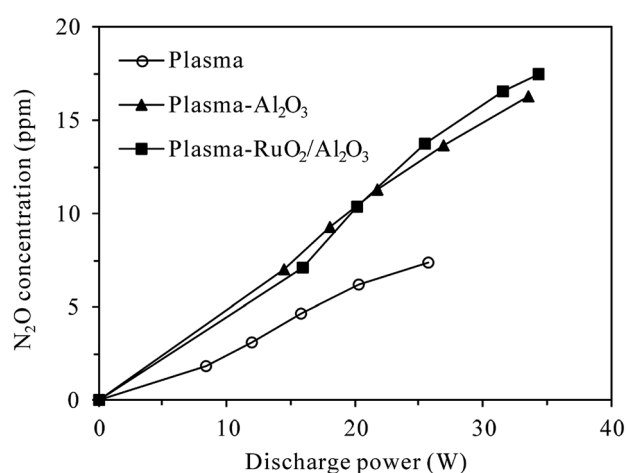


Fig. 6 Dependence of N₂O production on the discharge power in plasma and plasma-catalytic reactors at 300 °C (inlet N₂O: 0 ppm; O₂ content: 5%).



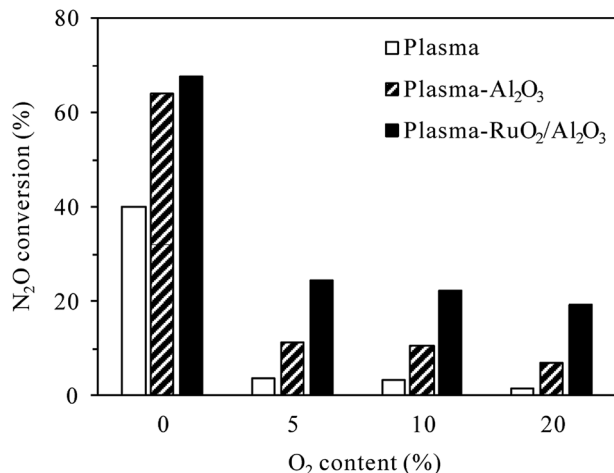
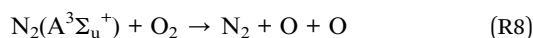


Fig. 7 Effects of O₂ content on N₂O conversion in plasma and plasma-catalytic reactors at 300 °C (inlet N₂O: 400 ppm; discharge power: 22 W for the plasma process and 34 W for the plasma-catalytic process).

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

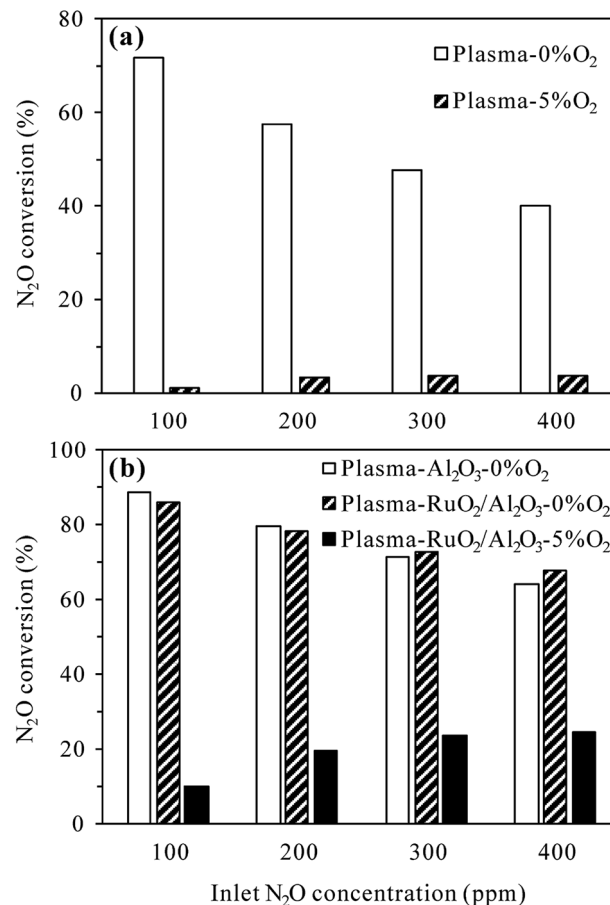


Fig. 8 Effects of inlet N₂O concentration on N₂O conversion in (a) plasma and (b) plasma-catalytic reactors at 300 °C (O₂ content: 0% or 5%; discharge power: 22 W for the plasma process and 34 W for the plasma-catalytic process).



(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,

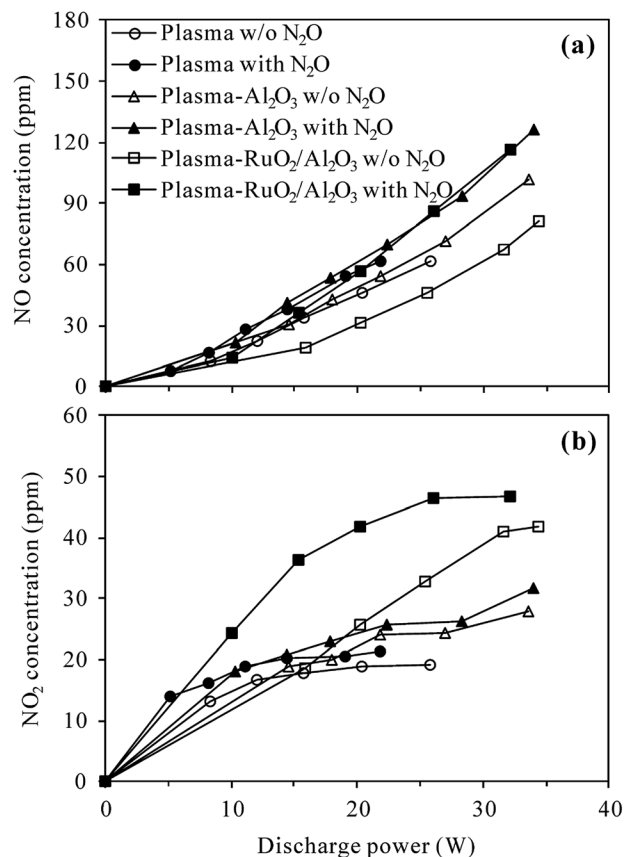


Fig. 9 Concentrations of (a) NO and (b) NO_2 formed with and without 400 ppm N_2O in the inlet gas of plasma and plasma-catalytic reactors at 300 °C (O_2 content: 5%).

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.

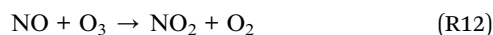
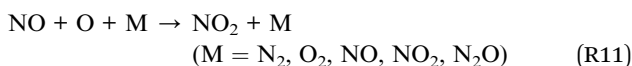
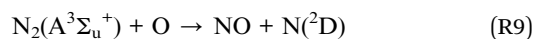
Overall, NO and NO_2 concentrations increased with the increase of discharge power and the presence of 400 ppm- N_2O in the N_2-O_2 mixture did not obviously change the variation trends of NO or NO_2 concentrations. For a given discharge power, however, higher concentrations of NO and NO_2 were always 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

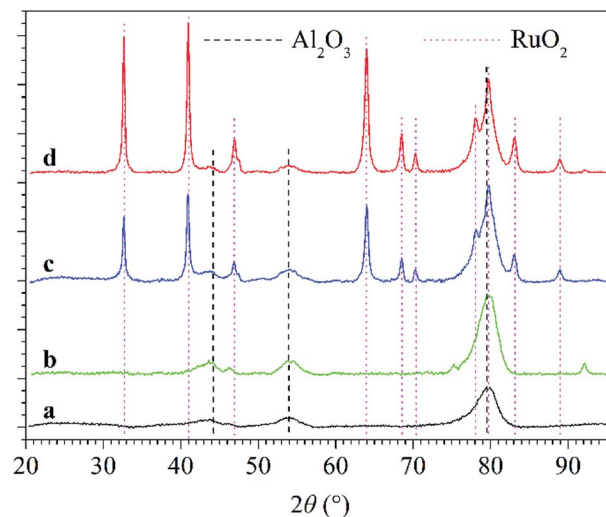


Fig. 10 XRD patterns of Al₂O₃ and RuO₂/Al₂O₃ catalysts: (line a) fresh Al₂O₃ catalyst; (line b) Al₂O₃ catalyst after use in plasma-catalytic conversion of N₂O at 300 °C; (line c) fresh RuO₂/Al₂O₃ catalyst; (line d) RuO₂/Al₂O₃ catalyst after use in plasma-catalytic conversion of N₂O at 300 °C.

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.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (grant numbers 21707004, 51638001) and the Natural Science Foundation of Beijing Municipality (grant number 8152011).

References

- 1 J. Pérez-Ramírez, F. Kapteijn, K. Schöffel and J. A. Moulijn, *Appl. Catal., B*, 2003, **44**, 117–151.
- 2 K. R. Sistani, M. Jn-Baptiste, N. Lovanh and K. L. Cook, *J. Environ. Qual.*, 2011, **40**, 1797–1805.
- 3 M. Konsolakis, *ACS Catal.*, 2015, **5**, 6397–6421.
- 4 A. Ates, A. Reitzmann, C. Hardacre and H. Yalcin, *Appl. Catal., A*, 2011, **407**, 67–75.

- 5 F. Zhang, X. Wang, X. Zhang, M. Turxun, H. Yu and J. Zhao, *Chem. Eng. J.*, 2014, **256**, 365–371.
- 6 M. Konsolakis, F. Aligizou, G. Goula and I. V. Yentekakis, *Chem. Eng. J.*, 2013, **230**, 286–295.
- 7 S. S. Kim, S. J. Lee and S. C. Hong, *Chem. Eng. J.*, 2011, **169**, 173–179.
- 8 Z. Liu, C. He, B. Chen and H. Liu, *Catal. Today*, 2017, **297**, 78–83.
- 9 H. L. Chen, H. M. Lee, S. H. Chen, M. B. Chang, S. J. Yu and S. N. Li, *Environ. Sci. Technol.*, 2009, **43**, 2216–2227.
- 10 J. V. Durme, J. Dewulf, C. Leys and H. V. Langenhove, *Appl. Catal., B*, 2008, **78**, 324–333.
- 11 X. Fan, T. L. Zhu, Y. F. Sun and X. Yan, *J. Hazard. Mater.*, 2011, **196**, 380–385.
- 12 Y. J. Wan, X. Fan and T. L. Zhu, *Chem. Eng. J.*, 2011, **171**, 314–319.
- 13 X. Fan, T. L. Zhu, Y. J. Wan and X. Yan, *J. Hazard. Mater.*, 2010, **180**, 616–621.
- 14 X. Fan, T. L. Zhu, M. Y. Wang and X. M. Li, *Chemosphere*, 2009, **75**, 1301–1306.
- 15 Q. Yu, Y. Gao, X. Tang, H. Yi, R. Zhang, S. Zhao, F. Gao and Y. Zhou, *Catal. Commun.*, 2018, **110**, 18–22.
- 16 A. Mizuno, *Catal. Today*, 2013, **211**, 2–8.
- 17 X. Hu, J. Nicholas, J. Zhang, T. M. Linjewile, P. D. Filippis and P. K. Agarwal, *Fuel*, 2002, **81**, 1259–1268.
- 18 G. B. Zhao, X. D. Hu, M. D. Argyle and M. Radosz, *Ind. Eng. Chem. Res.*, 2004, **43**, 5077–5088.
- 19 S. Mahammadunnisa, E. L. Reddy, P. R. M. K. Reddy and C. Subrahmanyam, *Plasma Processes Polym.*, 2013, **10**, 444–450.
- 20 Q. Trinh, S. H. Kim and Y. S. Mok, *Chem. Eng. J.*, 2016, **302**, 12–22.
- 21 D. H. Lee and T. Kim, N₂O decomposition by catalyst-assisted cold plasma, *20th Int. Symp. Plasma Chem.*, Philadelphia, USA, 2012.
- 22 H. Hu, H. Huang, J. Xu, Q. Yang and G. Tao, *Plasma Sci. Technol.*, 2015, **17**, 1043–1047.
- 23 J. Jo, Q. H. Trinh, S. H. Kim and Y. S. Mok, *Catal. Today*, 2018, **310**, 42–48.
- 24 K. Krawczyk and M. Młotek, *Appl. Catal., B*, 2001, **30**, 233–245.
- 25 K. Schmidt-Szałowski, K. Krawczyk and M. Młotek, *J. Adv. Oxid. Technol.*, 2007, **10**, 330–336.
- 26 G. Pekridis, C. Athanasiou, M. Konsolakis, I. V. Yentekakis and G. E. Marnellos, *Top. Catal.*, 2009, **52**, 1880–1887.
- 27 I. A. Kossyi, A. Y. Kostinsky, A. A. Matveyev and V. P. Silakov, *Plasma Sources Sci. Technol.*, 1992, **1**, 207–220.
- 28 M. P. Iannuzzi, J. B. Jeffries and F. Kaufman, *Chem. Phys. Lett.*, 1982, **87**, 570–574.
- 29 X. Tang, J. Wang, H. Yi, S. Zhao, F. Gao, Y. Huang, R. Zhang and Z. Yang, *Energy Fuels*, 2017, **31**, 13901–13908.
- 30 J. T. Herron and D. S. Green, *Plasma Chem. Plasma Process.*, 2001, **21**, 459–481.
- 31 K. Krawczyk, *IEEE Trans. Plasma Sci.*, 2009, **37**, 884–889.
- 32 G. B. Zhao, S. Garikipati, X. D. Hu, M. D. Argyle and M. Radosz, *AIChE J.*, 2005, **51**, 1800–1812.



Paper

- 33 G. Sathiamoorthy, S. Kalyana, W. C. Finney, R. J. Clark and B. R. Locke, *Ind. Eng. Chem. Res.*, 1999, **38**, 1844–1855.
- 34 S. Kanazawa, J. S. Chang, G. F. Round, G. Sheng, T. Ohkubo, Y. Nomoto and T. Adachi, *J. Electrostat.*, 1997, **40–41**, 651–656.
- 35 Y. S. Mok, J. H. Kim, I. S. Nam and S. W. Ham, *Ind. Eng. Chem. Res.*, 2000, **39**, 3938–3944.
- 36 M. S. Bak, W. Kim and M. A. Cappelli, *Appl. Phys. Lett.*, 2011, **98**, 011502.
- 37 Y. Zhang, X. Tang, H. Yi, Q. Yu, J. Wang, F. Gao, Y. Gao, D. Li and Y. Cao, *RSC Adv.*, 2016, **6**, 63946–63953.

