Dielectric Barrier Discharge Reactor for the Removal of NOx From Automotive Exhaust

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Dielectric barrier discharge reactor for the removal of NO\textsubscript{x} from automotive exhaust

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Abstract: In this study, a self-made wire-cylinder dielectric barrier discharge (DBD) reactor was used to remove NO\textsubscript{x}. The influence of electrical and gas parameters (e.g. structure, voltage, and frequency) and temperature on the NO\textsubscript{x} removal rate was studied systematically while operating the DBD reactor with a high-voltage positive–negative double pulse power supply. The experimental results showed that following conditions led to the optimal NO conversion rate and NO\textsubscript{x} removal rate: voltage of ±12 kV, pulse frequency up to 60 Hz, oxygen concentration at 6%, reaction temperature at 300°C, and C\textsubscript{2}H\textsubscript{2}:NO\textsubscript{x} ratio at 1.5. Under these conditions, the NO conversion rate and NO\textsubscript{x} removal rate reached the highest levels of 76.4% and 31.2%, respectively. Additionally, when the process was run in conjunction with a La\textsubscript{0.7}Sr\textsubscript{0.3}Ni\textsubscript{0.5}Mn\textsubscript{0.2}Fe\textsubscript{0.3}O\textsubscript{3} catalyst, the reactor efficiency increased markedly, and the NO conversion and NO\textsubscript{x} removal rates increased to 94.93% and 74.97%, respectively. The findings of this study demonstrate that DBD reactor technology shows promise for the removal of NO\textsubscript{x} from automotive waste streams.

Keywords: Dielectric barrier discharge; nitrogen oxide; electrical parameters; gas parameters; denitrification; perovskite-type catalyst

1. Introduction

Nitrogen oxide from automotive exhaust is widely recognized as an important air pollutant. High levels of nitrogen oxide can pose serious threats to human health, socioeconomic systems, and the ecological environment (Lin et al., 2010; Talebizadeh et al., 2014; Cai et al., 2019; Nguyen et al., 2019; Zhu et al., 2019; Liang et al, 2020; Yang et al., 2021). Hence, there is an
urgent need for new technologies that can reduce NO\textsubscript{x} emissions from automotive exhaust. Such improvements in emission reduction technologies would help to reduce nitrogen oxide concentrations in the atmosphere. In recent years, the application of low temperature plasma (Adnan et al., 2017) in pollutant control technology has attracted increasing levels of attention (Locke et al., 2006; Moreau, 2010; Vandenbroucke et al., 2011). A dielectric barrier discharge (DBD) device can be created by inserting at least one piece of insulating medium into the air gap between two metal electrodes to block the discharge channel through the air gap (Kogelschatz, 2003). Such devices represent a reliable method for the generation of low temperature plasma and are one of the earliest applied discharge methodologies. Since the 1980s, DBD technology has been used to control air pollutants around the world. Previous studies have demonstrated the removal of SO\textsubscript{2} under different conditions with DBD technology (e.g. Chang et al., 1991; Dhali and Sardja, 1991; Higashi et al., 1992) Furthermore, Mizuno et al. (1995) proved through experiments that the removal rate of NO\textsubscript{x} could be effectively improved by using water spray from a nozzle on a line-cylinder reactor. Jolibois et al. (2011) studied a wet plasma reactor with a three-electrode device. Under a background concentration of 100 ppm NO at a gas flow rate of 1 L/min, this reactor was found to be better at purifying waste gas than conventional technologies. Rajanikanth and Sushma (2006) used an independent reactor to generate N atoms and injected N atoms into a DBD reactor to improve the NO\textsubscript{x} removal rate. Compared with the denitrification rate of a single DBD reactor, this method increased the denitrification rate by 22%. Such a process can be performed at low temperatures. Hao et al. (2017) proposed a complex absorbent composed of sodium humate and sodium chlorite for the simultaneous removal of NO and SO\textsubscript{2}, and they achieved a conversion efficiency of 98%. At present, the main research directions for studies on the removal of NO\textsubscript{x} by DBD are focused on the following three aspects: the power supply, reactor structure, and chemical composition. Among these, the influence of the power supply can be studied through changes in the voltage type, power frequency, and so forth. The aim of this study was to improve the NO\textsubscript{x} removal rate from automotive exhaust by optimizing the power supply, reactor structure, and operational parameters of a DBD reactor. The study showed that the reactor had a good NO\textsubscript{x} removal efficiency and the removal of NO\textsubscript{x} was greatly enhanced in the presence of the catalyst.
2. Experimental apparatus and methods

2.1. Experimental system and equipment

2.1.1. Experimental system

The experimental system can be divided into the following three parts: gas path system, reaction system, and analysis system. The gas path system was composed of the gas cylinder, mass flow controller (MFC), tube furnace, and so on. The reaction gas (N\textsubscript{2}, O\textsubscript{2}, NO, CH\textsubscript{4}, etc.) was controlled by a mass flow meter in the MFC and was introduced into the reactor through a stainless steel tube with a diameter of 3 mm. In our research, the reactor was placed in the tube furnace after the reaction, and the gas was introduced into the instrument through a 6 mm stainless steel pipe.

The reaction system was composed of several parts. The diameter D of the high-voltage discharge electrode of the barrel-type DBD reactor, which consisted of a threaded copper rod, was 10 mm, the inner diameter d of the dielectric tube was 16 mm, and the quartz glass was 1.5 mm thick. The ground was constructed from heavy duty aluminium foil. A P60KV-D-RSG-II high-voltage positive–negative double pulse power supply was used; this power supply was developed by the Dalian University of Technology. Discharge parameters were measured by a digital storage oscilloscope (Agilent DSO-X-3054A), voltage probe (IWASTA HV-P60), and current probe (Pearson\textsuperscript{TM} model 411).

An analysis system was used to measure the performance of the reactor. Specifically, the NO\textsubscript{x} removal and NO conversion rate of the reacted gas were analysed by a nitrogen oxide analyser, and the O\textsubscript{3} production amount was analysed by an O\textsubscript{3} analyser.

The exhaust components of small displacement engines are related to the engine type and operating status. Generally, the concentration of oxygen is approximately 2–11\%, the concentration of NO\textsubscript{x} is approximately 100–500 ppm, and the ratio of hydrocarbons (HCs) to NO\textsubscript{x} is approximately 0–2. According to these values and the existing conditions in the laboratory, in our study, we adopted the following values: oxygen concentration range of 2–10\%, NO\textsubscript{x} concentration range of 100–500 ppm, and by using CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{2} to simulate HCs, a C\textsubscript{2}H\textsubscript{2} and NO\textsubscript{x} concentration ratio of 0–2.
2.1.2. Dielectric barrier discharge reactor

Diagrams of the DBD reactor are shown in Figs. 1 and 2. The reactor was made of quartz glass, and the corresponding wall thicknesses was 1.5 mm, while the inner diameters of the dielectric tubes were 16 mm. The tube length was 550 mm. The high-voltage electrodes consisted of a threaded copper bar, which had a diameter of 10 mm. In our research, the outside of the reactor was wrapped with aluminium foil to serve as the ground electrode and the length of the aluminium foil was adjustable; a copper wire was used for fixing the grounding. The two ends of the dielectric tube were sealed with a tetrafluoro joint and connected to a three-way valve to control the entry and exit of the reaction gas.

2.1.3. Power supply technical parameters

The power supply had the following characteristics: AC SINGLE-PHASE 220 V 10%, 501 Hz; rated output power of 600 VA. The pulse polarity was positive and negative bipolar, and the power supply output pulse peak voltages were as follows: positive pulse +5 kV to +50 kV, continuously adjustable; negative pulse -5 kV to -50 kV, continuously adjustable. The pulse repetition frequency was continuously adjustable from 0 to 200 Hz, with a pulse width ≤500 NS and pulse rise front ≤200 NS.

2.2. Experimental procedure and test methods

2.2.1. Experimental procedure

The experimental procedure consisted of the following steps.

(1) Connect the experimental instruments according to the flow chart of the experimental system shown in Fig. 3 and then, check the instruments to ensure that they are working properly. Set the mass flow measurement range according to the gas atmosphere required for the experiment.

(2) Open the valve to let in nitrogen and check whether the air tightness in the air passage is good.

(3) Preheat the nitrogen oxide analyser for 1 h, and preheat the mass flow meter for 0.5 h; adjust the mass flow meter to the experimental value as required. Record the initial nitrogen oxide concentrations after digital stabilization with the nitrogen oxide analyser.
(4) Turn on the power supply and the digital oscilloscope, set up the discharge parameters, adjust the voltage to the required value to carry out the discharge experiment, and record the concentration of the nitrogen oxide, instantaneous voltage, and current of the oscilloscope after the discharge is stable.

(5) After completing a set of tests, adjust the mass flow meter to change the volume and concentration of gas, and ventilate the gas in the air path. Repeat the above steps to start a new test after the air path becomes stable.

2.2.2. Experimental test methods

(1) Measurement of the discharge power

In the experiment, the discharge power was measured by the instantaneous power method with the discharge instantaneous voltage; the instantaneous current and voltage were recorded by an oscilloscope, and the effective energy $e$ was obtained by using Origin software:

$$E = \int_{T_0}^{T} u(t) g(t) dt$$  \hspace{1cm} (1)

$P = E / T$  \hspace{1cm} (2)

where $E$ is the pulse effective energy (J), $T_0$ is the starting time of the pulse front at the beginning of the pulse injection, $T$ is the effective time of the pulse, and $P$ is the effective power.

(2) Calculation of the nitrogen oxide removal rate

The formula for calculating the NO conversion rate is shown in equation (3):

$$\eta_1(\%) = \frac{C_{NO} - C_{NO}'}{C_{NO}} \times 100\%$$  \hspace{1cm} (3)

The formula for calculating the NO$_x$ removal rate is shown in equation (4):

$$\eta_2(\%) = \frac{C_{NOx} - C_{NOx}'}{C_{NOx}} \times 100\%$$  \hspace{1cm} (4)

The formula for calculating the NO$_2$ production quantity is shown in equation (5):

$$\Delta_{NO_2} = C_{NO_2}' - C_{NO_2}$$  \hspace{1cm} (5)

In these formulas, $\eta_1$ (%) is the NO conversion, $\eta_2$ (%) is the NO$_x$ removal rate, $\Delta_{NO_2}$ is the NO$_2$ production, $C_{NO}$ is the initial concentration of NO, $C_{NOx}$ is the concentration of NO$_2$ after
the reaction, $C_{\text{NO}}$ is the concentration of NO after the reaction, and $C_{\text{NO}_2}$ is the concentration of NO$_2$ after the reaction.

3. Results and discussion

3.1. Effect of electrical parameters on the NO$_x$ removal rate

3.1.1. Effect of voltage on NO$_x$ removal

The effects of voltage on NO conversion, NO$_x$ removal, and NO$_2$ production are presented in Figs. 4 and 5. The NO conversion rate and NO$_x$ removal rate increased with increasing voltage. After the voltage reached $\pm$12 kV, the NO conversion rate and NO$_x$ removal rate tended to stabilize. When the highest NO conversion value of 41.35% was reached, the highest NO$_x$ removal was 23.09%, while the highest NO$_2$ production was 44 ppm. These findings indicate that increases in the voltage have a beneficial effect on NO conversion, but when the voltage reaches a certain level, any further increase can have a negative effect on NO conversion. Under aerobic conditions, the discharge causes O$_2$ to produce O$^-$, O$_2^-$, and O$_3^-$. These ions move slowly, which will make subsequent discharges more difficult and weaken the discharge current. When O atoms and O$_2$ are oxidized to O$_3$, the O$_3$ reacts with NO to produce NO$_2$, but as the reaction proceeds, the concentration of NO$_2$ increases and the NO$_2$ reacts with O atoms to produce NO, which will reduce the removal efficiency of NO. The specific reactions are as follows:

$$O + O_2 \rightarrow O_3 \quad (6)$$

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (7)$$

$$O + NO \rightarrow NO_2 \quad (8)$$

$$NO_2 + O \rightarrow NO + O_2 \quad (9)$$

With an increase in voltage, the concentration of NO$_2$ increases, which leads to a decrease in the number of active O atoms and a reduction in NO oxidation reactions; additionally, the increase in voltage wastes energy and reduces the removal of NO. Based on the energy efficiency and NO conversion rate, 12 kV was determined to be the optimum voltage.

3.1.2. Effect of pulse frequency on the NO$_x$ removal rate
At a 2% oxygen concentration, Fig. 6 shows the effect of the pulse frequency on the NO\textsubscript{x} removal rate. As can be seen from the diagram, the NO conversion rate and NO\textsubscript{x} removal rate both increased when the pulse frequency increased from 30 to 60 Hz, and the values reached a maximum of 42.85% and 23.24%, respectively, when the pulse frequency was increased from 60 Hz to 70 Hz; meanwhile, the NO conversion rate and NO\textsubscript{x} removal rate decreased to 36.12% and 22.27%, respectively, when the pulse frequency was increased from 60 Hz to 70 Hz. In Fig. 6, the trend of NO\textsubscript{2} was the same as that of the NO, and in Fig. 7 the highest production quantity of NO\textsubscript{2} was 49 ppm. With an increase in pulse frequency, and the times and energy of the energy injection, active substances increased, which enhanced the removal of NO and NO\textsubscript{x}. After an increase in pulse frequency, a portion of the energy was consumed in the form of electromagnetic waves. A pulse frequency of 60 Hz was deemed to be optimal based on our research results.

3.2. Effect of gas parameters on the NO\textsubscript{x} removal rate

3.2.1. Effect of gas flow

Fig. 8 shows the relationship between the gas flow rate and NO conversion rate and NO\textsubscript{x} removal rate. Gas flow affects the residence time of the gas in the reactor and directly affects the NO conversion rate and NO\textsubscript{x} removal rate. Here, it can be seen from the diagram that higher gas flows were associated with lower NO conversion. As the gas flow increased from 0.7 to 1.1 L/min, the NO conversion decreased greatly from 42.85% to 35.78%. Beyond a gas flow rate of 1.1 L/min, the reduction in the NO conversion rate decreased, and the NO\textsubscript{x} removal rate decreased when the gas flow was 1.3 L/min; specifically, the NO\textsubscript{x} removal rate was 15.9% when the gas flow rate was 1.3 L/min. Fig. 9 shows that the NO\textsubscript{2} production decreased with an increase in the gas flow rate, and the decrease was smaller after the gas flow rate reached 1.1 L/min, which was the same trend observed for the NO conversion. In order to achieve an optimal pollutant gas treatment capacity, higher energy efficiency, and NO conversion rate, 1.1 L/min was selected as the experimental gas flow.

3.2.2. Effect of oxygen concentrations

The exhaust from an automobile contains relatively high concentrations of oxygen (2–10%).
Figs. 10, 11, and 12 present the curves for the NO conversion, NO\textsubscript{x} removal, and NO\textsubscript{2} production under different oxygen concentrations.

It can be seen from the diagram that the conversion and removal rate of NO and NO\textsubscript{x} decreased with increases in the oxygen concentration, and the conversion rate of NO stabilized after the oxygen concentration reached 6%; at a 6% oxygen concentration, with NO\textsubscript{x} concentrations of 100, 200, and 400 ppm, the conversion rates of NO were 33.54%, 28.44%, and 27.11%, respectively. As the oxygen concentration increased, the NO\textsubscript{x} removal rate for the three initial NO\textsubscript{x} concentrations displayed closer values, and the maximum NO\textsubscript{x} removal quantity reached 79 ppm in a 2% oxygen atmosphere. As can be seen from Fig. 12, the amount of NO\textsubscript{2} produced increased with an increase in oxygen concentrations. NO\textsubscript{2} is not produced in the absence of oxygen. Under aerobic conditions, N radicals in various states behave differently, as shown in the reactions depicted in equations (10) and (11):

\[
e + N_2 \rightarrow e + N(^4S) + N(^4S) \quad (10)
\]
\[
e + N_2 \rightarrow e + N(^4S) + N(^2D) \quad (11)
\]
\[
N(^2D) + O_2 \rightarrow NO + O \quad (12)
\]
\[
N(^2D) + NO \rightarrow N_2 + O \quad (13)
\]
\[
N(^4S) + NO \rightarrow N_2 + O \quad (14)
\]
\[
N(^4S) + O_2 \rightarrow NO + O \quad (15)
\]

\(N(^4S)\) is the excited state N radical. Because \(N(^2D)\) has a higher energy, this can react with O\textsubscript{2} at very high chemical energies, as shown in formula (12). Additionally, \(N(^4S)\) barely interacts with O\textsubscript{2}, through the following reaction equation \(e + N_2 \rightarrow e + N(^4S) + N(^2D)\) . Because the concentration of oxygen is much higher than the concentration of NO, this contributes to improvements in the production quantity of NO in formula (12), and the quantity is much higher than that in reaction (9); furthermore, NO will be produced continuously, although NO will be reduced by \(N(^4S)\) and the NO will be oxidized to NO\textsubscript{2} by O, O\textsubscript{2}, and O\textsubscript{3}. However, as the concentration of oxygen increases gradually, reaction (12) produces too
much NO to effectively remove NO. At low NO\textsubscript{x} concentrations, a large proportion of NO is converted to NO\textsubscript{2}, and this process reaches a dynamic equilibrium. It can be seen from Fig. 12 that when the NO\textsubscript{x} concentration is 200 ppm, the amount of NO\textsubscript{2} generated will be significantly higher than 100 ppm.

During the process of discharge, some O\textsubscript{2} is oxidized to O\textsubscript{3} by the action of high energy electrons and active radicals, which contributes to the oxidation of NO, but the amount of O\textsubscript{3} is not very large. As shown in Fig. 13, the ozone produced by the discharge at a NO\textsubscript{x} concentration of 400 ppm increased with an increase in the concentration of oxygen, but the ozone production tended to stabilize when the concentration of oxygen was at 6%. According to the different oxygen concentrations, the discharge process for the removal of NO\textsubscript{x} can be divided into the following three stages: (1) NO decomposition in an anaerobic atmosphere, (2) NO conversion into N\textsubscript{2} and NO\textsubscript{2} by reduction and oxidation at lower oxygen concentrations (2–5%), and (3) NO conversion into NO\textsubscript{2} by oxidation at higher oxygen concentrations (≥5%). A portion of the NO\textsubscript{2} can also react with NO and convert into other forms of NO\textsubscript{x} under the action of the discharge, so the amount of NO conversion can be higher than the amount of NO\textsubscript{2} produced. In consideration of the high oxygen content in automotive exhaust, a 6% oxygen concentration was selected as the basic oxygen concentration for subsequent experiments.

### 3.2.3. Effect of the initial concentration of NO\textsubscript{x} on the NO\textsubscript{x} removal rate

Fig. 14 shows the relationship between the NO conversion and NO\textsubscript{x} removal rate at different initial NO\textsubscript{x} concentrations. As shown, both the NO conversion rate and NO\textsubscript{x} removal rate increased at first and then decreased with increases in the initial NO\textsubscript{x} concentration. Both of the rates reached maximum values at an initial NO\textsubscript{x} concentration of 200 ppm, for which the rates were 33.54% and 16.84%, respectively. The NO conversion varied greatly with the initial NO\textsubscript{x} concentrations in the range of 100–400 ppm, and the value decreased steadily after 400 ppm; meanwhile, the NO removal rate varied greatly in the range of 100–500 ppm and decreased steadily after 500 ppm. We discussed the reason for this effect in Section 3.2.2.

Fig. 15 shows that the quantity of NO\textsubscript{2} generated increased with an increase in the initial concentration of NO\textsubscript{x}. The maximum NO\textsubscript{x} concentration was 61 ppm when the initial NO\textsubscript{x} concentration was 600 ppm. However, with an increase in the initial NO\textsubscript{x} concentration, there
was an abundance of NO and NO\textsubscript{2} in the oxygen-enriched gas system. A higher initial concentration of NO\textsubscript{x} led to a higher concentration of NO\textsubscript{2}, which made it difficult to oxidize NO\textsubscript{1}, so the growth rate of NO\textsubscript{2} production decreased gradually. Because the concentration of NO\textsubscript{x} in the tail gas ranged between 100 and 500 ppm, in combination with the experimental results for the NO conversion rate and NO\textsubscript{x} removal rate, 400 ppm was used as the initial concentration of NO\textsubscript{x} in subsequent testing.

3.2.4. Effect of HC reducing gas on NO\textsubscript{x} removal

Due to the large amount of HC gas in automotive exhaust, reductions in NO\textsubscript{x} driven by HC gas require further study.

3.2.4.1. Experimental study on NO\textsubscript{x} removal in the NO/O\textsubscript{2}/CH\textsubscript{4}/N\textsubscript{2} system

Figs. 16 and 17 show the influence of different additions of CH\textsubscript{4} on the NO conversion rate, NO\textsubscript{x} removal rate, and NO\textsubscript{2} production. It can be seen from Fig. 16 that the NO conversion rate increased with the increase in the amount of CH\textsubscript{4} added. When the concentration ratio reached 2, the NO conversion rate reached a maximum of 50.52%, which was 23% higher than that without the addition of CH\textsubscript{4}. The removal rate of NO\textsubscript{x} first increased and then decreased with the increase in the CH\textsubscript{4} addition. It reached a maximum of 16.4% when the concentration ratio was 1.5, which represents an increase of 6% compared with that without CH\textsubscript{4} addition.

Fig. 17 shows the influence of different CH\textsubscript{4} additions on NO\textsubscript{2} production. It can be seen from the figure that the production of NO\textsubscript{2} increased with the increase in the proportion of CH\textsubscript{4} and the initial concentration of NO\textsubscript{x}. When the concentration ratio reached 2, the NO\textsubscript{2} production reached a maximum of 85 ppm. As can be seen from the two figures, oxidation reactions mainly took place inside the reactor and involved the oxidization of NO to NO\textsubscript{2}, without a large number of reduction reactions. The main reason for this was that the electron energy required for the activation of CH\textsubscript{4} is greater than 10 eV, and it is difficult to activate CH\textsubscript{4} at room temperature (25°C) and atmospheric pressure or under the action of no catalyst. However, CH\textsubscript{4} can react with high-energy electrons and O atoms to generate various free radicals.
\[ CH_4 + e \rightarrow CH_2 + H_2 + e \]
\[ \rightarrow CH + H_2 + H + e \] (16)

\[ CH_4 + O \rightarrow OH + CH_3 \] (17)

\[ CH_4 + O(1D) \rightarrow CH_3OH \] (18)

CH₄ reacts with these radicals and O₂ to generate HO₂, which is a strong oxidizing radical.

HO₂ is the most important free radical for the oxidation of NO, and it oxidizes NO into NO₂.

As shown in formula (16), CH and CH₂ generated by the reaction can react with NO. Of course, O₃ oxidation of NO and other reactions that remove NO also occur.

3.2.4.2. Experimental study on NOx removal in the NO/O₂/N₂/C₂H₂ gas system

Fig. 18 shows the influence of C₂H₂ addition on the NO conversion rate and NOₓ removal rate. It can be seen from the experimental results that the NO conversion rate increased with an increase in the ratio between the concentration of C₂H₂ and the initial concentration of NOₓ.

When the ratio reached 1.5, the NO conversion rate reached the maximum value of 64.56%, which was 14% higher than that of the reduced gas with the same proportion of CH₄. With an increase in the concentration ratio of the two, the removal rate of NOₓ first increased and then decreased. When the concentration ratio was 1.5, it reached a maximum of 22.57%. Compared with the addition of CH₄ at the same proportion, the removal rate of NOₓ increased by 6%.

After the addition of C₂H₂, the following reactions occurred in the reactor:

\[ e + C_2H_2 \rightarrow C + CH_2 + e \] (19)

\[ \rightarrow CH + CH + e \]

\[ C_2H_2 + O \rightarrow CH_2 + CO \] (20)

\[ C_2H_2 + O_2 \rightarrow C_2H + HO_2 \] (21)

\[ CH + NO \rightarrow NCO + H \] (22)

\[ CH_2 + NO \rightarrow HCN + OH \] (23)

\[ HO_2 + NO \rightarrow NO_2 + OH \] (24)

High-energy electrons transfer energy to C₂H₂, which then dissociates to produce many
active radicals, like those shown in formula (19); formula (20) shows the most important reaction that consumes C$_2$H$_2$, and CH and CH$_2$ generated by that reaction continue to react with NO through formulas (21) and (22). While the HO$_2$ generated by the addition of CH$_4$ as discussed in the previous section is still generated after adding C$_2$H$_2$, it reacts with NO to generate NO$_2$ and further removes NO.

Fig. 19 shows the influence of different C$_2$H$_2$ additions on NO$_2$ production. It can be seen from the figure that the production of NO$_2$ increased with the increase in the concentration ratio of C$_2$H$_2$ to NO$_x$, and the maximum production of NO$_2$ was 74 ppm. Since the main reactions after the addition of C$_2$H$_2$ are formulas (19) and (20), the production of HO$_2$ with a strong oxidation potential is less than that with CH$_4$, so the production of NO$_2$ is less than that with CH$_4$ gas.

3.3. Effect of reaction temperature on the NO$_x$ removal rate

When automotive exhaust is discharged, the tail gas terminal temperature in the exhaust pipe is 100°C to 300°C. Fig. 20 shows the effect of the reaction temperature on NO conversion and NO$_x$ removal. As can be seen from the diagram, the conversion of NO increased significantly with an increase in the reaction temperature. The conversion of NO increased from 64.56% at room temperature to 76.40% at 300°C. Additionally, it can be seen that the temperature had a great influence on the NO conversion rate; the NO$_x$ removal rate also increased with the increase in the reaction temperature, from 22.57% at room temperature to 31.2% at 300°C.

Fig. 21 shows the effect of the reaction temperature on NO$_2$ production. The diagram shows that the reaction temperature had a great effect on the amount of NO$_2$ produced. During the change from room temperature to 100°C, the amount of NO$_2$ produced increased greatly, and then, the amount of NO$_2$ produced increased at smaller increments with further increases in the reaction temperature. When the reaction temperature was 300°C, the maximum concentration of NO$_2$ produced was 92 ppm.

It can be seen from the experimental results that the effect of the reaction temperature on DBD denitrification was obvious. An increase in reaction temperature led to an increase in the folding field strength, which induced N$_2$ and O$_2$ to collide with more high energy electrons,
and more N, O, N\textsubscript{2} (a') reacted with NO. The increase in reaction temperature can also increase
the amount of active radicals, such as CH, CH\textsubscript{2}, and C\textsubscript{2}H, which can further improve the NO\textsubscript{x}
removal efficiency. As the temperature of the reaction increases, the rate of the reaction
\[O + O\textsubscript{2} \rightarrow O\textsubscript{3}\] increases, and the production of more O\textsubscript{3} causes more NO to be oxidized to NO\textsubscript{2}.

### 3.4. Effect of concomitant use of the La\textsubscript{0.7} Sr\textsubscript{0.3} Ni\textsubscript{0.5} Mn\textsubscript{0.2} Fe\textsubscript{0.3} O\textsubscript{3} catalyst on the NO\textsubscript{x} removal rate

Based on the optimum electrical parameters and gas flow rate of 1.1 L/min, an oxygen
concentration of 6\%, NO\textsubscript{x} concentration of 400 ppm, C\textsubscript{2}H\textsubscript{2} concentration of ~600 ppm, and
temperature 300°C were chosen to investigate the effect of the use of a La\textsubscript{0.7} Sr\textsubscript{0.3} Ni\textsubscript{0.5}
Mn\textsubscript{0.2} Fe\textsubscript{0.3} O\textsubscript{3} catalyst. Fig. 22 shows the results for different systems involving the La\textsubscript{0.7}
Sr\textsubscript{0.3} Ni\textsubscript{0.5} Mn\textsubscript{0.2} Fe\textsubscript{0.3} O\textsubscript{3} catalyst in regard to the effect on NO conversion and NO\textsubscript{x} removal.
It can be seen that when the reaction temperature was 300°C, DBD synergy existed with the
La\textsubscript{0.7} Sr\textsubscript{0.3} Ni\textsubscript{0.5} Mn\textsubscript{0.2} Fe\textsubscript{0.3} O\textsubscript{3} catalyst and the efficiency was significantly higher than that
for the single use of catalyst. The NO conversion rate and NO\textsubscript{x} removal rate reached 94.93\%
and 74.97\%, respectively, which were far higher values than those obtained at room
temperature (32.56\% and 30.38\%) and at 300°C (35.81\% and 34.84\%) without discharge. As
can be seen from Fig. 22, the NO conversion and NO\textsubscript{x} removal efficiency were much higher
with the DBD in conjunction with the La\textsubscript{0.7} Sr\textsubscript{0.3} Ni\textsubscript{0.5} Mn\textsubscript{0.2} Fe\textsubscript{0.3} O\textsubscript{3} catalyst than without
the catalyst. In the previous sections, we analysed C\textsubscript{2}H\textsubscript{2} in terms of reaction ionization into
various strongly oxidizing free radicals and hydroxyl groups (CH, OH\textsubscript{2}, -OH) via formulas (19)
to (24). These strongly oxidizing free radicals and hydroxyl groups oxidize NO into higher-
order nitrogen oxides such as NO\textsubscript{2}, thus improving the conversion rate of NO. Meanwhile,
C\textsubscript{2}H\textsubscript{2} or other organic intermediate products can also be used as reducing agents. Under the
catalytic action of catalysts, redox reactions with NO\textsubscript{x} will take place that further improve the
removal rate of NO\textsubscript{x}.

### 4. Conclusion

In this study, we developed a self-made wire-cylinder dielectric barrier discharge (DBD)
reactor and used it to remove NO\textsubscript{x}. The main findings are as follows.

(1) The optimal voltage was ±12 kV, and the frequency was 60 Hz. The optimal gas flow rate was 1.1 L/min, the optimal oxygen concentration was 6\%, and the optimal initial concentration of NO\textsubscript{x} was 400 ppm.

(2) The NO conversion rate and NO\textsubscript{x} removal rate were improved by the addition of a HC reducing gas. In the system of N\textsubscript{2}/NO/O\textsubscript{2}/CH\textsubscript{4}, the NO conversion rate and NO\textsubscript{x} removal rate increased by 23\% and 6\%, respectively, compared with the condition in which reducing gas CH\textsubscript{4} was not added. In the system of N\textsubscript{2}/NO/O\textsubscript{2}/C\textsubscript{2}H\textsubscript{2}, after the addition of reducing gas C\textsubscript{2}H\textsubscript{2}, the NO conversion rate and NO\textsubscript{x} removal rate were further increased by 14\% and 6\%, respectively.

(3) In the system of N\textsubscript{2}/NO/O\textsubscript{2}/C\textsubscript{2}H\textsubscript{2}, the removal rate of NO\textsubscript{x} was improved by the increase in the reaction temperature. At 300\,^\circ\text{C}, the NO conversion and NO\textsubscript{x} removal rates reached a maximum of 76.4\% and 31.2\%, respectively.

(4) Further improvements were achieved with the concomitant use of the La0.7 Sr0.3 Ni0.5 Mn0.2 Fe0.3 O\textsubscript{3} catalyst in the system, whereby the NO conversion rate and NO\textsubscript{x} removal rate reached 94.93\% and 74.97\%, respectively. The synergistic effect of the catalyst was obvious.

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Declaration of competing interests

The authors declare no competing interests.

Authors Contributions

Dong Bingyan: Conceptualization, Methodology, Funding acquisition, Supervision
Zou Ying: Validation, Formal analysis, Writing - Original Draft, Writing - Review & Editing
Zhang Ping: Investigation, Resources
Luo Ting: Data Curation, Visualization
Li Zhendong: Project administration
Consent to Participate
The authors hereby assure that this study did not involve any human trials.

Consent to Publish
All the authors agreed to publish the study and did not object to their data being published in the journal. Before submitting a paper to a journal, we have ensured that all authors agree to publish their data.

Availability of data and materials
All data generated or analysed during this study are included in this published article [and its supplementary information files].

Ethical Approval
All writers hereby guarantee that this article has no ethical implications.

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Fig. 1. Schematic diagram of the dielectric barrier discharge reactor.

Fig. 2. Photograph of the quartz glass used in the dielectric barrier discharge reactor.
Fig. 3. Schematic diagram of the experimental system. 1. Gas cylinders, 2. mass flow controller, 3. valves, 4. dielectric barrier discharge reactors, 5. tube furnaces, 6. high voltage probe, 7. current probe, 8. high voltage positive–negative double pulse power supply, 9. oscilloscope, 10. infrared flue gas analyser, and 11. NO\textsubscript{x} analyser and O\textsubscript{3} analyser.
Fig. 4. Effect of voltage on the NO and NO\textsubscript{x} conversion and removal rate.

Fig. 5. Effect of voltage on NO\textsubscript{2} production.
Fig. 6. Effect of pulse frequency on the NO and NO\(_x\) conversion and removal rate.

Fig. 7. Effect of pulse frequency on NO\(_2\) production.
Fig. 8. Effect of gas flow on the NO\textsubscript{x} removal rate.

Fig. 9. Effect of the gas flow rate on the NO\textsubscript{2} production quantity.
Fig. 10. Effect of oxygen concentrations on the NO conversion rate.

Fig. 11. Effect of different oxygen concentrations on the NO\textsubscript{x} removal rate.
Fig. 12. Effect of different oxygen concentrations on NO$_2$ production.

Fig. 13. NO$_x$ ozone production at 400 ppm.
Fig. 14 Effect of different initial NOx concentrations on the NO and NOx conversion and removal rate.

Fig. 15. Effect of different initial NOx concentrations on the NO2 production quantity.
Fig. 16. Effect of CH₄ addition on the NO conversion rate and NOₓ removal rate.

Fig. 17. Influence of CH₄ addition on NO₂ production.
Fig. 18. Effect of C$_2$H$_2$ addition on the NO conversion rate and NO$_x$ removal rate.

Fig. 19. Effect of C$_2$H$_2$ additions on NO$_2$ production.
Fig. 20. Effect of the reaction temperature on NO conversion and NO\textsubscript{x} removal.

Fig. 21. Effect of the reaction temperature on NO\textsubscript{2} production.
Fig. 22. Effect of different systems on the NO conversion rate and NO\textsubscript{x} removal rate.
Figures

Figure 1

Schematic diagram of the dielectric barrier discharge reactor.

Figure 2

Photograph of the quartz glass used in the dielectric barrier discharge reactor.
Figure 3

Schematic diagram of the experimental system. 1. Gas cylinders, 2. mass flow controller, 3. valves, 4. dielectric barrier discharge reactors, 5. tube furnaces, 6. high voltage probe, 7. current probe, 8. high voltage positive–negative double pulse power supply, 9. oscilloscope, 10. infrared flue gas analyser, and 11. NOx analyser and O3 analyser.
Figure 4

Effect of voltage on the NO and NOx conversion and removal rate.

NO/2%O₂/N₂

\( f = 55 \text{Hz} \)

\( Q = 0.7 \text{L/min} \)

\( C_{\text{NOx}} \approx 400 \text{ppm} \)
Figure 5

Effect of voltage on NO2 production.

NO/2%O₂/N₂
f = 55Hz
Q = 0.7L/min
C \(_{(NOx)}\) ≈ 400ppm
Figure 6

Effect of pulse frequency on the NO and NOx conversion and removal rate.
Figure 7

Effect of pulse frequency on NO2 production.
Figure 8

Effect of gas flow on the NOx removal rate.
Figure 9

Effect of the gas flow rate on the NO2 production quantity.
Figure 10

Effect of oxygen concentrations on the NO conversion rate.
Figure 11

Effect of different oxygen concentrations on the NOx removal rate.
Figure 12

Effect of different oxygen concentrations on NO2 production
Figure 13

NOx ozone production at 400 ppm.
Figure 14

Effect of different initial NOx concentrations on the NO and NOx conversion and removal rate.

N₂/NO/O₂  Q = 1.1 L/min
U = ± 12 kV  f = 60 Hz
O₂ = 6%
Figure 15

Effect of different initial NOx concentrations on the NO2 production quantity.
Figure 16

Effect of CH4 addition on the NO conversion rate and NOx removal rate.

- $N_2/O_2/NO/CH_4$
- $U = \pm 12$ kV
- $f = 60$ Hz
- $O_2 = 6\%$
- $NO_x = 400$ ppm
- $Q = 1.1$ L/min
Figure 17

Influence of CH4 addition on NO2 production.
Figure 18

Effect of C2H2 addition on the NO conversion rate and NOx removal rate.
Figure 19

Effect of C2H2 additions on NO2 production.

NO/O2/C2H2/N2
U =±12kV
f =60Hz
O2 =6%
Q =1.1L/min
NOx =400ppm
Figure 20

Effect of the reaction temperature on NO conversion and NOx removal.
Figure 21

Effect of the reaction temperature on NO2 production.

\[ \text{NO/\text{N}_2/\text{O}_2/\text{C}_2\text{H}_2} \]

\[ \text{NO}_x = 400 \text{ppm} \]

\[ Q = 1.1 \text{L/min} \quad \text{O}_2 = 6\% \]

\[ U = \pm 12 \text{kV} \quad f = 60 \text{Hz} \]
Figure 22

Effect of different systems on the NO conversion rate and NOx removal rate.

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