Role of Oxygen in the Plasma Catalytic Removal of NOx

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Abstract
Combined system of non-thermal plasma and catalytic process was investigated. The plasma reactor oxidizes NO to NO₂. The plasma reactor alone can not reduce the NOx (NO+NO₂) level effectively, but the increase in the ratio of NO₂ to NO as a result of plasma discharge can lead to enhancing NOx removal efficiency even at lower temperatures over the catalyst surface. In the present work, the effect of oxygen content during the plasma catalytic reduction of NOx is studied. Two different catalysts were used in the experiments such as V₂O₅/TiO₂ and Cr₂O₃/TiO₂. The effect of flow rate on the plasma catalysis was also studied.

Keywords: Plasma Reactor, Plasma Catalytic Removal, Plasma Catalysis, Pulse Corona Reactors.

1. Introduction
Pulse corona reactors, which have been demonstrated to be effective in treating NOx from thermal power plants, convert NO into NO₂ and eventually into HNO₃. This HNO₃ is later neutralized into useful agricultural products. But the same approach cannot be applicable to the other exhaust sources such as engine exhausts and small-scale industrial sources. The desired approach in such cases would be to reduce NOx into N₂ and O₂. In this context, non-thermal plasma technique combined with selective catalytic reduction assumes importance as this technique can reduce NOx into molecular oxygen and nitrogen. The two main steps in this process are (a) non-thermal plasma converting NO into NO₂ and (b) selective catalytic reduction of NO and NO₂ in presence of ammonia [1-3].
In the area of selective catalytic reduction of NOx, the performance of SCR is elevated by the increase in the ratio of NO₂ to NO [4]. This result indicates that catalytic removal of NOx at relatively low temperature is possible when a part of NO is converted to NO₂. Since, the content of NO in total NOx is usually around 95% in practical exhaust, the performance was always limited and required high temperatures for the efficient operation. One easy and inexpensive method to increase the portion of NO₂ in NOx may be non-thermal plasma technology as its capability to oxidize NO to NO₂ has been proved elsewhere. Researchers have shown the possibility of enhanced NOx removal by combining non-thermal plasma with SCR [5-8].
In the present work, the effect of oxygen content during the plasma catalytic reduction of NOx has been studied. Two different catalysts were used in the experiments such as V₂O₅/TiO₂ and Cr₂O₃/TiO₂. The effect of flow rate on the plasma catalysis was also studied.

2. Experimental Setup

2.1. Description of the Experimental Setup

The schematic of the reactor system composed of non-thermal plasma reactor and catalytic reactor is presented in Figure 1. The coaxial plasma reactor makes use of dielectric barrier discharge operated with AC high voltage. A glass tube (inner diameter: 25.8 mm; outer diameter: 30.2 mm) was utilized as the dielectric material and a 1/8” stainless steel rod was used as the discharging electrode to which AC high voltage was applied. The space between the glass tube and the discharging electrode was filled with glass beads of 5 mm in diameter. The effective length of the plasma reactor where discharge takes place is 31 cm. A 1.0 μF capacitor was connected to the plasma reactor in series to measure the discharge power.

Two honeycomb catalysts were used in the present studies such as V₂O₅/TiO₂ (20 cells per square inch) and Cr₂O₃/TiO₂ (cells per square inch). The content of vanadium in the catalyst was 5.0 wt. %, and the apparent volume of the honeycomb was 31 cm³ (1.8×1.8×9.7 cm³), which was used for the calculation of space velocity defined as the ratio of feed gas flow rate to reactor volume.

All the experiments were carried out at a gas temperature of 150 °C. For this, the reactor was kept in an oven to maintain the desired gas temperature. To ensure proper heating-up of the feed gas to a given temperature, the stainless steel tube connected to the reactor inlet was wound several times within the oven, which acted as a heat exchanger. The main components of the feed gas stream were nitrogen and oxygen whose flow rates were adjusted by mass flow controllers (MFC) (Model 1179A, MKS Instruments, Inc.). The flow rates of NO (5.0 % v/v balanced with N₂), NO₂ (2.0 % v/v balanced with N₂) and ethylene (pure) were also controlled by mass flow controllers, and they were mixed with N₂ and O₂. In most of the experiments, the flow rate of the feed gas stream was 5 L/min (at room temperature). But some experiments were carried out by changing the gas flow rate. The NOx concentration was fixed at 300 ppm. The concentrations of NO and NO₂ were analyzed by a chemiluminescence NO-NO₂-NOₓ analyzer (Model 42C, Thermo Environmental Instruments, Inc.).

The reactor was energized by AC voltage at 60 Hz. The voltage was varied from 4 to 14 kV to change the discharge power. The voltage applied to the discharging electrode was measured by a 1000:1 high voltage probe (PVM-4, North Star Research, Corp.) and a digital oscilloscope (TDS 3032, Tektronix). For the measurement of the voltage between both ends of the 1.0 μF capacitor, a 10:1 voltage probe (Tektronix P6139A) was used. The measurement of input power was carried out using a digital power meter (Model WT 200, Yokogawa).
2.2. Discharge Power Measurement

The method adopted to measure the discharge power in the present experiments is as follows. A 1.0 μF capacitor was connected in series with the reactor as shown in the Figure 1. Since the dielectric barrier discharge reactor can be considered as a capacitor, the charge stored in the capacitor (1.0 μF) is equal to that in the reactor. The charge stored in the capacitor (Q) is the product of capacitance and voltage (CV, C: capacitance; V: voltage), which can be directly read by the voltage between both ends of the capacitor. In other words, the charge stored in the capacitor is equal to \(10^{-6}\) times the voltage.

Figure 1 Reactor system composed of non-thermal plasma reactor and catalytic reactor (schematic)

![Reactor system](image)

Figure 2 (a) shows the voltage waveforms measured at the discharging electrode and at the 1.0 μF capacitor, and Figure 2 (b) shows the charge-voltage plot at the corresponding voltage. The area of the parallelogram in Figure 2(b) conforms to the discharge energy per one cycle, and the average discharge power can be obtained by multiplying the discharge energy per one cycle by AC frequency (i.e. 60 Hz). For example, in Figure 2 (b), the discharge energy per cycle at 12 kV was found to be 7.33 mJ/cycle. Hence the average discharge power is 7.33 \(\times 10^{-3}\) J/cycle \(\times 60\) Hz = 0.44 W. For convenience, in the present case the area of parallelogram was calculated by comparing the total mass of the graph with that of the parallelogram. It was assumed that the thickness of the paper was uniform throughout. We compared both methods of calculating the area of the parallelogram and the results were found to agree well within 5 %.
3. Results and Discussion

Initial experiments were carried out using the plasma reactor by varying the oxygen content in the gas mixture. Figure 3 shows variation of NO concentration as a function of energy density at different oxygen contents. When the gas mixture contained no oxygen, the NO removal was very less. The NO removal in the absence of oxygen takes place as
NO + N → N₂ + O \hspace{1cm} (1)

The presence of ethylene cannot help in the conversion of NO, as ethylene needs the presence of oxygen radicals to be dissociated into active radicals. When the oxygen content was increased to 5%, 10% and 20%, the NO conversion was more than 95%. The NO conversion in the gas mixtures with oxygen content more than 5% takes place as

NO + O → NO₂ \hspace{1cm} (2)

The presence of ethylene in the gas mixture greatly helps the oxidation of NO to NO₂.

**Figure 3** Variation of NO concentrations as a function of energy density at different oxygen contents

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Figure 4 shows the NOx removal efficiencies obtained by plasma catalytic reduction at different oxygen contents when V₂O₅/TiO₂ catalyst is used. Energy density zero corresponds to the catalytic activity. In the absence of oxygen, the catalytic activity is less with NOx removal efficiency being 20%. With increase in oxygen content, the catalyst could remove more NOx. When the plasma is applied, the NOx removal efficiencies tend to increase in all cases. However, in the absence of oxygen, the NOx removal efficiencies were lesser as plasma is unable to oxidize NO₂. For the efficient selective catalytic reduction of NOx, the gas mixture should contain equimolar concentrations of NO and NO₂. With increase in the oxygen content, higher NOx removal efficiencies were obtained. The NOx removal efficiency obtained was more than 85% when oxygen content was 20%. The next figure (Figure 5) shows the effect of gas flow rate on the plasma catalysis. It can be found that the removal efficiencies were not affected by the gas flow rate. With the gas flow rate of 2.5 L/min, the catalyst showed better activity and the activity decreased with
increase in the flow rate. However, the plasma catalysis was not affected by the increase in the gas flow rate and NOx removal efficiencies of more than 80% were obtained in all the cases. This shows that still higher gas flow rates can be treated with this system.

**Figure 4** NOx removal efficiencies obtained by plasma catalytic reduction at different oxygen contents when V2O5/TiO2 catalyst

![Figure 4](image)

**Figure 5** Effect of gas flow rate on the plasma catalysis

![Figure 5](image)

Figure 6 shows the NOx removal efficiencies obtained when Cr2O3/TiO2 catalyst was employed in the plasma catalytic reactor. The trends were similar to those obtained with V2O5/TiO2, but the removal efficiencies were much lesser. This shows
that not all the catalysts can be suitable for the purpose of employing them in plasma catalysis. This catalyst simply converted back the NO\textsubscript{2} back into NO while removing only less amount of NO\textsubscript{x}. It can be seen clearly from the Figure 7 where NO, NO\textsubscript{2} and NO\textsubscript{x} concentrations are shown. The plasma reactor converts most of the NO into NO\textsubscript{2}, but when NO\textsubscript{2} enters the catalyst it is reduced back to NO as seen from high NO concentrations in the Figure 7.

**Figure 6** NO\textsubscript{x} removal efficiencies obtained when Cr\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2} catalyst was employed in the plasma catalytic reactor

![Figure 6](image)

**Figure 7** NO, NO\textsubscript{2} and NO\textsubscript{x} concentrations

![Figure 7](image)
Figure 8 shows the differences in the performances of the two catalysts used in the present study. Cr₂O₃/TiO₂ catalyst may not be a suitable candidate for plasma catalysis.

**Figure 8** Differences in the performances of the two used catalysts

![Graph showing NOx removal efficiency vs. Energy density](image)

4. Conclusion

Effect of oxygen content in the gas stream was investigated and it was found that higher contents of oxygen helps in oxidizing NO to NO₂ in order that there is equimolar concentrations of NO and NO₂ for the catalyst to reduce. The present technique could treat more volumes of gases consisting of the pollutants. It is also concluded that not all kinds of SCR catalysts are useful for plasma catalytic reduction of NOx.

References