Effect of NO/NO$_2$ Concentration Ratio on Nitrogen Oxides Removal in the Plasma Assisted Catalytic Process

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Abstract

When nitrogen oxides are mixed with air, the ratio of NO to NO\textsubscript{2} is changed as energy density in the dielectric barrier discharge process. And the change of NO/NO\textsubscript{2} ratio in the plasma process could affect the removal rate of NO\textsubscript{x} in the catalytic process. In the experiments, we have investigated that the effect of NO/NO\textsubscript{2} ratio on removal efficiency in the catalytic process with changing the ratio of NO to NO\textsubscript{2}, and the experimental results were compared with those obtained from plasma assisted catalytic process. The temperatures of catalyst were varied in the range from 100 to 300 \textdegree C. Gas flow rate was 10 \textit{l/min} and the initial concentration of NO\textsubscript{x} was approximately 500 ppm. The ratios of NO to NO\textsubscript{2} were varied from 3.4:1 to 1:4. The optimum NO/NO\textsubscript{2} ratio for the highest efficiency was 2:3, and the removal efficiency of NO\textsubscript{x} was 34.6 \% in the catalytic process. This removal trend is similar to that obtained in the plasma assisted catalytic process. In the plasma assisted catalytic process, the optimum energy density for the highest NO\textsubscript{x} removal was 67 J/\textit{l} at the temperature of 100 \textdegree C. At the energy density, the ratio of NO to NO\textsubscript{2} was approximately 2:3 in the plasma process. The removal rate was 52 \% in the hybrid process. The removal trend at 200 \textdegree C is also similar to that obtained in the plasma assisted catalytic process. In the plasma catalytic hybrid process, the optimum energy density for the highest NO\textsubscript{x} removal was 50 J/\textit{l}, and the ratio of NO to NO\textsubscript{2} in the plasma reactor was approximately 1:1 at the energy density. The removal rate was approximately 80 \% in the plasma assisted catalytic process.
## Background of Study

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<th>Conventional NOx Emissions Control Technologies</th>
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<td>Lowering combustion temperatures</td>
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<td>Careful air/fuel control during combustion</td>
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<tr>
<td>Reducing the nitrogen content of fuels</td>
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<td>Injection of water or steam</td>
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<th>Advanced NOx Emission Control Technologies</th>
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<tr>
<td>NOx Catalysts</td>
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<tr>
<td>Selective Catalytic Reduction</td>
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<tr>
<td>Plasma Technology</td>
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<td>Hybrid Systems (Plasma + Catalyst)</td>
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</table>

**Cold Start Emissions**
- NOx, HCs, VOCs

**Excess emissions**
- first 5 ~ 15 minutes or 5 ~ 15 km, after the vehicle starts.

## Combined Systems for Reducing NOx

**Plasma process**
- NO $\rightarrow$ NO\textsubscript{2}

**Catalytic process**
- NO\textsubscript{2} $\rightarrow$ N\textsubscript{2}, O\textsubscript{2}

**NOx** $\rightarrow$ **N\textsubscript{2}, O\textsubscript{2}**
Plasma reactions

\[ \text{e} + \text{O}_2 \rightarrow \text{e} + \text{O}(^3\text{P}) + \text{O}(^1\text{P}, \, ^1\text{D}) \] (1)

\[ \text{e} + \text{N}_2 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O} \] (2)

\[ \text{O}(^3\text{P}) + \text{NO} + \text{M} \rightarrow \text{NO}_2 + \text{M} \] (3)

\[ \text{O}(^3\text{P}) + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \] (4)

\[ \text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2 \] (5)

\[ \text{N}(^2\text{D}) + \text{O}_2 \rightarrow \text{NO} + \text{O} \] (6)

\[ 4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \] (7)

NH$_3$ SCR reactions

At a high temperature over 300 °C

At a low temperature below 200 °C

\[ 6\text{NO}_2 + 8\text{NH}_3 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O} \] (8)

\[ 2\text{NO}_2 + 2\text{NH}_3 \rightarrow \text{N}_2 + \text{H}_2\text{O} + \text{NH}_4\text{NO}_3 \] (9)

\[ \text{NO} + \text{NO}_2 + 2\text{NH}_3 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O} \] (10)

The Experimental Setup for Plasma Catalytic Hybrid System
The Principle of Dielectric Barrier Discharge

- Electron multiplication
- Space charge formation
- Ionization
- Dissociation & excitation
- Chemical reactions

The advantages
- DBD can be operated stably at ambient conditions by mature technique of commercial ozone generator.
- It can be readily applied for abating the emission of gaseous air pollutants.
- The dielectrics acts as a stabilizing material leading to the formation of a large number of micro-discharge.

DBD Reactor

- Applied Voltage: 0~20 kV (AC, 60 Hz)
- Current: 0 ~ 5 mA
- Dielectric material: pylex glass
  - I.D: 44mm
  - Thickness: 3 mm
- Discharge electrode: sus 304
  - Diameter: 40 mm
  - Length: 500 mm

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Diagram of DBD Reactor:

- Gas outlet
- Discharge electrode
- Copper film tape
- Pyrex tube
- Teflon cap
- Gas inlet
The Conversion Characteristics of NOx in DBD Reactor

- **Initial conc.** NO: 400 ppm, NO₂: 56 ppm
- **Flow rate:** 10 LPM
- **Temperature:** R.T
- **Mixing gas:** Air

**Graph:**
- Concentration (ppm) vs. Energy density (J/L)
- NO
- NO₂
- NOx

Chemical species detected:
- NO
- NO₂
- NOx
- N₂O
- CH₄
- CO₂
- NO
- HNO₃

Reaction:

\[ \text{N}_2 + \text{O}_2 + \text{NO} \quad (\sim 220 \text{ ppm}) \quad \text{at 13 kV} \]
The Removal of NOx in the Catalytic process

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Before catalyst</th>
<th>After catalyst</th>
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<tbody>
<tr>
<td></td>
<td>NO (ppm)</td>
<td>NO2 (ppm)</td>
</tr>
<tr>
<td>100 °C</td>
<td>396</td>
<td>77</td>
</tr>
<tr>
<td>200 °C</td>
<td>400</td>
<td>66</td>
</tr>
<tr>
<td>300 °C</td>
<td>398</td>
<td>63</td>
</tr>
</tbody>
</table>

The Effect of Temperature and SED on NOx Conversion in the Plasma Catalytic Hybrid Process

- Initial NOx concentration: 470 ppm
- Flow rate: 10 LPM
- Temperature: 100 ~ 300 °C
- NH3: 240 ppm
- Mixing gas: Air
The Conversion of NOx in the Catalytic Process

Control of NO/NO2

V2O5-WO3/TiO2 Catalyst

Removal efficiency (%)

The ratio of NO to NO2

The ratio of NO to NO2

Removal efficiency (%)

Energy density (J/L)

Removal efficiency (%)

Energy density (J/L)
1. In the dielectric barrier discharge reactor, NO was converted to NO₂ with a high efficiency.
2. In NH₃-SCR process, NOx removal was affected by the ratio of NO to NO₂.
3. We investigated the synergetic effect of the plasma catalytic hybrid process in reducing NOx.
4. We observed that the ratio of NO to NO₂ affected the NOx removal rate in the plasma catalytic hybrid process.
5. The optimum energy density and the ratio of NO to NO₂ for the maximum NO removal were existed in the plasma catalytic hybrid system.