Simultaneous Reduction of CH\textsubscript{4} and NO\textsubscript{x} of NGOC/LNT Catalysts for CNG buses

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CNG 버스용 NGOC/LNT 촉매의 CH\textsubscript{4}와 NO\textsubscript{x}의 동시 저감

Abstract: Natural gas is a clean fuel that discharges almost no air-contaminating substances. This study examined the simultaneous reduction of CH\textsubscript{4} and NO\textsubscript{x} of NGOC/LNT catalysts for CNG buses related to the improvement of the de-CH\textsubscript{4}/NO\textsubscript{x} performance, focusing mainly on identifying the additive catalysts, loading of the washcoat, stirring time, and types of substrates. The 3wt. % Ni-loaded NGOC generally exhibited superior CH\textsubscript{4} reduction performance through CH\textsubscript{4} conversion, because Ni is an alkaline, toxic oxide, and exerts a reducing effect on CH\textsubscript{4}. A excessively small loading resulted in insufficient adsorption capacity of harmful gases, whereas too high loading of washcoat caused clogging of the substrate cells. In addition, with the economic feasibility of catalysts considered, the appropriate amount of catalyst washcoat loading was estimated to be 124g/L. The NO\textsubscript{x} conversion rate of the NGOC/LNT catalysts stirred from 200°C to 550°C for 5 hours showed 10-15% better performance than the NGOC/LNT catalysts mixed for 2 hours over the entire temperature range. The NGOC/LNT catalysts exhibited approximately 20% higher de-CH\textsubscript{4} performance on the ceramic substrates than on the metal substrates.

Keywords: Catalyst, CH\textsubscript{4}, Compressed Natural Gas, Metal, NO\textsubscript{x}, Palladium
Accordingly, regulation on emission gases are becoming stricter [1-2]. Natural gas is a clean fuel that discharges almost no air-contaminating substance. It is mainly used as the primary fuel source for the compressed natural gas (CNG) bus. The application of natural gas, with its many advantages as a fuel, is anticipated to spread more widely, because of the rich deposits of shale gas available at present, the development of innovative drilling technology, and its stable price [3]. At present, city buses are legally required to use CNG fuel, the primary content of which is CH\textsubscript{4}. The currently commercialized after-treatment system for CH\textsubscript{4} and NOx reduction for CNG buses is implemented based on a theoretical air-fuel ratio and uses a three-way catalyst. Recently, this system has been operated under a lean air-fuel ratio condition, with a separately mounted oxidation catalyst and de-NOx catalyst [4-9]. However, operation under a theoretical air-fuel ratio adversely affects fuel-efficiency and increases CO\textsubscript{2} emission. Further the after-treatment system of lean air-fuel ratio type has increased installation cost and difficulty because of the size of the catalyst unit. From a long-term perspective, this study targets development of a natural gas oxidation catalyst (NGOC)/lean NOx trap (LNT) + NGOC/selective catalytic reduction (SCR) combined unit for a simple “one-canning two-brick system” that can simultaneously reduce emission of both CH\textsubscript{4} and NOx for CNG buses. Such reduction is in accordance with the post Euro 6 emission regulation, which are challenging to comply with and render this study more meaningful. This study primarily focuses on identifying the additive catalysts, loading amount of washcoat and stirring time and types of substrates, related with improvement of de-CH\textsubscript{4}/NOx performance.

2. Experimental

2.1 Catalyst preparation and characterization

NGOC/LNT

Catalysts were prepared through the conventional impregnation method. After maintaining the room temperature of a beaker at 80°C, a supporter comprised of 50% zeolite (Z) and 50% γ-Al\textsubscript{2}O\textsubscript{3} (Al), Table 1 was added to 500cc of distilled water in accordance with the required content and stirred. We also inserted additive catalysts including MgO and CeO\textsubscript{2} at certain contents and stirred the resultant mixture for 2 h. Then, precious metals, i.e., Pt, Pd and Rh, were mixed for 2 h at the required contents and in the order listed. After washing with distilled water twice, the resultant slurry was placed in a drying machine at a temperature of 80°C and dehydrated for 12 h. After milling, the catalyst powder was placed in 50 cc distilled water and 7 or 8 thin coatings were applied onto ceramic substrate, with the mixer temperature maintained at 60°C. Then, coating of 80 g/L (400 cells per square inch (CPSI)) was applied. Following reduction of the coated catalysts for 30 min, at 500°C, with H\textsubscript{2} 10%/N\textsubscript{2} bal., the specimens were calcinated in air for 2 h to manufacture NGOC/LNT catalysts. The Brunauer – Emmett – Teller (BET) method was used to measure the specific surface areas, pore volumes and pore size distributions of the catalyst samples (ASAP Q2 2020, Micromeritics). Prior to these measurements, all samples were degassed at 1×10\textsuperscript{-4} Torr. The adsorption isotherms were obtained after degassing the pre-adsorbed hydrogen at 300°C at 1×10\textsuperscript{-6} Torr for 0.5 h.

2.2 Experimental apparatus and method

Catalytic tests of the prepared NGOC/LNT were performed using the monolithic type in a model gas reaction system [10] was composed of a gas-supply component, a catalyst reaction component, a CO/H\textsubscript{2} injection component, an analyzer, and a control device. The total flow rate of the model gas was 2 L/min. The water content was adjusted to 1.5% by the saturated water vapor pressure. The gas composition after the catalytic reaction was measured at intervals of 1 s using a gas analyzer (VarioPlus Industrial, MRU...
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Instruments, Inc.). To evaluate the performance, we tested the de-CH₄/NOₓ performance of the NGOC/LNT catalysts under normal conditions from 100 to 600°C. The CH₄ conversion was calculated from the relation.

\[
\text{CH}_4 \text{ conversion} = \frac{[(\text{CH}_4)_{\text{in}} - (\text{CH}_4)_{\text{out}}]}{\text{CH}_4_{\text{in}}} \times 100\% \quad \cdots (1)
\]

In Eq. (1), \((\text{CH}_4)_{\text{in}}\) and \((\text{CH}_4)_{\text{out}}\) are CH₄ concentrations at the catalyst inlet and outlet, respectively. Experimental conditions of additive catalysts and loading amount were performed under lean conditions with NGOC catalyst.

![Fig. 1. After-treatment system for reducing both the CH₄ and NOₓ](image)

Table 1. Model gas conditions for evaluating NGOC/LNT catalyst performance

<table>
<thead>
<tr>
<th>Gas components</th>
<th>Lean condition</th>
<th>Rich condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_4) (ppm)</td>
<td>500</td>
<td>0</td>
</tr>
<tr>
<td>NO (ppm)</td>
<td>500</td>
<td>0</td>
</tr>
<tr>
<td>CO (ppm)</td>
<td>700</td>
<td>30,000</td>
</tr>
<tr>
<td>(\text{O}_2) (%)</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>(\text{H}_2\text{O}) (%)</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>(\text{N}_2)</td>
<td>Balance</td>
<td>Balance</td>
</tr>
<tr>
<td>SV (h⁻¹)</td>
<td>28,000</td>
<td>28,000</td>
</tr>
</tbody>
</table>

Table 2. Experimental conditions for evaluating de-CH₄/NOₓ

<table>
<thead>
<tr>
<th>Items</th>
<th>Conditions</th>
<th>Composition</th>
<th>Catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Additive catalysts</td>
<td>Lean</td>
<td>1Pt-3Pd-1Rh-5MgO/90(Al50:Z50)</td>
<td>NGOC</td>
</tr>
<tr>
<td>Loading amount</td>
<td>Lean</td>
<td>1Pt-3Pd-1Rh-5MgO/3CeO₂/8(Al50:Z50)</td>
<td>NGOC</td>
</tr>
<tr>
<td>Stirring time</td>
<td>Lean/Rich</td>
<td>1Pt-3Pd-1Rh-5MgO/3Ni-6CeO₂-5Cr-15Ba/63(Al50:Z50)</td>
<td>NGOC/LNT</td>
</tr>
<tr>
<td>Substrate</td>
<td>Lean/Rich</td>
<td>1Pt-3Pd-1Rh-5MgO/3Ni-6CeO₂-5Cr-15Ba/63(Al50:Z50)</td>
<td>NGOC/LNT</td>
</tr>
</tbody>
</table>

Table 3. Specification of several NGOC catalysts according to additive catalysts

<table>
<thead>
<tr>
<th>No</th>
<th>Composition(wt%)</th>
<th>BET surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Mean pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1Pt-3Pd-1Rh/95(Al50:Z50)</td>
<td>400.006</td>
<td>0.498</td>
<td>4.981</td>
</tr>
<tr>
<td>2</td>
<td>1Pt-3Pd-1Rh-5MgO/90(Al50:Z50)</td>
<td>407.232</td>
<td>0.53</td>
<td>5.211</td>
</tr>
<tr>
<td>3</td>
<td>1Pt-3Pd-1Rh-5CeO₂/90(Al50:Z50)</td>
<td>376.642</td>
<td>0.513</td>
<td>5.42</td>
</tr>
<tr>
<td>4</td>
<td>1Pt-3Pd-1Rh-5Cr/90(Al50:Z50)</td>
<td>401.192</td>
<td>0.521</td>
<td>5.2</td>
</tr>
<tr>
<td>5</td>
<td>1Pt-3Pd-1Rh-5MnO₂/90(Al50:Z50)</td>
<td>416.03</td>
<td>0.577</td>
<td>5.519</td>
</tr>
<tr>
<td>6</td>
<td>1Pt-3Pd-1Rh-5La/90(Al50:Z50)</td>
<td>391.841</td>
<td>0.52</td>
<td>5.32</td>
</tr>
<tr>
<td>7</td>
<td>1Pt-3Pd-1Rh-5MoO₃/90(Al50:Z50)</td>
<td>341.329</td>
<td>0.496</td>
<td>5.782</td>
</tr>
<tr>
<td>8</td>
<td>1Pt-3Pd-1Rh-5La/90(Al50:Z50)</td>
<td>399.107</td>
<td>0.519</td>
<td>5.176</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1 The effect of additive catalysts of NGOC catalyst

The catalysts are divided into the main catalyst, additive catalyst (promoter) and supporter, and the performance depends on the additive catalysts loaded in the NGOC. Therefore, to improve the harmful gas reduction performance of the NGOC catalysts, an experiment was conducted in which seven types of additive catalysts (MgO, CeO₂, Cr, Ni, Mn, MoO₃ and La) were loaded with 5wt% content.

Fig. 2 shows a TEM image including a single promoter substance of NGOC catalysts as well as the 7 types of NGOC catalysts with additive catalysts loaded. Fig. 2(a) shows Pd catalysts selective for CH₄ reduction; the rest of additive catalysts are divided into metal and metalloid (La). Fig. 2(b) shows a TEM image including 7 types of metals (Pt, Pd and Rh),

The test condition of NGOC/LNT catalysts on stirring time and substrates types were performed under lean/rich condition. Fig. 1 shows an after-treatment system to be developed for reducing both CH₄ and NOₓ. Table 1-3 show the experimental conditions and catalysis compositions.
transition metals and of metalloid, 5wt% each, were loaded onto the basic supporter, alumina and zeolites; the supporter helped the metals dispersed in good conditions.

Fig. 3 shows the performance of de-CH\textsubscript{4}/NO\textsubscript{x} based on promoter catalyst substances. In this figure, the CH\textsubscript{4} reduction performance is highest for the NGOC loaded with 5Ni, at 65\%, when the catalyst temperature reached 500\°C after the same NGOC had oxidized CH\textsubscript{4} at 350\°C. NO conversion rate tends to indicate higher values for the NGOC loaded with 1. STD, 4. 5Cr, 5. 5Ni, at a moderate temperature between 350\°C and 500\°C. In Table 3, the BET specific surface areas indicate better conditions for the NGOC catalysts loaded with 5Cr and 5Ni, at 401.192 and 416.03 m\textsuperscript{2}/g, respectively, compared with the standard (STD) catalyst of 1Pt-3Pd-1Rh/95(Al\textsubscript{50}:Z\textsubscript{50})(400.006m\textsuperscript{2}/g); the pore volumes were also improved to 0.521 and 0.577cm\textsuperscript{3}/g, respectively, over 0.498cm\textsuperscript{3}/g for the STD catalyst. These conditions promote growth of micropores on the catalyst surface and active sites, improving the catalytic performance. Optimization of the Ni and Cr transition metal contents, with improved low-temperature activation, may be necessary for improved CH\textsubscript{4} reduction performance, as CH\textsubscript{4} has a more tightly bound structure than NO\textsubscript{x} with a lower activation energy.

The Cr [11-16] and Ni [17-19] transition metals are useful for catalyst activation. Cr is a highly acidic substance with a body-centered cubic crystal structure, 1.66 electro-negativity and 652.9 kJ/mol primarily ionization energy. The melting point is 1,890\°C and the atomic mass is 51.996 g/mol, with one peripheral electron participating in chemical reactions. Cr loading is frequently used for polymerization of ethylene, alkene hydrogeneration reactions, and oxidization-reduction reaction between NO and CO particles. This transition metal, which has a strong energy bond with the nearest oxygen, helps stabilize metal oxides. Further, the Ni transition metal is a low-alkaline oxide with a face-centered cubic crystal structure. Its atomic mass is 58.693 g/mol and it has 1.91 electro-negativity, with 737.19 kJ/mol primary ionization energy and two peripheral electrons. Ni plays a critical role in catalyst synthesis. The 5 wt\% Ni loaded NGOC exhibited superior CH\textsubscript{4} reduction performance; thus, the Ni transition metal is more selective than Cr. This may possibly be explained by the fact that Ni is an alkaline, toxic oxide and is, there easily activated when mixed with chemically stabilized CH\textsubscript{4}. 

**Fig. 2.** SEM/TEM image of additive catalysts

**Fig. 3.** The effect of additive catalysts
Simultaneous Reduction of CH$_4$ and NOx of NGOC/LNT Catalysts for CNG buses

Fig. 4. The effect of Cr and Ni additive catalysts

Fig. 4 shows that, in Fig. 3, the Ni and Cr loaded NGOC catalysts exhibited relatively higher performance in purifying harmful gas, so we manufactured a NGOC loaded with Ni and Cr, each of 3 and 5wt% content to design a NGOC/LNT catalyst structure. In Fig. 4 (a), for CH$_4$ conversion rate, the 3Ni loaded NGOC catalyst generally showed a better performance in CH$_4$ reduction, starting to oxidize at 350°C to 400°C. At a temperature of 500°C, the 5Ni loaded NGOC exhibited a better performance for reducing CH$_4$; transition metal Ni was more selective than Cr. This may possibly be explained by the fact that Ni is an alkaline, toxic oxide so easily activated when mixed with CH$_4$, chemically stabilized. Although there may be a slight error in experimental results due to the catalyst preparation and experimental evaluation, in Fig.4(b), in terms of NO conversion rate, the NGOC catalyst loaded with 5Cr and 3Cr showed, overall, a better catalyst activation at mid and low temperatures than the two types of NGOC loaded with Ni. In reducing NO at a low temperature, the appropriate amount is 5Cr. As mentioned above, this is because Cr is a strong acid oxide so readily reacts to stabilized metal oxides as well as oxidization and reduction of between NO and CO particles. In manufacturing NGOC/LNT, to improve CH$_4$ and NOx reducing effect, it is estimated that an appropriate loading amount of transition metals, Ni and Cr, can help reduce harmful gas.

3.2 The effect of washcoat loading amount and stirring time

The washcoat loading amount coated onto automobile catalysts plays an important role in catalyst design and should be determined appropriately, with the impact of harmful gas and the cost of catalysts taken into consideration. In particular, the NGOC/LNT catalysts on the front play important roles in development of a combined NGOC/LNT+NGOC/SCR system, so we determined a proper washcoat loading amount, by considering the conversion rate of harmful gas based on 3 types of washcoat loading amounts.

Fig. 5. De-CH$_4$/NOx performance according to loading amount
Fig. 5 shows de-CH\textsubscript{4}/NOx performance based on washcoat loading amounts. The 80g/L NGOC catalyst with the lowest loading amount showed the lowest CH\textsubscript{4} oxidation ability, which started to oxidize at 375°C to reach 550°C and LOT 50. However, the 170g/L NGOC catalyst with the greatest catalyst loading amount started to oxidize at 375°C to indicate a conversion rate of 80% at 600°C. The NGOC catalyst loaded with an appropriate amount of 124g/L washcoat began to oxidize at 375°C and showed the highest de-CH\textsubscript{4} removing performance as the temperature reached 50 0°C and LOT50. In Fig. 5(b), the NO conversion rate was indicated the highest for the NGOC catalyst with the lowest washcoat loading amount of 80g/L for the entire temperature range. For the de-NOx conversion rate, 170g/L led to the highest value, followed by 124g/L. To small amount of loading results in insufficient adsorption capacity of harmful gas while too much loading of caused the substrate cells to be clogged. In addition, with the economic feasibility of catalysts considered, an appropriate amount of catalyst washcoat loading is estimated to be 124g/L.

Fig. 6 shows the de-CH\textsubscript{4}/NOx performance for mixing hours of 2 and 5, during the NGOC and LNT is coupled. At a catalyst temperature of 200°C, any CH\textsubscript{4} stabilized instructure is not oxidized. NGOC/LNT catalysts compounded by mixing time of 2 and 5 hours started to reduce CH\textsubscript{4} at 350°C, by 10% or less. When the catalyst temperature reached 550°C, the two types of NGOC/LNT catalysts showed a cleaning effect of 37%, with almost no gaps in CH\textsubscript{4} reducing performance. In reducing CH\textsubscript{4}, the main catalyst of Pd plays the key role and the precious metal dispersion of Pd was estimated not improved over the mixing time. In Fig. 6(b), when it comes to NOx conversion rate, NGOC/LNT catalysts stirred from 200°C to 550°C for 5 hours showed a better performance than NGOC/LNT catalysts mixed for 2 hours, by 10-15% at the entire temperature range. This is estimated to be the result of chemical reactions between catalysts and promoters which eventually increased active sites of catalysts along the boundary of different substances. Particularly, the increase of NOx absorption by BaO (barium oxide) and faster reaction of catalysts to oxidization and reduction may have improved the performance of NGOC/LNT catalysts mixed for 5 hours.

![Graph](image.png)

Fig. 6. De-CH\textsubscript{4}/NOx performance according to stirring time

![Graph](image.png)

Fig. 7. Behavior of CH\textsubscript{4} and NOx at 350°C
Fig. 7 shows the behavior of harmful gas at 350°C against the effect of two types of NGOC/LNT catalysts. There is almost no difference between the two types of NGOC/LNT catalysts in terms of behaviors of CH₄ and NOₓ gas, except that the 5-hour stirred catalyst has a lower density. This is because the long, 5-hour mixing increased active sites of BaO and, accordingly, the amount of NOₓ absorbed. As a result, we could not observe improvement of CH₄ reduction performance in the 5-hour mix NGOC/LNT catalysts but increase of active sites of NOₓ absorbents.

3.3 The effect of substrates type of NGOC/LNT catalysts

Above, to improve the ability for simultaneous reduction of harmful CH₄ and NOₓ gases emitted from CNG buses, we deduced the appropriate composition of NGOC/LNT catalyst, by observing the effects for different precious metals and additive catalysts. Next, to further improve the de-CH₄/NOₓ performance, we examined the effect of the substrate on this performance, by coating NGOC/LNT catalysts with equal loads (120g/L) on the ceramic and metal substrates, which are widely used for automobiles. Note that the metal substrate is known to have high thermal conductivity and good low-temperature activity [1].

Fig. 8 shows photographs of specimens with washcoat coatings on the different ceramic and metal substrates. The substrate on the left is a ceramic substrate (SiO₂-Al₂O₃-MgO, 50/35/14wt%) composed of 400 CPSI silica and alumina. The substrate on the right is a metal substrate (Fe-Cr-Ni, 51.24/23.87/17.49 wt%) compose of Fe-Cr-Ni, which was coated with catalyst materials of equal amounts. The metal substrate was wound around a steel use stainless (SUS) pipe with 20 mm diameter, as densely as possible. Fig. 9 shows the de-CH₄/NOₓ cleaning performance under “lean/rich” test conditions for the coated substrates. The NGOC/LNT catalysts on the ceramic substrate began to oxide CH₄ at 325°C, reaching 550°C and LOT 50; this corresponds to a de-CH₄ removal performance that is approximately 20% higher than that of the NGOC/LNT catalysts on the metal substrate. The conversion rates for the catalysts on the ceramic and metal substrates were moderate, at approximately 30%, and were attributed to two-type reaction (oxidization/reduction) by each catalyst. Overall, the NGOC/LNT catalysts on ceramic substrate exhibited superior performance to their metal counterparts. This is because the washcoats loaded on the metal substrates were highly concentrated on the side, in contrast to those deposited on the honeycomb shapes of the ceramic substrates; thus, their dispersion was irregular, as shown Fig. 8. This is despite the fact that the same amount of washcoating was allocated to each group of substrates. The metal is thought to have had higher thermal conductivity than the ceramic substrate. This would have caused problem with the washcoating, and consequently, deterioration of the catalytic performance due to the catalyst structure, despite the superior low-temperature activation performance of the metal substrate.
4. Conclusions

This study examined the effect of the additive catalysts, loading amount of washcoat and stirring time and types of substrates, related with improvement of de-CH₄/NOx performance of NGOC/LNT catalyst.

1) The best CH₄ conversion rate was generally exhibited by an NGOC catalyst loaded with 3wt% Ni. Ni is an alkaline, toxic oxide, easily activated when mixed with chemically stabilized CH₄.

2) To small amount of loading results in insufficient adsorption capacity of harmful gas while too much loading of washcoat caused the substrate cells to be clogged. The economic feasibility of catalysts considered, an appropriate amount of catalyst washcoat loading was estimated to be 124g/L.

3) NOx conversion of NGOC/LNT catalysts stirred for 5 hours showed a better performance than NGOC/LNT catalysts mixed for 2 hours, by 10-15% at the entire temperature range.

4) On ceramic substrates, corresponding to a de-CH₄ performance approximately 20% higher than that of the NGOC/LNT catalysts on metal substrates.

References


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Combustion Engineering, After-treatment engineering, Newable energy