Simultaneous Reduction of CH₄ and NOx of NGOC/LNT Catalysts for CNG buses

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CNG 버스용 NGOC/LNT 촉매의 CH₄와 NOx의 동시 저감
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Abstract Natural gas is a clean fuel that discharges almost no air-contaminating substances. This study examined the simultaneous reduction of CH₄ and NOx of NGOC/LNT catalysts for CNG buses related to the improvement of the de-CH₄/NOx 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 CH₄ reduction performance through CH₄ conversion, because Ni is an alkaline, toxic oxide, and exerts a reducing effect on CH₄. 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 NOx 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-CH₄ performance on the ceramic substrates than on the metal substrates.

요약 친연 가스는 공기 오염 문제를 거의 배출하지 않는 깨끗한 연료입니다. 이 연구의 목표는 CNG 버스용 NGOC/LNT (친연가스산화촉매/질소산화물흡착촉매)촉매의 메탄의 질소산화물 동시 저감에 관한 연구로 메탄의 질소산화물 저감 성능 개선과 관련하여 촉매, washcoat 담지량, 교반 시간 및 담체 종류에 대해 주로 조절을 두었다. 더구나, 니켈은 알칼리성의 독성산화물로 메탄에 영향을 미치는 효과가 있기 때문에, 3wt% 니켈 담긴 친연가스산화촉매는 일반적으로 메탄 전환율을 통해 우수한 메탄 감소 성능을 나타낸다. 담체에 담지량이 적으면 유해 가스의 흡착력이 충분히 없고 위치 코르가 너무 많이 담지되면 담체의 상이 막히게 되었다. 촉매의 경제적을 고려할 때 촉매에 담지되는 양은 124g/L가 적절하다. 물질이다. 5시간 동안 교반된 NGOC/LNT 촉매의 200에서 550도 까지 NOx 전환율은 2시간 동안 교반된 NGOC/LNT 촉매보다 전체 온도 범위에서 10-15% 우수한 성능을 보였다. 메탈 담체의 NGOC/LNT 촉매는 메탈 담체보다 약 20% 수준의 높은 메탄 저감 성능을 나타냈다.

Keywords : Catalyst, CH₄, Compressed Natural Gas, Metal, NOx, Palladium

1. Introduction

In recent years, the social problems caused by toxic gases from vehicles and internal combustion engines using fossil fuels, which affect both the environment and human health, have become more serious.

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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 CH₄. The currently commercialized after-treatment system for CH₄ 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 CO₂ 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 CH₄ 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-CH₄/NOX performance.

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-Al₂O₃ (Al), Table1 was added to 500cc of distilled water in accordance with the required content and stirred. We also inserted additive catalysts including MgO and CeO₂ 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 H₂ 10%/N₂ bal., the specimens were calcined air for 2h 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 1×10⁻⁴ Torr. The adsorption isotherms were obtained after degassing the pre-adsorbed hydrogen at 300°C at 1×10⁻⁶ Torr for 0.5h.

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/H₂ 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
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:

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

In Eq. (1), ([CH₄]ₜₐₚ and ([CH₄]ₜₒᵤₜ 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>CH₄(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>O₂(%)</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>H₂O(%)</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>N₂</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-5X/90 (Al₂O₃:ZrO₂)</td>
<td>NGOC</td>
</tr>
<tr>
<td>Loading amount</td>
<td>Lean</td>
<td>1Pt-3Pd-1Rh-3MgO-3CeO₂/90 (Al₂O₃:ZrO₂)</td>
<td>NGOC</td>
</tr>
<tr>
<td>Stirring time</td>
<td>Lean/Rich</td>
<td>1Pt-3Pd-1Rh-3MgO-3Ni-6CoO₃-5Cr-15BaO₃/63 (Al₂O₃:ZrO₂)</td>
<td>NGOC/LNT</td>
</tr>
<tr>
<td>Substrate</td>
<td>Lean/Rich</td>
<td>1Pt-3Pd-1Rh-3MgO-3Ni-6CoO₃-5Cr-15BaO₃/63 (Al₂O₃:ZrO₂)</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(Al₂O₃:ZrO₂)</td>
<td>460.006</td>
<td>0.498</td>
<td>4.981</td>
</tr>
<tr>
<td>2</td>
<td>1Pt-3Pd-1Rh-5MgO/90 (Al₂O₃:ZrO₂)</td>
<td>407.232</td>
<td>0.53</td>
<td>5.211</td>
</tr>
<tr>
<td>3</td>
<td>1Pt-3Pd-1Rh-3CeO₂/90 (Al₂O₃:ZrO₂)</td>
<td>376.642</td>
<td>0.513</td>
<td>5.42</td>
</tr>
<tr>
<td>4</td>
<td>1Pt-3Pd-1Rh-5Cr/90 (Al₂O₃:ZrO₂)</td>
<td>401.192</td>
<td>0.521</td>
<td>5.2</td>
</tr>
<tr>
<td>5</td>
<td>1Pt-3Pd-1Rh-3Ni/90(Al₂O₃:ZrO₂)</td>
<td>416.03</td>
<td>0.577</td>
<td>5.519</td>
</tr>
<tr>
<td>6</td>
<td>1Pt-3Pd-1Rh-5Mn/90 (Al₂O₃:ZrO₂)</td>
<td>391.841</td>
<td>0.52</td>
<td>5.32</td>
</tr>
<tr>
<td>7</td>
<td>1Pt-3Pd-1Rh-3MoO₃/90 (Al₂O₃:ZrO₂)</td>
<td>341.329</td>
<td>0.496</td>
<td>5.782</td>
</tr>
<tr>
<td>8</td>
<td>1Pt-3Pd-1Rh-5La/90 (Al₂O₃:ZrO₂)</td>
<td>399.107</td>
<td>0.519</td>
<td>5.176</td>
</tr>
</tbody>
</table>

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.

### 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),
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-CH₄/NOₓ based on promoter catalyst substances. In this figure, the CH₄ 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 CH₄ 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 50 0°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 m²/g, respectively, compared with the standard (STD) catalyst of 1Pt-3Pd-IrRh/95(Al50:Z50)(400.06m²/g); the pore volumes were also improved to 0.521 and 0.577cm³/g, respectively, over 0.498cm³/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 CH₄ reduction performance, as CH₄ has a more tightly bound structure than NOₓ 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 hydrogenation reactions, and oxidation-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 58.699 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 CH₄ 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 CH₄.

![SEM/TEM image of additive catalysts](image1)

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

![CH₄ conversion(%)](image2)

(a) CH₄ conversion(%)

![NO conversion(%)](image3)

(b) NO conversion(%)

**Fig. 3.** The effect of additive catalysts
Simultaneous Reduction of CH₄ and NOx of NGOC/LNT Catalysts for CNG buses

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. 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 CH₄ conversion rate, the 3Ni loaded NGOC catalyst generally showed a better performance in CH₄ 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 CH₄; 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 CH₄, 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,
Fig. 5 shows de-CH₄/NOx performance based on washcoat loading amounts. The 80g/L NGOC catalyst with the lowest loading amount showed the lowest CH₄ 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-CH₄ 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-CH₄/NOx performance for mixing hours of 2 and 5, during the NGOC and LNT is coupled. At a catalyst temperature of 200°C, any CH₄ stabilized instructure is not oxidized. NGOC/LNT catalysts compounded by mixing time of 2 and 5 hours started to reduce CH₄ 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 CH₄ reducing performance. In reducing CH₄, 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 oxidation and reduction may have improved the performance of NGOC/LNT catalysts mixed for 5 hours.

Fig. 6. de-CH₄/NOx performance according to stirring time

Fig. 7. Behavior of CH₄ 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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