Catalytic performance of Ag/Al₂O₃-C₂H₅OH-Cu/Al₂O₃ system for the removal of NOₓ from diesel engine exhaust

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Combination of Ag/Al₂O₃-C₂H₅OH-Cu/Al₂O₃ is a promising system for the removal of NOₓ from diesel engine exhaust.

Abstract

The selective catalytic reduction (SCR) of NOₓ by C₂H₅OH was studied in excess oxygen over Ag/Al₂O₃ catalysts with different Ag loadings at lab conditions. The 4% Ag/Al₂O₃ has the highest activity for the C₂H₅OH-SCR of NOₓ with a drawback of simultaneously producing CO and unburned THC in effluent gases. An oxidation catalyst 10% Cu/Al₂O₃ was directly placed after the Ag/Al₂O₃ to remove CO and unburned THC. Washcoated honeycomb catalysts were prepared based on the 4% Ag/Al₂O₃ and 10% Cu/Al₂O₃ powders and tested for the C₂H₅OH-SCR of NOₓ on a diesel engine at the practical operating conditions. Compared with the Ag/Al₂O₃ powder, the Ag/Al₂O₃ washcoated honeycomb catalyst (SCR catalyst) has a similar activity for NOₓ reduction by C₂H₅OH and the drawback of increasing the CO and unburned THC emissions. Using the SCR + Oxi composite catalyst with the optimization of C₂H₅OH addition, the diesel engine completely meets EURO III emission standards.

Keywords: Selective catalytic reduction; NOₓ; Ag/Al₂O₃; Cu/Al₂O₃; Honeycomb; Diesel engine exhaust

1. Introduction

Nitrogen oxides (NOₓ) in exhaust gases have caused serious air pollution in urban areas. In order to meet the increasingly stringent emission standards, the removal of NOₓ from diesel engine is always at the forefront of efforts for the environmental air pollution improvement. The selective catalytic reduction of NOₓ (SCR of NOₓ) is a potential method to remove NOₓ from oxygen rich exhausts. The SCR of NOₓ by ammonia or urea has become a fairly mature technology for stationary applications (Nakajima, 1991; Fritz and Pitchon, 1997). However, it is not suitable to apply this technology to mobile applications such as diesel trucks and some lean-burn gasoline cars for obvious reasons (ammonia slip, etc). A more attractive solution for this type of NOₓ reduction is to use hydrocarbon (HC-SCR) as reducing agent.

Up to now, multifarious catalysts such as zeolitic oxide, base oxide/metal and noble metal catalysts have been found to be effective for the HC-SCR of NOₓ in the presence of excess oxygen (Fritz and Pitchon, 1997; Traa et al., 1999; Burch et al., 2002). Among them, it is commonly accepted that the Ag/Al₂O₃ catalyst with 2% Ag loading is one of the most promising catalysts due to its high activity for the SCR of NOₓ by hydrocarbons and oxygenated hydrocarbons in the presence of excess oxygen (Miyadera, 1993; Bethke and Kung, 1997; Kung et al., 1997; Meunier et al., 1999; Kameoka et al., 2000; Shimizu et al., 2000; Eränen et al., 2003). However, it is reported that the reduction of NOₓ by hydrocarbons over Ag/Al₂O₃ is usually suppressed by H₂O and SO₂ (Miyadera and Yoshida, 1993). In our previous studies (Sumiya 2009).
we had found that the Ag/Al₂O₃ catalyst exhibits a high activity for the SCR of NOx with H₂O in the presence of H₂O and SO₂, but the best performance of Ag/Al₂O₃ is achieved with 4% Ag loading which is not in agreement with the reported results. Moreover, we noticed that a large amount of CO is produced during the SCR of NOx with C₃H₆ and C₂H₅OH over the Ag/Al₂O₃, and a substantial amount of unburned THC is also detected in the effluent gases besides the CO when using C₂H₅OH as a reductant. Eränen et al. (2003) also reported that there is a considerable production of CO during the SCR of NOx with octane over the Ag/Al₂O₃, and CO can be completely eliminated when they add a commercial noble metal oxidation catalyst directly after the Ag/Al₂O₃. However, Eränen et al. (2003) found at the same time that the NOx conversions dramatically decrease because of the addition of the oxidation catalyst, which indicates that noble metal catalyst is not suitable to set after Ag/Al₂O₃ for CO removal during the SCR of NOx.

In this paper, the Ag/Al₂O₃ powder catalysts with various Ag loadings were prepared and studied for the SCR of NOx by C₂H₅OH in excess oxygen. Furthermore, the Ag/Al₂O₃ washcoated honeycomb catalyst was prepared based on Ag/Al₂O₃ powder catalyst and tested for the removal of NOx from diesel engine exhaust using C₂H₅OH as a reducing agent on a diesel engine at the practical operating conditions. In addition, an attempt was made to remove CO and unburned THC by combining the Ag/Al₂O₃ with an oxidation catalyst 10% Cu/Al₂O₃ under both laboratory and practical operating conditions.

2. Materials and methods

2.1. Catalyst preparation

2.1.1. Preparation of Ag/Al₂O₃ and Cu/Al₂O₃ powders

Ag/Al₂O₃ with different loadings and 10 wt.% Cu/Al₂O₃ catalysts were prepared by an impregnation method as follows: Al₂O₃ powder was added into an appropriate amount of silver and copper nitrate aqueous solution, respectively. The samples were dried at 120 °C for 12 h and calcinated at 600 °C for 3 h in air.

2.1.2. Preparation of washcoated honeycomb catalysts

Washcoated honeycomb catalysts were prepared using the 4% Ag/Al₂O₃ and the 10% Cu/Al₂O₃ powders (denoted as SCR and Oxi catalyst, respectively). Mixing 100 g powder and 400 g water using a ball mill prepared washcoat slurries. Cordierite honeycombs with 400 cells per square inch (90 mm in diameter and 110 mm in length) were dipped into the washcoat slips and excess slurry was blown out with an air knife. The samples were then dried and calcinated at 600 °C for 3 h. The washcoat loading was 110 g L⁻¹ after calcination.

2.2. Catalyst characterization

BET surface area, pore volume and pore diameter were obtained from N₂ adsorption isotherms measured at 77 K using an ASAP 2000 instrument (Micromeritics Co., USA). The data of Ag/Al₂O₃ catalysts with different loadings are given in Table 1. Powder X-ray diffraction (XRD) measurements of catalysts were carried out on a Rigaku D/max-RB X-Ray Diffractometer (Japan) with a Cu Kα radiation and operated at 40 kV and 40 mA. The patterns were taken in the 2θ range of 20°–70° at a scan speed of 6° min⁻¹.

2.3. Catalyst characterization

2.3.1. Powder catalyst test

The activity tests for the SCR of NOx by C₂H₅OH over Ag/Al₂O₃ catalysts were performed with a fixed-bed quartz flow reactor (15 mm in diameter, 500 mm in length) by passing a mixture gas of NO/C₂H₅OH/O₂/H₂O/ N₂ = 800 ppm/1656 ppm/10 vol.%/10 vol.%/balance at a total flow rate of 4000 cm³ min⁻¹ [Catalyst: 1.2 g; W/F (W, weight of catalyst; F, total flow) = 0.018 g s⁻¹ cm⁻³; gas hourly space velocity (GHSV): 50,000 h⁻¹] within the temperature range of 200–600 °C. C₂H₅OH was supplied with a micro-pump into the gas steam and vaporized by a coiled heater at the inlet of the reactor. After reaching the steady state, the effluent gas was analyzed by (AVL Di Gas, 4000 light) for HC and CO concentration analysis and a chemiluminescence based NO/NO₂/NOx analyzer (42C-HL, Thermo Environmental Instrument Inc.) for NOx conversion analysis.

2.3.2. Washcoated honeycomb catalyst engine test

Diesel engine testing of the catalysts was conducted on the washcoated cordierite honeycombs. An apparatus diagram for the activity test of catalysts is shown in Fig. 1. The test engine was a Sofim 8140–43C diesel engine (Displacement 2.8 L, compression ratio 18.5:1, rated power/ Speed 76 kW/3600 rpm). A portion of the exhaust gas was extracted and passed through a particulate trap. The catalysts were exposed to the exhaust gas with C₂H₅OH injected into the exhaust in front of the catalyst. A temperature range from 220 to 550 °C was conducted. The tests were conducted under the following conditions: Engine speed 195 rpm, Torque 195 Nm (full load), THC/NOx = 6% (molar ratio). In addition, catalyst was tested for the EURO III European Stationary Cycle (EURO III EESC) at 13-mode test cycle (Fig. 2). The 2.4 L Ag/Al₂O₃ and 2.4 L Cu/Al₂O₃ washcoated honeycomb catalysts were used in the diesel engine testing. NOx, THC and CO conversions were measured with a gas analyzer (CEB-2, AVL).

3. Results and discussion

3.1. Powder catalysts tests

Fig. 3 shows the NOx conversions for the SCR of NOx by C₂H₅OH over Ag/Al₂O₃ catalysts with different Ag loadings at various temperatures. The NOx conversions significantly increased in the wide temperature range of 200–600 °C with increasing silver loading from 2% to 4%, and the curve of NOx conversion shifted towards lower temperatures. Further increase of the silver loading from 4% to 8% still enhanced the NOx conversion at low temperatures but decreased the NOx conversion at high temperatures. In addition, the highest NOx conversion (ca. 99%) was obtained at 4% Ag loading, and the average conversion of NOx was ca. 90% in the wide temperature range of 300–600 °C. The results above show that the 4% Ag/Al₂O₃ is the optimal catalyst in its series catalysts, and is very effective for the removal of NOx using C₂H₅OH as a reductant.

Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Pore volume (cc g⁻¹)</th>
<th>Pore diameter (Å)</th>
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<tr>
<td>2% Ag/Al₂O₃</td>
<td>239.8</td>
<td>0.7235</td>
<td>122.9</td>
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<tr>
<td>4% Ag/Al₂O₃</td>
<td>222.4</td>
<td>0.7107</td>
<td>124.9</td>
</tr>
<tr>
<td>6% Ag/Al₂O₃</td>
<td>211.8</td>
<td>0.6950</td>
<td>126.2</td>
</tr>
<tr>
<td>8% Ag/Al₂O₃</td>
<td>209.9</td>
<td>0.6493</td>
<td>130.3</td>
</tr>
</tbody>
</table>

C. Zhang et al. / Environmental Pollution 147 (2007) 415–421
BET results of the catalysts are shown in Table 1. The specific surface area of Ag/Al₂O₃ catalysts gradually decreased with increasing the Ag loading. XRD patterns of a series of Ag/Al₂O₃ catalysts are shown in Fig. 4. Only the Al₂O₃ phase was detected as the Ag loading increased from 2% to 6%, but the Ag₂O and Ag phases were observed with the 8% Ag loading due to the increase of Ag₂O and Ag particles sizes. On the other hand, the test data in Fig. 3 show that the optimum Ag loading is 4% for Ag/Al₂O₃ during the SCR of NOₓ. This implies that the activity of Ag/Al₂O₃ for the SCR of NOₓ is closely related to Ag loading, the specific surface area and the dispersion of active phases.

The results above show that the Ag/Al₂O₃ has a very high activity for the SCR of NOₓ by C₂H₅OH. However, as shown in Fig. 5B, a large amount of CO was produced during the SCR of NOₓ by C₂H₅OH over the 4% Ag/Al₂O₃. With the increase of the reaction temperature, CO concentration gradually increased and reached the maximum value 800 ppm at 350 °C. In addition, we noticed that there was a considerable amount of unburned THC in the effluent gases during the process. In order to eliminate the harmful CO and unburned THC, we added an oxidation catalyst 10% Cu/Al₂O₃ directly after the 4% Ag/Al₂O₃ to form a composite catalyst. As shown in Fig. 5, the composite catalyst exhibited a very similar activity for NOₓ reduction compared with the Ag/Al₂O₃ alone, just a slight decrease in the high temperature range. Furthermore, only a trace amount of CO was detected, and the concentrations of THC were also greatly reduced in effluent gases during the C₂H₅OH-SCR of NOₓ.

Fig. 1. Apparatus diagram for activity test of washcoated honeycomb catalysts.

Fig. 2. The 13 operating conditions of the EURO III ESC.

Fig. 3. NOx conversion for the SCR of NOx by C₂H₅OH over Ag/Al₂O₃ catalysts with different Ag loadings [2% (■), 4% (○), 6% (▲), 8% (▼)] at various temperatures. Reaction conditions: NO 800 ppm, C₂H₅OH 1565 ppm, O₂ 10%, H₂O 10%, N₂ balance, GHSV = 50,000 h⁻¹.
3.2. Honeycomb catalyst engine test

On the basis of the results at lab conditions, the Ag/Al₂O₃ washcoated honeycomb catalyst was prepared and investigated for the removal of NOₓ from diesel exhaust using C₂H₅OH as a reducing agent on a diesel engine at the practical operating condition.

In order to investigate the influence of THC/NOₓ ratio, the temperature and GHSV on NOₓ conversion, impact of the exhaust components should be eliminated. Therefore, the engine was operating in the same mode with 3450 rpm at full load in the following experiment. The THC/NOₓ ratio in effluent gas was changed by C₂H₅OH injection. The temperature at the inlet of the catalyst was adjusted by the heat exchanger, and GHSV was changed by the bypass valve (as shown in Fig. 1).

Fig. 6 shows the catalytic activity of diesel engine test of the Ag/Al₂O₃ washcoated honeycomb catalyst (SCR) with various THC/NOₓ ratios (2.3–6.2) and a fixed GHSV of 90,000 h⁻¹. The GHSV is defined as the ratio of the flow rate of the flue gas to the volume of the honeycomb catalyst. The experiment was carried out with a particulate filter, which can reduce the content of the particulate contained in effluent gases. It could be seen that the THC/NOₓ ratio has an important influence on the NOₓ (Fig. 6A) and CO (Fig. 6C) conversions, but no obvious influence on THC conversion (Fig. 6B). Fig. 6A shows that the NOₓ conversion was increased with the increase of the THC/NOₓ ratio. As shown in Fig. 6C, the CO conversions were negative in the whole temperature range, which means that CO was also produced during the process over the Ag/Al₂O₃ honeycomb catalyst. With the increase of the THC/NOₓ ratio, the production of CO was also greatly increased. In addition, although the THC (Fig. 6B) conversions were almost constant with increasing the THC/NOₓ ratio, the THC concentration was augmented in exhaust gases at most of operating conditions due to the increase of unburned THC, especially at the lower temperature range. On the basis of the results, the following investigation was performed at a fixed THC/NOₓ ratio of 3.4, which was mostly appropriate for the system above.

Fig. 7 shows the catalytic activity of the Ag/Al₂O₃ honeycomb catalyst (SCR catalyst) with different GHSVs (30,000, 50,000, 80,000 h⁻¹) at a fixed THC/NOₓ ratio of 3.4. As shown in Fig. 7A, the honeycomb catalyst showed a very high activity for the removal of NOₓ at the GHSV of 30,000 h⁻¹. The maximal conversion of NOₓ was up to 93%, and the average conversion of NOₓ was ca. 77% in the wide temperature range of 270–470 °C. Those results are similar to our results in the laboratory scale test, which indicates that Ag/Al₂O₃ has a realistic potential in reducing NOₓ under real diesel engine exhaust conditions. Increasing the GHSV from 30,000 to 50,000 and 80,000 h⁻¹, the catalytic activity for the removal of NOₓ was gradually decreased. The curve of NOₓ conversion was shifted towards higher temperatures, and the average conversion of
NOx was only ca. 52% in the wide temperature range of 290–
490 °C at the GHSV of 80,000 h⁻¹. Fig. 7B shows that THC
conversions have no obvious change with the increase of
GHSV. In addition, as shown in Fig. 7C, CO production was
also decreased with the increase of GHSV from 30,000 to
50,000 and 80,000 h⁻¹. According to the results above, it can
be seen that CO production is in direct proportion to the
NOx conversion, so we propose that CO is not mainly produced
from partial oxidation of HC, but from the SCR-C₂H₅OH of
NOx process.
3.3. EURO III ESC test of honeycomb catalysts

In order to make the original Sofim 8140-43 C EURO II diesel engine to meet EURO III standards, the catalytic system for the removal of NOx was tested and optimized at the 13-mode test cycle for heavy duty diesel engines.

Table 2 shows the EURO III ESC test results with different catalysts. It should be noted that the C2H5OH was not injected at idle speed. It could be seen that the NOx emission is much lower than the original engine one over the SCR catalyst, which meet the EURO III regulation. But the drawback was the great increase of the THC and CO emissions, which exceeded the EURO III limits. As a result, certain measures should be taken to reduce HC and CO simultaneously, such as using an oxidation catalyst with a low light-off temperature, or optimizing the strategy of the C2H5OH addition.

According to the results of powder catalyst tests (Fig. 5), the Cu/Al2O3 honeycomb catalyst (Oxi catalyst) was added directly after the SCR catalyst to reduce THC and CO. It can be seen from the Table 2 that the SCR + Oxi composite catalyst not only reduce NOx emission, but also make the CO much lower than the limits. The HC emission was also reduced from over twice as much as the limits to just a little higher. Therefore, the SCR + Oxi composite catalyst is more effective than a single SCR catalyst for meeting EURO III regulation. However, because the HC emission still does not meet EURO III standard, the addition of C2H5OH should be optimized.

As shown in Fig. 7A, the SCR catalyst showed a high activity for NOx reduction only in the middle range of temperatures such as 300–450 °C. At lower temperatures (<300 °C), the NOx conversion was lower, and the addition of C2H5OH would cause the great increase of the THC emission without obviously improving the NOx conversion. In this case, without adding C2H5OH, the THC emission would be greatly reduced although the NOx emission would be slightly increased. At higher temperatures (>450 °C), NOx conversion was also very low. In this case, the ambient temperature air could be introduced into the exhaust pipe to cool the temperature of exhaust gas to the temperature range of high NOx conversion, and then the NOx conversion would be increased.

As shown in Fig. 2, the exhaust temperatures were relatively low at modes 1, 3, 5, 7, 9 and 11, so C2H5OH was not added due to the low NOx conversion. On the other hand, adequate C2H5OH was added for NOx reduction at the high conversion temperature range of modes 2, 4, 6, 8, 12 and 13. In addition, the exhaust temperature was too high at mode 10, so the ambient temperature air was introduced along with the addition of C2H5OH. The strategy of the C2H5OH addition is shown in Fig. 8.

The EURO III ESC test results after optimization are shown in Fig. 9. It was shown that NOx and CO emissions are nearly the same as that before optimization, but HC emission is greatly reduced, making the engine meet EURO III standards.

4. Conclusions

The 4% Ag/Al2O3 has a high activity for the C2H5OH-SCR of NOx with the drawback of simultaneously producing CO and unburned THC in effluent gases. Compared with the Ag/Al2O3 powder, the Ag/Al2O3 washcoated honeycomb catalyst (SCR catalyst) has a similar activity for NOx reduction by C2H5OH and the drawback of increasing CO and unburned THC concentrations in effluent gases. Using the 10% Cu/Al2O3 washcoated honeycomb catalyst (Oxi catalyst) with

Table 2
EURO III ESC test results

<table>
<thead>
<tr>
<th>Emissions</th>
<th>CO (g kW⁻¹ h⁻¹)</th>
<th>THC (g kW⁻¹ h⁻¹)</th>
<th>NOx (g kW⁻¹ h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EURO III limits</td>
<td>2.1</td>
<td>0.66</td>
<td>5.0</td>
</tr>
<tr>
<td>Original engine</td>
<td>1.307</td>
<td>0.355</td>
<td>6.924</td>
</tr>
<tr>
<td>SCR</td>
<td>3.482</td>
<td>1.431</td>
<td>2.668</td>
</tr>
<tr>
<td>SCR + Oxi</td>
<td>0.098</td>
<td>0.709</td>
<td>3.654</td>
</tr>
</tbody>
</table>

THC/NOx = 3.4.

Fig. 9. Test results after optimization of C2H5OH addition.
the optimization of C2H5OH addition, the emissions of NOx, THC and CO can meet EURO III standards over the SCR + Oxi composite catalyst under the 13-mode test cycle.

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References


