

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

Changbin Zhang^a, Hong He^{a,*}, Shijin Shuai^b, Jianxin Wang^b

^a State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

^b State Key Laboratory of Automotive Safety and Energy, Tsinghua University, Beijing, China

Received 19 May 2006; accepted 24 May 2006

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

Abstract

The selective catalytic reduction (SCR) of NO_x 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 NO_x 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 NO_x 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 NO_x 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.

© 2006 Elsevier Ltd. All rights reserved.

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

1. Introduction

Nitrogen oxides (NO_x) in exhaust gases have caused serious air pollution in urban areas. In order to meet the increasingly stringent emission standards, the removal of NO_x from diesel engine is always at the forefront of efforts for the environmental air pollution improvement. The selective catalytic reduction of NO_x (SCR of NO_x) is a potential method to remove NO_x from oxygen rich exhausts. The SCR of NO_x 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 NO_x 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 NO_x 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 NO_x 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 NO_x by hydrocarbons over Ag/Al₂O₃ is usually suppressed by H₂O and SO₂ (Miyadera and Yoshida, 1993). In our previous studies (Sumiya

* Corresponding author. Tel.: +86 10 6284 9123; fax +86 10 6292 3563.

E-mail address: honghe@cees.ac.cn (H. He).

et al., 1998; He et al., 2004; Yu et al., 2004; Wu et al., 2005), we had found that the Ag/Al₂O₃ catalyst exhibits a high activity for the SCR of NO_x with C₂H₅OH 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 NO_x 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 NO_x 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 NO_x 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 NO_x.

In this paper, the Ag/Al₂O₃ powder catalysts with various Ag loadings were prepared and studied for the SCR of NO_x 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 NO_x 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 × 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 K α radiation and operated at 40 kV and 40 mA. The patterns were taken in the 2 θ range of 20–70° at a scan speed of 6° min⁻¹.

Table 1

BET surface area, pore volume and pore diameter of Ag/Al₂O₃ catalysts with different Ag loadings

Catalyst	BET surface area (m ² g ⁻¹)	Pore volume (cc g ⁻¹)	Pore diameter (Å)
2% Ag/Al ₂ O ₃	239.8	0.7235	122.9
4% Ag/Al ₂ O ₃	222.4	0.7107	124.9
6% Ag/Al ₂ O ₃	211.8	0.6950	126.2
8% Ag/Al ₂ O ₃	209.9	0.6493	130.3

2.3. Catalytic testing

2.3.1. Powder catalyst test

The activity tests for the SCR of NO_x 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/1565 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 stream 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/NO_x analyzer (42C-HL, Thermo Environmental Instrument Inc.) for NO_x 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/3600r/min). 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 3450 rpm, Torque 195 Nm (full load), THC/NO_x 2.3–6.2 (molar ratio). In addition, catalyst was tested for the EURO III European Stationary Cycle (EURO III ESC) 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. NO_x, 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 NO_x conversions for the SCR of NO_x by C₂H₅OH over Ag/Al₂O₃ catalysts with different Ag loadings at various temperatures. The NO_x conversions significantly increased in the wide temperature range of 200–600 °C with increasing silver loading from 2% to 4%, and the curve of NO_x conversion shifted towards lower temperatures. Further increase of the silver loading from 4% to 8% still enhanced the NO_x conversion at low temperatures but decreased the NO_x conversion at high temperatures. In addition, the highest NO_x conversion (ca. 99%) was obtained at 4% Ag loading, and the average conversion of NO_x 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 NO_x using C₂H₅OH as a reductant.

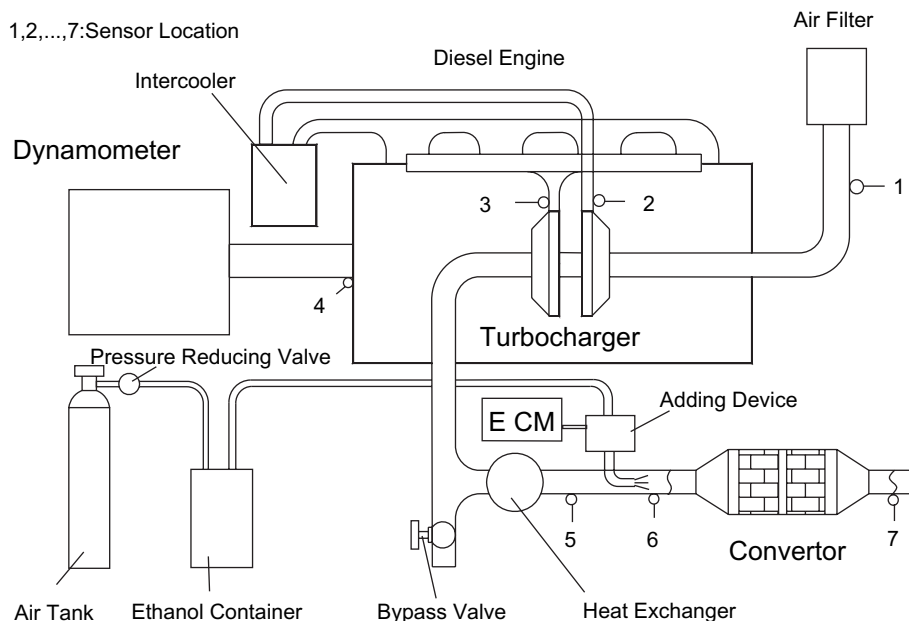


Fig. 1. Apparatus diagram for activity test of washcoated honeycomb catalysts.

BET results of the catalysts are shown in Table 1. The specific surface area of $\text{Ag}/\text{Al}_2\text{O}_3$ catalysts gradually decreased with increasing the Ag loading. XRD patterns of a series of $\text{Ag}/\text{Al}_2\text{O}_3$ catalysts are shown in Fig. 4. Only the Al_2O_3 phase was detected as the Ag loading increased from 2% to 6%, but the Ag_2O and Ag phases were observed with the 8% Ag loading due to the increase of Ag_2O and Ag particles sizes. On the other hand, the test data in Fig. 3 show that the optimum Ag loading is 4% for $\text{Ag}/\text{Al}_2\text{O}_3$ during the SCR of NO_x . This implies that the activity of $\text{Ag}/\text{Al}_2\text{O}_3$ for the SCR of NO_x is closely related to Ag loading, the specific surface area and the dispersion of active phases.

The results above show that the $\text{Ag}/\text{Al}_2\text{O}_3$ has a very high activity for the SCR of NO_x by $\text{C}_2\text{H}_5\text{OH}$. However, as shown in Fig. 5B, a large amount of CO was produced during the SCR of NO_x by $\text{C}_2\text{H}_5\text{OH}$ over the 4% $\text{Ag}/\text{Al}_2\text{O}_3$. 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% $\text{Cu}/\text{Al}_2\text{O}_3$ directly after the 4% $\text{Ag}/\text{Al}_2\text{O}_3$ to form a composite catalyst. As shown in Fig. 5, the composite catalyst exhibited a very similar activity for NO_x reduction compared with the $\text{Ag}/\text{Al}_2\text{O}_3$ 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 $\text{C}_2\text{H}_5\text{OH}$ -SCR of NO_x .

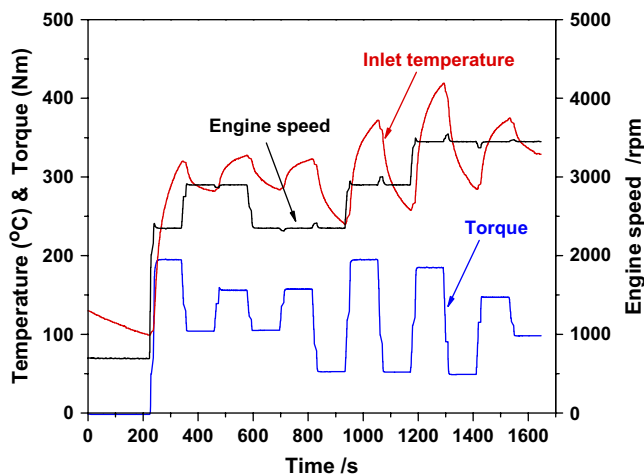


Fig. 2. The 13 operating conditions of the EURO III ESC.

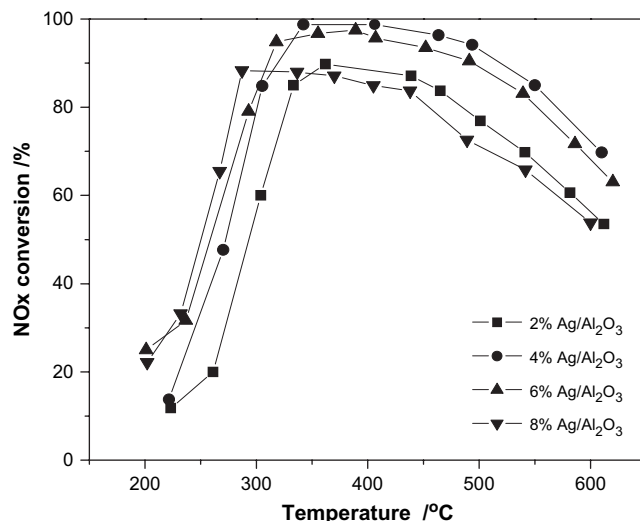


Fig. 3. NO_x conversion for the SCR of NO_x by $\text{C}_2\text{H}_5\text{OH}$ over $\text{Ag}/\text{Al}_2\text{O}_3$ catalysts with different Ag loadings [2% (■), 4% (●), 6% (▲), 8% (▼)] at various temperatures. Reaction conditions: NO 800 ppm, $\text{C}_2\text{H}_5\text{OH}$ 1565 ppm, O_2 10%, H_2O 10%, N_2 balance, $\text{GHSV} = 50,000 \text{ h}^{-1}$.

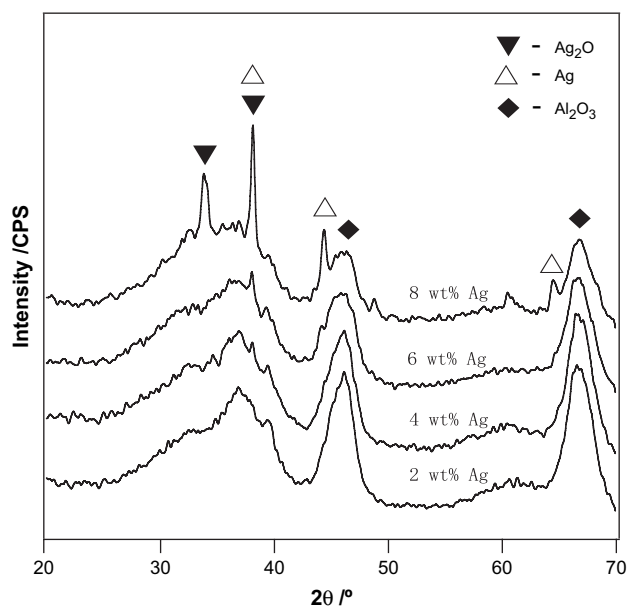


Fig. 4. XRD patterns of Ag/Al₂O₃ catalysts with different Ag loadings.

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 NO_x 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/NO_x ratio, the temperature and GHSV on NO_x 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/NO_x 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/NO_x 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/NO_x ratio has an important influence on the NO_x (Fig. 6A) and CO (Fig. 6C) conversions, but no obvious influence on THC conversion (Fig. 6B). Fig. 6A shows that the NO_x conversion was increased with the increase of the THC/NO_x 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/NO_x ratio, the production of CO was also greatly increased. In addition, although the THC (Fig. 6B) conversions were almost constant with increasing the THC/NO_x ratio, the THC concentration was augmented in exhaust gases at most of operating conditions due to the increase of unburned THC,

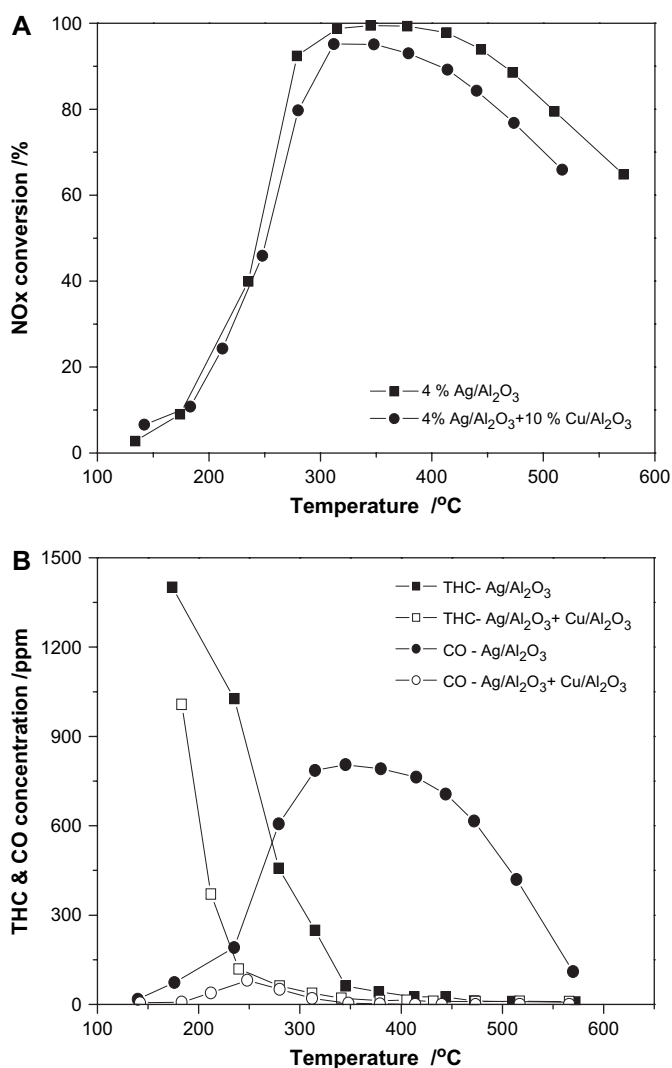


Fig. 5. NO_x conversions (A) and THC, CO concentrations (B) in the effluent gases during the SCR of NO_x by C₂H₅OH over 4% Ag/Al₂O₃ and 4% Ag/Al₂O₃ + 10% Cu/Al₂O₃ catalysts at various temperatures. Reaction conditions: NO 800 ppm, C₂H₅OH 1565 ppm, O₂ 10%, H₂O 10%, N₂ balance, GHSV = 50,000 h⁻¹.

especially at the lower temperature range. On the basis of the results, the following investigation was performed at a fixed THC/NO_x 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/NO_x ratio of 3.4. As shown in Fig. 7A, the honeycomb catalyst showed a very high activity for the removal of NO_x at the GHSV of 30,000 h⁻¹. The maximal conversion of NO_x was up to 93%, and the average conversion of NO_x 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 NO_x 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 NO_x was gradually decreased. The curve of NO_x conversion was shifted towards higher temperatures, and the average conversion of

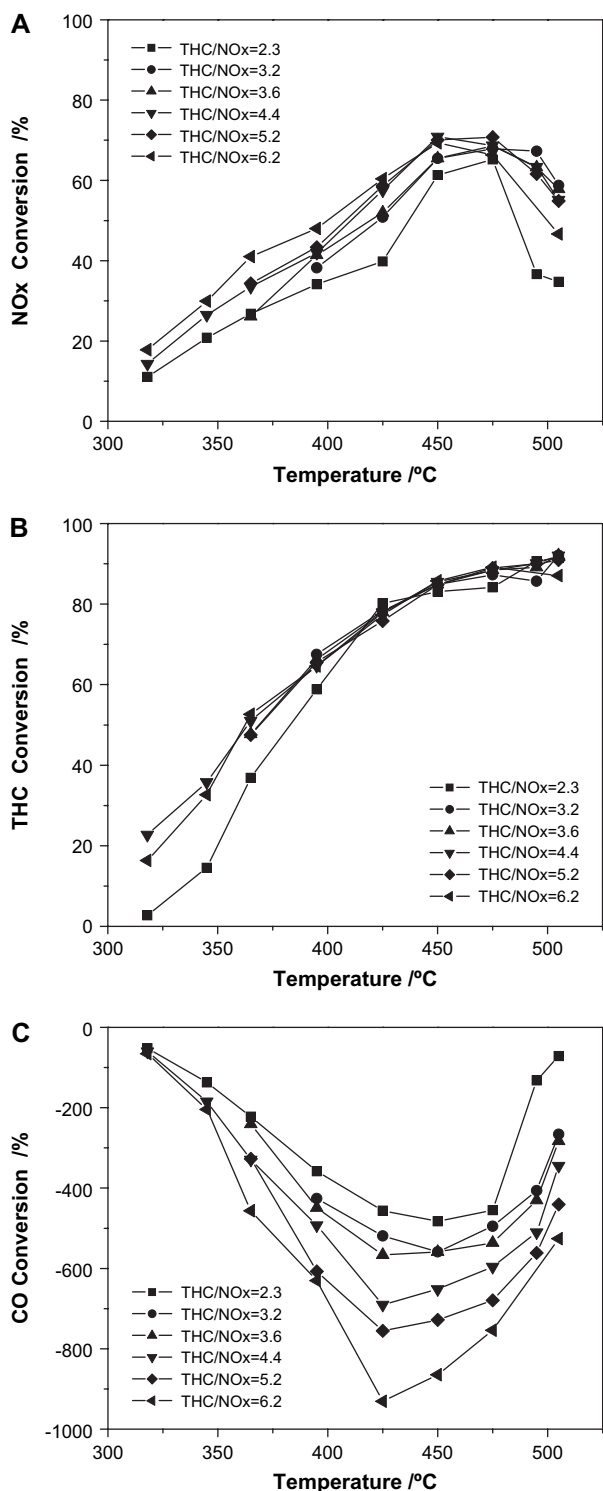


Fig. 6. Effect of THC/NO_x ratio [2.3 (■), 3.2 (●), 3.6 (▲), 4.4 (▼), 5.2 (◆), 6.2 (◄)] on the catalytic activity. (A) NO_x conversion, (B) THC conversion, (C) CO conversion. Operating conditions: Engine speed 3450 rpm, Torque 195 Nm (full load), GHSV = 90,000 h⁻¹.

NO_x 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

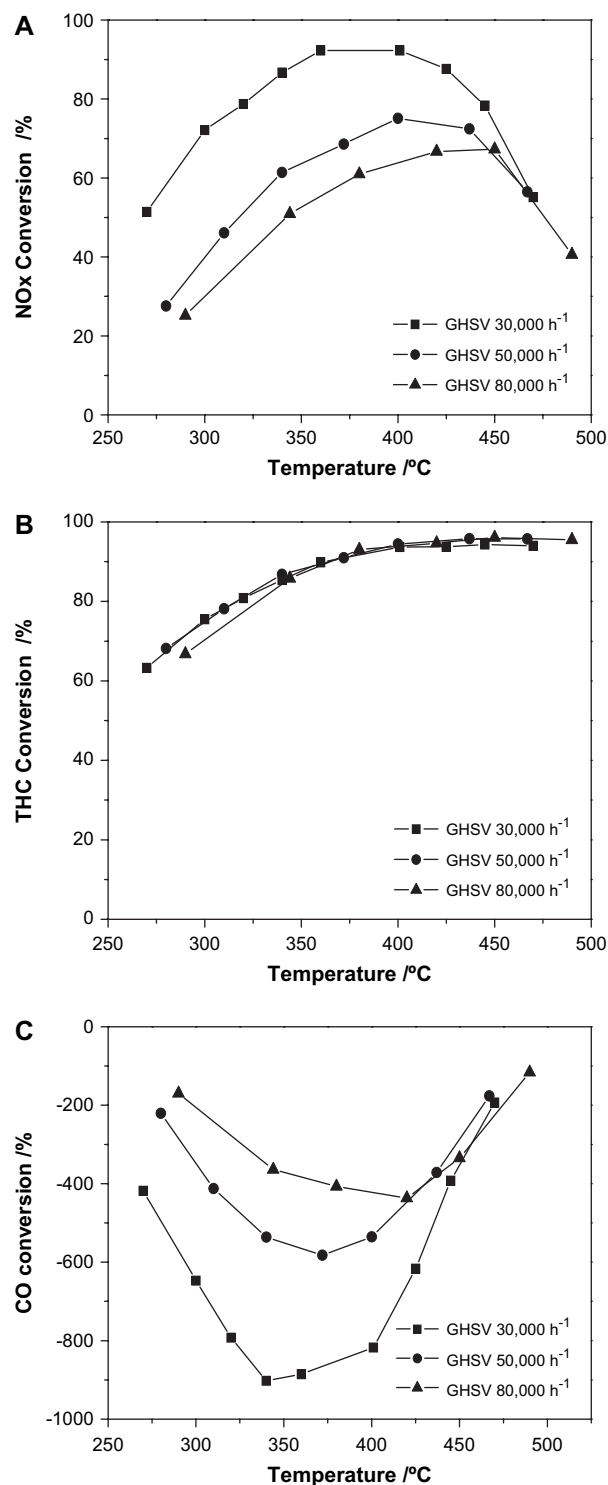


Fig. 7. Effect of GHSV [30,000 h⁻¹ (■), 50,000 h⁻¹ (●), 80,000 h⁻¹ (▲)] on the catalytic activity. (A) NO_x conversion, (B) THC conversion, (C) CO conversion. Operating conditions: Engine speed 3450 rpm, Torque 195 Nm (full load), THC/NO_x ratio 3.4.

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 NO_x conversion, so we propose that CO is not mainly produced from partial oxidation of HC, but from the SCR-C₂H₅OH of NO_x 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 NO_x 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 NO_x 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 NO_x 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 NO_x reduction only in the middle range of temperatures such as 300–450 °C. At lower temperatures (<300 °C), the NO_x conversion was lower, and the addition of C₂H₅OH would cause the great increase of the THC emission without obviously improving the NO_x conversion. In this case, without adding C₂H₅OH, the THC emission would be greatly reduced although the NO_x emission would be slightly increased. At higher temperatures (>450 °C), NO_x 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 NO_x conversion, and then the NO_x 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 NO_x conversion. On the other hand, adequate C₂H₅OH was added for NO_x reduction at the high conversion temperature range of modes 2, 4, 6, 8, 12

Table 2
EURO III ESC test results

Emissions	CO (g kW ⁻¹ h ⁻¹)	THC (g kW ⁻¹ h ⁻¹)	NO _x (g kW ⁻¹ h ⁻¹)
EURO III limits	2.1	0.66	5.0
Original engine	1.307	0.355	6.924
SCR	3.482	1.431	2.668
SCR + Oxi	0.098	0.709	3.654

THC/NO_x = 3.4.

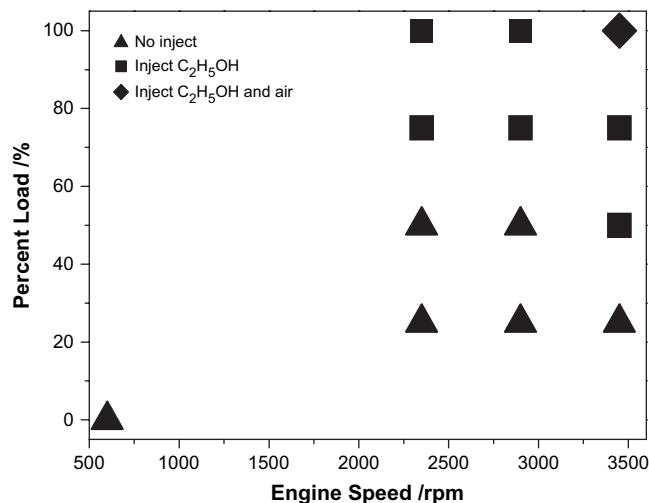


Fig. 8. The optimization of C₂H₅OH addition.

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 NO_x 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 NO_x 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 NO_x 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

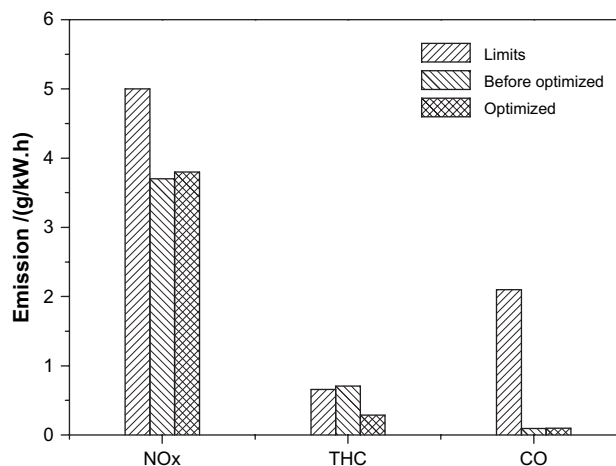


Fig. 9. Test results after optimization of C₂H₅OH addition.

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

Acknowledgments

This work was financially supported by the National Science Fund for Distinguished Young Scholars of China (20425722) and the Innovation Program of the Chinese Academy of Sciences (KZCX3-SW-430).

References

- Bethke, K.A., Kung, H.H., 1997. Supported Ag catalysts for the lean reduction of NO with C₃H₆. *J. Catal.* 172, 93–102.
- Burch, R., Breen, J.P., Meunier, F.C., 2002. A review of the selective reduction of NO_x with hydrocarbons under lean-burn conditions with non-zeolitic oxide and platinum group metal catalysts. *Appl. Catal. B.* 39, 283–303.
- Eränen, K., Lindfors, L.E., Klingstedt, F., Murzin, D.Y., 2003. Continuous reduction of NO with octane over a silver/alumina catalyst in oxygen-rich exhaust gases: combined heterogeneous and surface-mediated homogeneous reactions. *J. Catal.* 219, 25–40.
- Fritz, A., Pitchon, V., 1997. The current state of research on automotive lean NO_x catalysis. *Appl. Catal. B.* 13, 1–25.
- He, H., Yu, Y.B., Liu, J.F., Zhang, R.D., Zhang, C.B., Wang, J., 2004. Selective catalytic reduction of NO_x in the presence of excess oxygen, II. SCR of NO_x with oxo-organic compounds over Ag/Al₂O₃. *Chin. J. Catal.* 25, 460–466.
- Kameoka, S., Ukisu, Y., Miyadera, T., 2000. Selective catalytic reduction of NO_x with CH₃OH, C₂H₅OH and C₃H₆ in the presence of O₂ over Ag/Al₂O₃ catalysts: role of surface nitrate species. *Phys. Chem. Chem. Phys.* 2, 367–372.
- Kung, M.C., Bethke, K.A., Yan, J., Lee, J.H., Kung, H.H., 1997. Catalysts for lean NO_x reduction: structure-property relationship. *Appl. Surf. Sci.* 121/122, 261–266.
- Meunier, F.C., Breen, J.P., Zuzaniuk, V., Olsson, M., Ross, J.R.H., 1999. Mechanistic aspects of the selective reduction of NO by propene over alumina and silver-alumina catalysts. *J. Catal.* 187, 493–505.
- Miyadera, T., 1993. Alumina-supported silver catalysts for the selective reduction of nitric oxide with propene and oxygen-containing organic compounds. *Appl. Catal. B.* 2, 199–205.
- Miyadera, T., Yoshida, K., 1993. Alumina-supported catalysts for the selective reduction of nitric oxide by propene. *Chem. Lett.* 9, 1483–1486.
- Nakajima, F., 1991. Air pollution control with catalysis -past, present and future. *Catal. Today* 10, 1–20.
- Shimizu, K., Satsuma, A., Hattori, T., 2000. Catalytic performance of Ag-Al₂O₃ catalyst for the selective catalytic reduction of NO by higher hydrocarbons. *Appl. Catal. B.* 25, 239–247.
- Sumiya, S., Saito, M., He, H., Feng, Q.C., Takezawa, N., 1998. Reduction of lean NO_x by ethanol over Ag/Al₂O₃ catalysts on the presence of H₂O and SO₂. *Catal. Lett.* 50, 87–91.
- Traa, Y., Burger, B., Weitkamp, J., 1999. Zeolite-based materials for the selective catalytic reduction of NO_x with hydrocarbons. *Micr. Mes. Mater.* 30, 3–41.
- Wu, Q., He, H., Yu, Y.B., 2005. In situ DRIFTS study of the selective catalytic reduction of NO_x with alcohols over Ag/Al₂O₃ catalyst: Role of surface enolic species. *Appl. Catal. B.* 61, 107–113.
- Yu, Y.B., He, H., Feng, Q.C., Gao, H.W., Yang, X., 2004. Mechanism of the selective catalytic reduction of NO_x by C₂H₅OH over Ag/Al₂O₃. *Appl. Catal. B.* 49, 159–171.