An Ethanol SCR for NOx Purification: Performance Evaluation on Engine Bench and Demonstration on Bus

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ABSTRACT

NOx –SCR over Ag/Al₂O₃ catalyst using ethanol (C₂H₅OH) as a reductant has proven its ability to significantly reduce NOx emission in a simulated engine exhaust gas environment. However the real engine exhaust gas environment is too complicated to be simulated. Therefore, the performance evaluation of the Ag/Al₂O₃ catalyst in real exhaust gas environment is necessary. Moreover, the ethanol dosing device and control strategy also need to be validated for the practical use.

In this paper, firstly the catalyst performance and its sulfur tolerance was tested on an engine test bench and the effect of the catalyst on PM emission was investigated. Then the aftertreatment system composed of Ag/Al₂O₃ catalyst + Cu/TiO₂ catalyst + Pt/TiO₂ catalyst and ethanol dosing control based on open loop control was designed, and the diesel engine emission with the aftertreatment system was tested according to ESC test cycle. Finally, the whole aftertreatment system was integrated on a bus and demonstrated.

The performance test results showed that under the conditions of fresh catalyst and SV=30,000 h⁻¹, high NOx conversion (up to 90%) can be obtained in the range of temperature 350~450°C. The aging test showed that sulfur absorbed on catalyst surface is the main reason for catalyst deactivation.

The Ag/Al₂O₃ catalyst can effectively decrease the soluble organic fraction (SOF) in PM, but has little effect on dry soot (DS). The catalyst can also decrease the sulfate slightly when the exhaust temperature is below 410°C, but dramatically increase the sulfate when the temperature is about 470°C. Totally, the PM emission can be decreased more than half of the raw engine out when the exhaust temperature is 336°C, but increased a little when the temperature is over 470°C.

The emissions based on ESC test cycle showed that the engine with the aftertreatment system can completely meet EURO III regulations. Bus demonstration test result showed that the NOx conversion was less then 15%, which indicated that ethanol SCR has some obstacles to be overcome in vehicle road running.

INTRODUCTION

The progressive tightening of the emission standards for heavy-duty diesel vehicles around the world presents great challenges for the engine development and environmental protection. Reduction of both NOx and PM is now the focus of diesel engine emission control. However, since there is a trade-off relationship between NOx and PM, simultaneous reduction of both by conventional engine modification technologies is very difficult and limited [1]. Therefore, the aftertreatment technologies are necessary for diesel engines to meet future stringent emission standards. There exist two basic approaches to achieve the limits of Euro 4 beyond: (1) Optimize the combustion to lower NOx emission, but lead a high PM emission. Then use a particulate filter in the exhaust to clean the PM. (2) Optimize the combustion to lower PM emission, but lead a high NOx emission. Then use a DeNOx catalyst in the exhaust to clean the NOx.

Usually, the exhaust gas recirculation (EGR) is used as a primary engine modification technology to lower the NOx emission, but causing the fuel penalty. Moreover the particulate filters normally need additional fuel injection to regenerate the filtered particulates. All of these lead to an increase of the fuel consumption. Normally, the high- pressure multiple injection, the injection advance and the charge flow control are adopted to decrease PM formation in combustion chamber, which will result in a high NOx emission. But the high NOx emission usually means good combustion. Therefore, the second approach is a better choice from the energy saving point of view.

Among the various NOx aftertreatment technologies, the selective catalytic reduction (SCR) and lean NOx trap
(LNT) are the most promising selections. But use of LNT will require sophisticated control of frequent fuel-rich pulses to form a reductive atmosphere for converting the absorbed NOx, which will lead to an excessive fuel penalty. Moreover the precious metal loading of LNT will increase the cost of the aftertreatment. Compared with LNT catalyst, SCR catalyst has advantages of higher NOx conversion efficiency, lower cost and less sulfur sensitivity. Recently, aqueous urea is commonly used as a reductant, which releases the ammonia by thermal and hydrolytic decomposition. However, there are some drawbacks in use of urea SCR, such as the excess slip of unwanted urea and urea by-products, the high requirement for aqueous urea products and supplement, the high freezing point of aqueous urea, the corrosion of urea solution. Therefore lots of new SCR catalysts utilizing hydrocarbons and oxygenated hydrocarbons as reductants have been studied [2]. Among these HC-SCR catalysts, Ag/Al₂O₃ catalyst utilizing ethanol as a reductant has been identified as a promising NOx reduction catalyst for diesel engines, which has a high NOx selective reduction and a low sensitivity to water vapor and SO₂[2].

In a simulated exhaust gas environment, the SCR with oxygenated hydrocarbon reductants over Ag/Al₂O₃ was studied by the author[4]. It was shown that in the whole temperature range, the ethanol has a higher activity of NOx conversion, and also has a wider working temperature range (310~610°C) with the highest conversion efficiency up to 90%. However the real engine exhaust gas environment is too complicated to be simulated. Consequently, the research of the Ag/Al₂O₃ catalyst performance in real exhaust gas environment is necessary.

EXPERIMENT SETUP

EXPERIMENTAL FACILITY

Figure 1 shows the schematic diagram of the test bench. The test engine is YC4112ZLQ diesel engine. The engine specification can be found in Table 1. Gaseous emissions and PM were sampled from raw exhaust streams before and after catalyst. NOx, THC and CO emissions were measured by AVL CEB II exhaust gas analyzer, and PM by AVL SPC 472 particulates collector.

Ethanol was added in the upstream of SCR catalyst by using an air-assisted injection system, which is composing of ethanol tank, fuel pump, fuel rail, ethanol injector, air compressor and electronic control module (ECM). Fuel pump supplies the ethanol into the fuel rail, where the ethanol pressure maintains about 0.3 MPa. Ethanol flow rate can be controlled by the ECM automatically based on engine speed, load and averaged SCR temperature (calculated from the thermocouple before and after SCR). Moreover, the ECM can be controlled in manual mode, in which the pulse width can be changed when needed. High pressure air from engine air compressor assists the atomization and diffusion of the ethanol spray.

During the evaluation of the light-off behavior on engine test bench, the exhaust temperature was increased every around 40-50 °C by changing the engine speed and load (the NOx emission concentration has to be kept constant at the same time with careful selection). The temperature was then maintained constant for around 10 minutes to obtain a steady state running before the temperature was moved to the next point. Moreover, the space velocity maintained constant by using a by-pass valve.

<table>
<thead>
<tr>
<th>Engine Mode</th>
<th>YC4112ZLQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>4-cylinder,4-stroke, in-line, turbocharging, intercooler</td>
</tr>
<tr>
<td>Displacement</td>
<td>5.12 L</td>
</tr>
<tr>
<td>Compress ratio</td>
<td>17.5</td>
</tr>
<tr>
<td>Fuel pump</td>
<td>BH4P120R1402</td>
</tr>
<tr>
<td>Rated power/speed</td>
<td>132kW / 2300r/min</td>
</tr>
<tr>
<td>Max toque/speed</td>
<td>660N.m / 1300-1500n/min</td>
</tr>
</tbody>
</table>

CHARACTERISTICS OF TESTED CATALYSTS

Silver loading has a great influence on the Ag/Al₂O₃ catalyst performance. The high loading will decrease the selective performance at high temperature and lead to a NOx conversion decrease, while low loading of silver will decrease the NOx conversion at low temperature. The investigation in the previous research shows that the silver loading of 4 wt.% has an optimal NOx conversion in a wide temperature range when using ethanol as a reductant [4,5]. Therefore the Ag/Al₂O₃ catalysts used in this paper have a silver loading of 4 wt.%. In order to remove the by-products of the SCR reaction and avoid the reductant slip, a diesel oxidation catalyst (DOC) is needed [5, 6]. There are two kinds of DOC used: Cu/TiO₂ and Pt/TiO₂ catalysts. The Cu/TiO₂ catalyst has a Cu loading of 10 wt. %, the Pt/TiO₂ catalyst has a Cu loading of 10 wt. %. The catalysts were coated onto cordierite monolith substrates with a cell density of 200 cpsi. The geometric dimension of the catalyst was...
140×100 mm (diameter×length), giving a catalyst volume of approximately 1.54 liters per block. The Ag/Al2O3 wascoated loading on monolith was about 130 g/L while the Cu/TiO2 about 110 g/L. During the evaluation test of the catalysts, 3 blocks Ag/Al2O3 catalysts were assembled in the exhaust pipe. However, in application test of the catalysts, 6 blocks of Ag/Al2O3 catalysts, 2 blocks of Cu/TiO2 and 2 blocks of Pt/TiO2 catalysts were integrated as shown in the Figure 5, which can ensure the space velocity is lower than 50,000 h⁻¹ under the condition of the maximum exhaust mass flow.

**TEST FUEL AND REDUCTANT**

One kind of oxygenated diesel fuel blend (hereafter named BE25) was used in the test which is composed of 5 wt.% ethanol, 20 wt.% bio-diesel and 75 wt.% 0# fossil diesel. All the fuels were purchased from the market. Table 2 shows the property of the fuels. The selected BE25 has a potential to reduce the PM emission and to be an alternative to diesel fuel [7].

The reductant ethanol used in this study was fuel-grade (denatured with gasoline), which has an ethanol content more than 95 wt. %.

| Table 2. Property of the fuels |
|---------------------|-----------------|-----------------|-----------------|
| Fuel               | Oxygen content wt% | Specific enthalpy MJ/kg | Sulfur content (ppm) |
| BE25               | 3.8              | 40.8            | 262             |
| 0# diesel          | 0                | 42.5            | 350             |
| Bio-diesel         | 11               | 38.0            | 0               |
| ethanol            | 35               | 27.0            | 0               |

**PERFORMANCE EVOLUTION OF CATALYST**

**PERFORMANCE OF Ag/Al2O3 IN THE SCR OF NOX**

Figure 2 shows the NOx conversion, CO slip and THC slip as a function of ethanol:NOx molar ratio when the fresh Ag/Al2O3 catalysts were used. Before the nE:nNOx ratio equal to 1.0, the NOx conversion apparently increases with increasing of the nE:nNOx ratio, while the CO and THC slip increase too. The NOx conversion gets max when nE:nNOx=1, and then NOx conversion keep almost constant when the nE:nNOx ratio increase, but the CO and THC slip continue increase.

Many investigations showed that CO is a by-product of SCR reaction when Ag/Al2O3 used as catalyst [4, 5, 6]. The CO partially from the SCR reaction’s key step: isocyanate (NCO) reaction with NO generates N2 and CO. As CO can’t be avoid in NOx selective reduction reaction, additional catalyst for cleaning up these by-product is needed. Miyadera[6] show that Cu/TiO2 + Pt/TiO2 have a excellent performance in cleaning up system when put behind the Ag/Al2O3 catalyst, In which the by-products such as NH3, CH3CN, and HCN were reduced by Cu/TiO2, while the other by-products such as CO and CH3CHO were reduced by Pt/TiO2. Therefore the same system was selected in this work.

**SULFUR TOLERANCE**

Figure 3 shows the light-off behaviors of the catalyst under the conditions of the fresh and aged 30 hours while the nE:nNOx ratio maintains 1.5 and the NOx concentration is around 1500 ppm. From the figure, for the fresh catalyst with SV=30,000 h⁻¹, it is found that a high NOx conversion (up to 90%) can be obtained in the range of inlet temperature 350~450 °C. However, the NOx conversion begins to decrease when the inlet temperature is over 450 °C, because some unselective oxidation reactions (combustion) of the ethanol gradually increase with the increasing of the temperature. For the fresh catalyst with SV=50,000 h⁻¹, it has the same trend but a little low NOx conversion.

In order to investigate the sulfur tolerance of the Ag/Al2O3 catalyst, an aging test was conducted. Generally the sulfate will be easily deposited on the
monolith in low temperature, since at higher temperature the sulfur can be desorbed from the catalyst surface. Therefore a low temperature aging cycle was selected, in which the highest temperature was below 400°C. 0# diesel was selected as fuel during the aging cycle as it has a high level of S than BED25. The range of SV was about 10,000~30,000 h⁻¹ during the aging cycle. After 30 hours aging, the light-off behavior was tested again under the same two space velocity conditions as shown in Figure 3. The test results show that the aged catalyst activation was deteriorated under both space velocities. The deterioration extent under SV=50,000 h⁻¹ is larger than that under SV=30,000 h⁻¹, which indicates that the aging process is more severe in the high space velocity.

Table 3 shows the comparison of the component between the coating of fresh and 30 hours aged Ag/Al₂O₃ catalysts. The sulfur content increases dramatically, which indicates that the sulfur absorbed on catalyst surface is a main reason for the catalyst activation decreasing after aging test.

Table 3 Comparison between the coating of fresh and 30 hours aged Ag/Al₂O₃ catalysts

<table>
<thead>
<tr>
<th>Component</th>
<th>O wt%</th>
<th>Al wt%</th>
<th>Ag wt%</th>
<th>S wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh catalyst</td>
<td>43.82</td>
<td>49.77</td>
<td>5.09</td>
<td>0</td>
</tr>
<tr>
<td>After aged 30 hours</td>
<td>43.68</td>
<td>46.77</td>
<td>4.59</td>
<td>1.66</td>
</tr>
</tbody>
</table>

THE EFFECT OF THE PM EMISSION

To investigate the effect of the Ag/Al₂O₃ catalyst on PM emission, the engine-out PM sampled before the catalyst and the PM after the catalyst were measured at different catalyst inlet temperatures under the condition of SV=50,000 h⁻¹ and with the ethanol been injected (nₑ:nNOₓ=1.5). Then the PM collected on the filter was separated into soluble organic fraction (SOF), sulfate and dry soot (DS) to investigate the effect of the catalyst on different compositions of the PM. The SOF was determined through extraction of the filter paper with PM on it, the organic solvent used here was CH₂Cl₂, the extraction was used again with pure water as solvent, the pure water was weighed two times, and the mass difference of the water was sulfate mass, the DS would be still stay on the filter paper. Thus the three components could be separated.

Figure 4 shows the comparison of the PM emission before and after SCR catalyst under different inlet temperatures. It was found that the SOF was reduced in the whole range of the inlet temperature when the exhaust gas flows through the Ag/Al₂O₃ catalyst; moreover the reduction of SOF was increased with the increasing of the inlet temperature. This is mostly because of the oxidation capability of the Ag/Al₂O₃ catalyst. However the DS was almost unchanged before and after the SCR catalyst in the whole temperature range. When the inlet temperature is below 410 °C, the sulfate will decrease slightly, however the reduction of sulfate will decrease with the increasing of the inlet temperature. The sulfate was increased dramatically when the inlet temperature is at 470 °C. This is because the sulfate is easy to be absorbed on the surface of the catalyst under the low temperature and desorbed under the high temperature, which indicates that the catalyst activation loss due to the sulfur poisoning can be recovered by a desulfurization process under the high temperature condition. However the oxidation of the SO₂ to SO₃ to from sulfate by Ag/Al₂O₃ catalyst may partially contribute to the sulfate increasing at high inlet temperature. In general, the PM emission can be decreased more than half of the original engine-out under the condition of inlet temperature of 336 °C, but increased a little when the inlet temperature is 470 °C because of the desulfurization process. Since most of the sulfate in the PM come from the sulfur in fuel, the final effect of the Ag/Al₂O₃ catalyst on PM emission is dependent on the temperature and fuel sulfur content.

The result of Ag/Al₂O₃ catalyst aging test and the effect of PM emission test show that fuel sulfur content has a great influence on the catalyst activation and final tailpipe emission. Therefore the low sulfur fuel should be used when the Ag/Al₂O₃ catalyst was used as an aftertreatment.

![Figure 4. Comparison of PM emission before and after SCR catalyst](image)

CATALYST APPLICATION

For the practically using of the Ag/Al₂O₃ catalyst, an aftertreatment system, which composed of Ag/Al₂O₃ catalyst + Cu/TiO₂ + Pt/TiO₂ catalyst, was integrated firstly. Figure 5 shows the CAD model of the Exhaust
pipe and catalyst containers. 3 block Ag/Al$_2$O$_3$ catalyst, 1 block Cu/TiO$_2$ catalyst and 1 block Pt/TiO$_2$ catalyst were integrated in each container. To have an even distribution of the exhaust gas flow and equal distribution of reductant though the two line of catalyst, the exhaust pipe and containers designed to have a symmetric layout. Then a dosing control strategy based on open loop control was developed. Finally the engine out emission and tail out emission based on ESC test cycle was measured.

**ETHANOL DOSING STRATEGY**

Figure 6 shows the Ethanol dosing control based on open loop control. The NOx concentration MAP and Exhaust flux MAP, which consists of a 2-dimensional look up table filled based on engine bench test result, were a function of engine speed and load and given out in figure 7. It represents roughly amount of NOx to be converted and magnitude of the space velocity. Also the effect of engine intake air temperature to the NOx emission is taken into account. The NOx conversion rate was predicted by combining the catalyst temperature, SV and catalyst aging time. Then the basic pulse width was set based on amount of NOx and conversion rate. Finally the Pulse width was adjusted by a function depending on the Voltage of injector.

The engine speed measured by a speed sensor, and load by a displacement sensor on accelerator pedal. The catalyst temperature calculated by a model based on temperature measured before and after SCR.

**ESC TEST CYCLE RESULT**

Figure 8 shows the change of the catalyst inlet temperature, engine torque and engine speed in an ESC test mode. It was found that the exhaust gas temperature was over 300 °C in most of the test modes, which indicates that the NOx conversion efficiency can be maintained on a high level. Table 5 shows the NOx, CO and THC emissions under the ESC tests. It was found that engine emission can meet the Euro III by use of the combined catalyst system. The average NOx conversion efficiency is about 64.5% with high ethanol consumption, about 6% of fuel consumption by weight. However the high ethanol consumption results from the high engine-out NOx emission, which is even higher than Euro I limit.
measured per second. Figure 9 shows the test emission results. It was found that the NOx conversion is very high at most of the run points and the CO emission after the catalyst is lower than the engine-out during the most of the test cycle. However there is almost no NOx conversion in four modes which were corresponding to the four THC slip peaks. As shown in Figure 8, the exhaust temperature was increased quickly in the four modes. However the catalyst temperature was increased slowly because of its high thermal inertia. Therefore the excessive ethanol, leading to a THC slip peak, was dosed to accelerate the light-off of the catalyst. As shown in Figure 9, the NOx conversion can quickly get to a high level by this excessive dosing strategy.

![Figure 9. Engine out emission and tailpipe emission during the ESC test cycle](image)

**DEMONSTRATION ON BUS**

Base upon the performance evaluation on the engine test, the integrated aftertreatment system was installed on a bus to carry out the demonstration of the ethanol SCR to assess its performance in the real road running.

The bus chosen for the demonstration was 29 seats sight-seeing bus powered by a YC 4112, 5.12 liter,132 kW diesel engine. Figure 10 gives the installation of the SCR system on demonstration bus. The composition of the aftertreatment system was the same as the one used on bench engine, which was put before the silencer. Ethanol container was set next to the fuel tank. The air used for assisting ethanol injection was coming from the air compressor set on bus, the air pressure was about 0.6~0.8 MPa in ordinary operation condition.

In road running, two AVL DiGas 4000 are used to simultaneously measure the emissions before and after the SCR catalyst. Moreover the exhaust gas temperature before and after the catalyst was measured by two thermal couples. As the bus was used for sightseeing, the road selected for the demonstration was a typical road from Beijing to a scenery spot in suburb of Beijing.

![Figure 10. Installation of the SCR system on demonstration bus](image)

Figure 11 gives the exhaust gas temperature and NOx concentration before and after the SCR. It can be found that the inlet gas temperature and NOx concentration changed frequently during the whole test process. The mean NOx conversion was less then 15%, far from the NOx conversion attained on engine bench test.

The inlet gas temperature profile over the road running is shown in Figure 12. It can be seen that the temperature of inlet gas is between 300 and 400 °C for the majority of the time, and the inlet gas temperature above 300 °C is about 75% of the total time.

![Figure 12. Exhaust gas temperature and NOx concentration](image)
lower the light-off temperature and thermal capacity of the catalyst.

![Inlet gas temperature](image1)

**Figure 11.** On-road result of temperature and NOx emission

![Temperature/℃](image2)

**Figure 12.** Inlet temperature distribution during road demonstration

### CONCLUSION

1. The NOx conversion efficiency will go up with the increase of the ethanol dosage, but causing the great increase of the CO emission and THC emission at the same time. As CO is a by-product of NOx selective reduction reaction, additional oxidation catalyst for cleaning up is needed.

2. Under the condition of fresh catalyst and SV=30,000 h\(^{-1}\), high NOx conversion (up to 90%) can be obtained in the range of 350~450 °C, while it is reduced at higher and lower temperature. However the NOx conversion decreased after 30 hours aging test. Component comparison between the coating of fresh and 30 hours aged Ag/Al\(_2\)O\(_3\) catalysts indicated that sulfur absorbed on catalyst surface is a main reason of catalyst's activation decreasing

3. Investigating of Ag/Al\(_2\)O\(_3\) catalyst's effect of the PM emission showed that it can effectively decrease the SOF of PM, but no effect of DS. The Ag/Al\(_2\)O\(_3\) catalyst can decrease the sulfate slightly when temperature low then 410 °C, but dramatically increase the sulfate when the inlet temperature at 470 °C. Totally, the PM emission can be decreased more than half of the original engine out under the condition of inlet temperature=336°C, but increased a little when inlet temperature=470 °C.

4. In the evaluation test on engine bench, an aftertreatment system composed of Ag/Al\(_2\)O\(_3\) catalyst + Cu/TiO\(_2\) catalyst + Pt/TiO\(_2\) catalyst and ethanol dosing control based on open loop control were designed. The engine emission based ESC test cycle showed that engine can be completely meet EURO III regulations with an original NOx emission of 13.06 g/kW.h.

5. Bus demonstration test result showed that the NOx conversion was less then 15%, which indicated that the ethanol SCR has to be improved to be activated in the lower exhaust temperature during the real road running.

### ACKNOWLEDGMENTS

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