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Study of NOx selective catalytic reduction by ethanol over Ag/Al_2O_3 catalyst on a HD diesel engine

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Abstract

The selective catalytic reduction (SCR) of NOx by ethanol over Ag/Al_2O_3 catalyst has been proven to significantly reduce NOx emission in a simulated engine exhaust gas environment in our previous research. However, the exhaust gas from real engines is too complicated to be simulated. Therefore, the Ag/Al_2O_3 catalyst is needed to be evaluated for its application on real diesel engines.

In this paper, firstly the catalyst performance was evaluated on an engine test bench and the effect of the catalyst on PM emission was investigated. Then, an integrated aftertreatment system composed of Ag/Al_2O_3 catalyst + Cu/TiO_2 catalyst + Pt/TiO_2 catalyst and ethanol dosing based on open loop control was designed and established. Finally the diesel engine emissions with the aftertreatment system were tested on the ESC test cycle.

The result showed that under the condition of fresh catalyst and space velocity (SV) = 30,000 h^{-1}, a high NOx conversion (up to 90%) can be obtained in the range of temperature 350–450 °C. The NOx conversion efficiency will go up with the increase of the ethanol dosage, but cause the great increase of the CO emission and THC emission at the same time. Under the condition of inlet temperature = 400 °C and ethanol to NOx mole ratio (n_E:n_{NOx}) = 1.5, the NOx conversion can maintain above 70% when the space velocity is less than 50,000 h^{-1}. The aging test showed that sulfur absorbed on catalyst surface is the main reason for the deterioration of the catalyst activation.

Additionally, the Ag/Al_2O_3 catalyst can effectively reduce the soluble organic fraction (SOF) in particulate matter (PM), but have no effect on dry soot (DS). The Ag/Al_2O_3 catalyst can decrease the sulfate slightly when the inlet temperature is below 410 °C, but dramatically increase the sulfate when the inlet temperature is above 470 °C. Totally, the PM emission can be decreased more than half of the original engine-out emission under the condition of inlet temperature 336 °C, but increased a little when inlet temperature is above 470 °C.

The engine emissions based on the ESC test showed that the engine with the aftertreatment system can completely meet EURO III regulations.

Keywords: NOx reduction; Selective catalytic reduction (SCR); Emission control; Ethanol

1. 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 IV beyond:

(1) Optimize the combustion to lower NOx emission, but lead a high PM emission. Then use a particulate filter in the aftertreatment 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 aftertreatment to clean the NOx.

Usually, the exhaust gas recirculation (EGR) is used as a primary engine modification technology to lower the NOx emission, but cause 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

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Table 1
Engine specification

Engine model	YC4112ZLQ
Type	4-Cylinder, 4-stroke, in-line, turbocharging, intercooling
Displacement	5.12 L
Compression ratio	17.5
Fuel pump	BH4P120R1402
Rated power/speed	132 kW/2300 r/min
Max toque/speed	660 N m/1300–1500 r/min

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 concerned [3]. But use of LNT will require sophisticated control of frequent fuel-rich pulses to form a reductive atmosphere for reverting 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 the LNT catalyst, the SCR catalyst has advantages of higher NOx conversion efficiency, lower cost and less sulfur sensitivity. Recently, aqueous urea is commonly used as a reductive agent, 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 products, the high standard level of 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 evaluated HC-SCR catalysts, Ag/Al_2O_3 catalyst utilizing ethanol as a reductant has been identified as a promising NOx reduction catalyst in diesel engines, which has a high NOx selective reduction and a low sensitivity to water vapor and SO_2 [2].

In a simulated exhaust gas environment, the selective catalyst reduction of NOx with oxygenated hydrocarbon reductants over Ag/Al_2O_3 was studied by the author [4]. It was shown that in the whole temperature range, the ethanol (C_2H_5OH) 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/Al_2O_3 catalyst performance in real diesel engine exhaust gas environment is necessary.

2. Experiment setup

2.1. Experimental apparatus

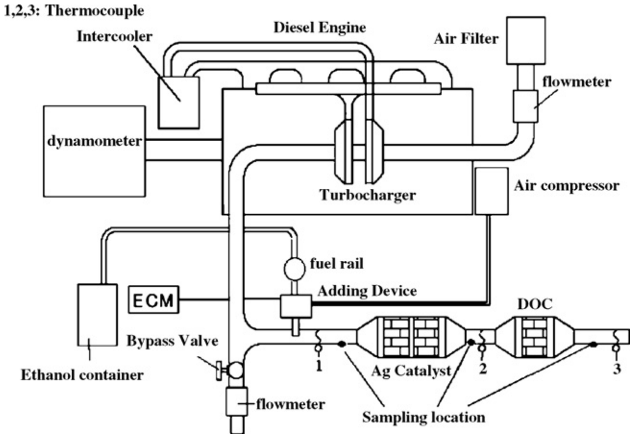

Fig. 1. Schematic of engine bench and sample location.

Fig. 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 CEBII 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 min 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.

2.2. Characteristics of tested catalysts

Sliver loading has a great influence on the Ag/Al_2O_3 catalyst performance. The high loading will decrease the selective performance at high temperature and lead to a NOx conversion decrease, while low loading of sliver will decrease the NOx conversion at low temperature. The investigation in the previous research shows that the sliver 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/Al_2O_3 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/TiO_2 and Pt/TiO_2 catalysts. The Cu/TiO_2 catalyst has a Cu loading of 10 wt. %. The catalysts were coated onto cordierite monolith substrates with a cell

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

density of 200 cpsi. The geometric dimension of the catalyst was 140 mm × 100 mm (diameter × length), giving a catalyst volume of approximately 1.54 L per block. The Ag/Al_2O_3 wash-coated loading on monolith was about 130 g/L while the Cu/TiO_2 about 110 g/L. During the evaluation test of the catalysts, three blocks Ag/Al_2O_3 catalysts, one block Cu/TiO_2 and one block Pt/TiO_2 catalysts were assembled in the exhaust pipe as shown in Fig. 1. However in application test of the catalysts, six blocks of Ag/Al_2O_3 catalysts, two blocks of Cu/TiO_2 and two blocks of Pt/TiO_2 catalysts were integrated as shown in the Fig. 7, which can ensure the space velocity is low than 50,000 h^{-1} under the condition of the maximum exhaust mass flow.

2.3. Tested 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 then 95 wt%.

3. Performance evaluation of the catalysts

3.1. Performance of the Ag/Al_2O_3 catalyst

Fig. 2 shows the NOx conversion, CO slip and THC slip as a function of ethanol:NOx mole ratio (n_E:n_{NOx}) when the fresh Ag/Al_2O_3 catalyst was used. Before the ratio equals to 1.0, the NOx conversion apparently increases with the increasing of the ratio, and the CO and THC slip also increase. The NOx conversion achieves the maximum point when n_E:n_{NOx} = 1, and then NOx conversion keeps almost constant when the ratio increases, but the CO and THC slip continue to increase.

Many studies showed that the CO is the by-product of the NOx SCR by ethanol when Ag/Al_2O_3 is used as the catalyst [4–6]. The CO partially comes from the key step of the SCR reactions: isocyanate (NCO) reacting with NO generates N_2 and CO. As the CO cannot be avoided in NOx selective reduction reactions, additional catalyst to remove the by-product is needed.

Fig. 3 shows the light-off behaviors of the catalyst under the conditions of the fresh and aged 30 h while the n_E:n_{NOx} 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.

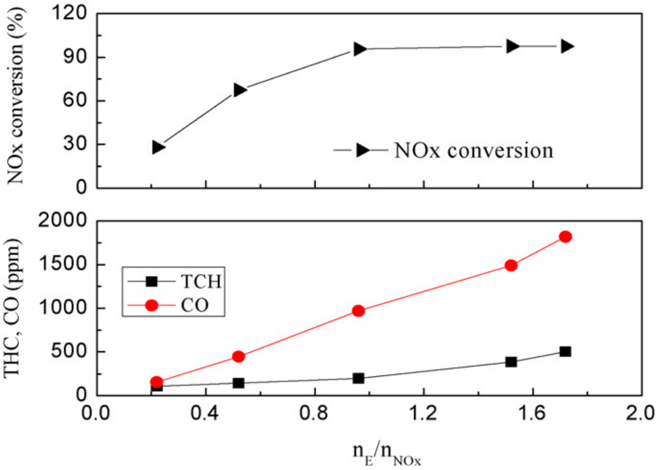

Fig. 2. NOx conversion, CO and THC slip vs. n_E:n_{NOx} ratio (engine speed 1726 r/min, torque 475 N m, exhaust temperature 410 °C, SV 30,000 h^{-1}, NOx 1500 ppm).

In order to investigate the sulfur tolerance of the Ag/Al_2O_3 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 is below 400 °C. After 30 h aging, the light-off behavior was tested again under the same two space velocity conditions as shown in Fig. 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 h aged Ag/Al_2O_3 catalysts. The sulfur content increases dramatically, which indicates that the sulfur

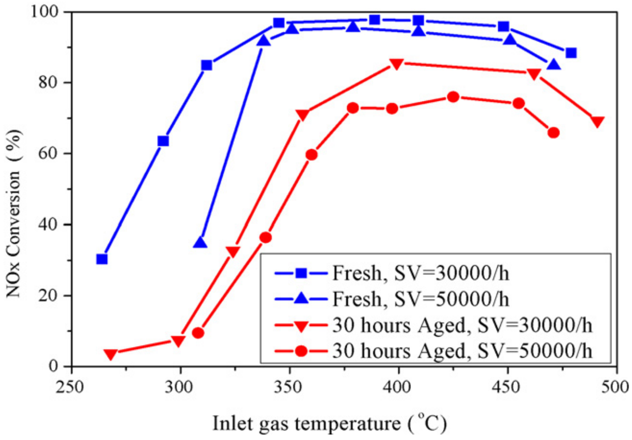

Fig. 3. NOx conversion vs. temperature (n_E:n_{NOx} = 1.5, NOx 1500 ppm).

Table 3
Comparison between the fresh and the aged coating of Ag/Al_2O_3 catalyst

Component	O (wt%)	Al (wt%)	Ag (wt%)	S (wt%)
Fresh	43.82	49.77	5.09	0
Aged	43.68	46.77	4.59	1.66

absorbed on catalyst surface is a main reason for the catalyst activation decreasing after aging test.

The result of Ag/Al_2O_3 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/Al_2O_3 catalyst was used as an aftertreatment.

The NOx conversion potential changing with the space velocity is an important characteristic of the catalyst, which will determine the final volume of the catalyst for a practical application. Generally in the real application, the catalyst is expected to have a high conversion with a small catalyst volume for low cost and compact space consideration; therefore the catalyst should maintain high conversion efficiency even under the high space velocity. Fig. 4 shows the NOx conversion versus space velocity under the condition of inlet temperature 400 °C and n_E:n_{NOx} = 1.5. It can be found that the NOx conversion maintains above 70% when the space velocity is below 50,000 h^{-1}. However the NOx conversion decreases linearly with the increasing of the space velocity, and under the condition of SV = 80,000 h^{-1}, the NOx conversion decreases to less than 50%.

3.2. *Effect of the Ag/Al_2O_3 catalyst on PM emission*

To investigate the effect of the Ag/Al_2O_3 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 n_E:n_{NOx} = 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. Fig. 5 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/Al_2O_3 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/Al_2O_3 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. 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. Since most of the sulfate in the PM come from the sulfur in fuel, the final effect of the Ag/Al_2O_3 catalyst on PM emission is dependent on the temperature and fuel sulfur content.

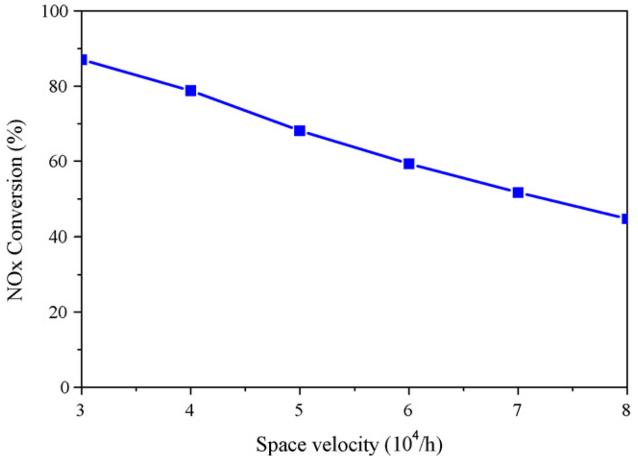

Fig. 4. NOx conversion vs. space velocity (inlet temperature 400 °C,0 n_E:n_{NOx} = 1.5).

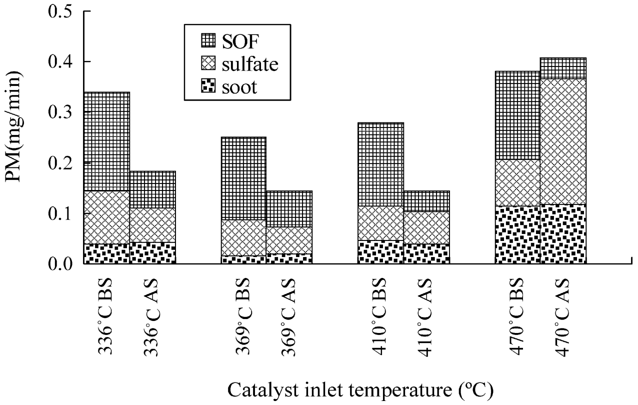

Fig. 5. Comparison of PM emission before and after SCR catalyst (BS: sampled before SCR; AS: sampled after SCR. SV = 50,000 h^{-1}, n_E:n_{NOx} = 1.5).

The result of Ag/Al_2O_3 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/Al_2O_3 catalyst was used as an aftertreatment.

3.3. *Performance of the combined catalysts*

As mentioned above, the CO slip cannot be avoided in NOx selective reduction reaction, therefore additional catalyst for removing the by-product CO was needed. Moreover the THC slip is also needed to be cleaned up. Two kinds of DOC catalysts were selected to be integrated into the catalyst assembly as shown in Table 4, where DOC1 indicates two block Cu/TiO_2 catalyst and DOC2 indicates one block Cu/TiO_2 + one block Pt/TiO_2. Fig. 6 gives the NOx, CO, THC emissions measured at the engine-out, after the SCR catalyst, after the SCR cata-

Table 4
Catalyst assemblies

	SCR catalyst	DOC catalyst
SCR	Three blocks Ag/Al_2O_3	None
SCR + DOC1	Three blocks Ag/Al_2O_3	Two blocks Cu/TiO_2
SCR + DOC2	Three blocks Ag/Al_2O_3	One block Cu/TiO_2 + 1 block Pt/TiO_2

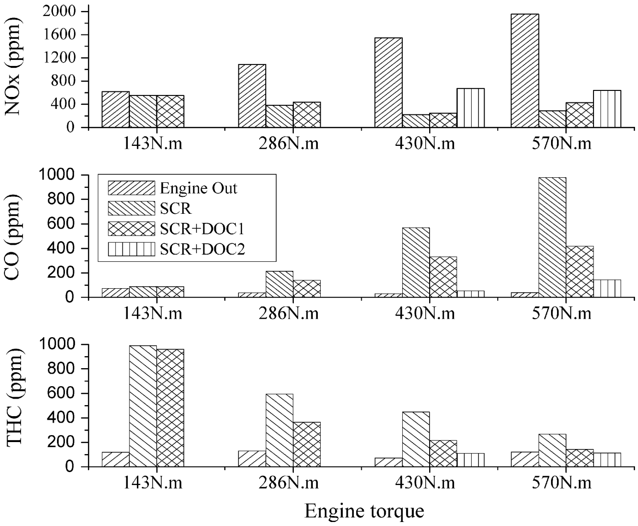

Fig. 6. NOx, CO and THC emissions of different catalyst assemblies (engine speed = 1800 r/min, n_E:n_{NOx} = 1.5).

lyst and DOC assemblies under the different engine torques. From the figure, it can be seen that DOC1 cannot efficiently remove the CO and THC emissions. And DOC2 can efficiently remove the CO and THC emissions but slightly decrease the NOx conversion.

Miyadera's research [6] showed that high-activity noble metal catalysts were unsuitable to be placed directly after the Ag/Al_2O_3 catalyst, because over these noble metal catalysts, some by-products like CH_3CN, HCN, and NH_3 were mainly oxidized to NOx and their conversion to N_2 was very limited. The research also indicated that low-activity Cu/TiO_2 catalysts can efficiently convert the by-products into N_2 but had a low efficiency to remove CO and CH_3CHO. So a two-component catalyst, $Cu/TiO_2 + Pt/TiO_2$ has an excellent performance in removing when put behind the Ag/Al_2O_3 catalyst, where the by-products such as NH_3, CH_3CN, and HCN were reduced by Cu/TiO_2, while other by-products such as CO and CH_3CHO were reduced by Pt/TiO_2. Finally three-component combined catalysts, $Ag/Al_2O_3 + Cu/TiO_2 + Pt/TiO_2$ were selected in the following application for diesel engines.

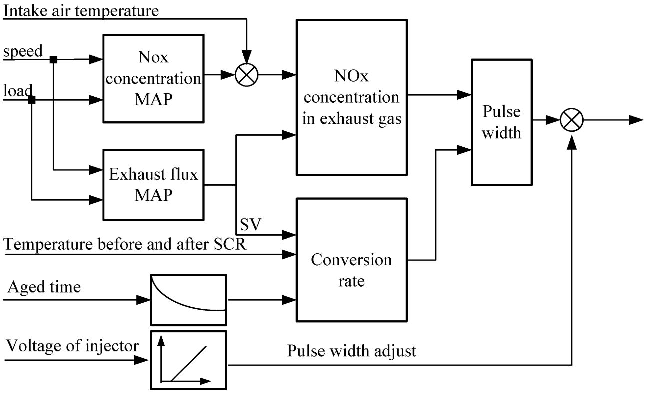

Fig. 8. Reductant dosing strategy based on the open loop control.

3.4. Application of the catalysts

For a practical application of the Ag/Al_2O_3 catalyst, both NOx and CO, THC have to be reduced to meet the stringent standards, therefore an aftertreatment system consisting of $Ag/Al_2O_3 + Cu/TiO_2 + Pt/TiO_2$ catalysts should be considered. Fig. 7 shows the CAD model of the exhaust pipe and integrated catalysts assembly. Three blocks of Ag/Al_2O_3 catalyst, one block of Cu/TiO_2 catalyst and one block of Pt/TiO_2 catalyst were assembled in each of two converters. To have a uniform distribution of the exhaust gas flow and balanced distribution of reductant through the two lines of the catalysts, the exhaust pipes and the converters are designed to have a symmetric layout. Then a dosing control strategy based on an open loop control was developed. Finally the engine-out emissions and tailpipe emissions based on ESC test cycle were measured.

3.4.1. Ethanol reductant dosing strategy

Fig. 8 shows the ethanol dosing control based on the open loop control. The NOx concentration MAP and exhaust flux MAP, which consist of a two-dimensional look-up table filled with engine bench test results, were a function of engine speed and load. It represents roughly the amount of NOx to be converted and the space velocity. Also the effect of the engine intake air temperature on the NOx emission is taken into account. The NOx conversion efficiency was predicted by combining the catalyst temperature, SV and catalyst aging time. Then the basic

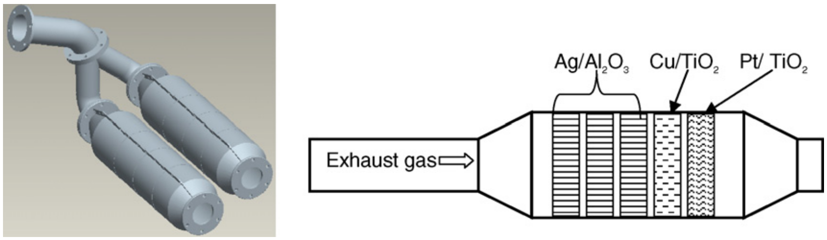

Fig. 7. . CAD model of exhaust pipe and catalysts layout in converter.

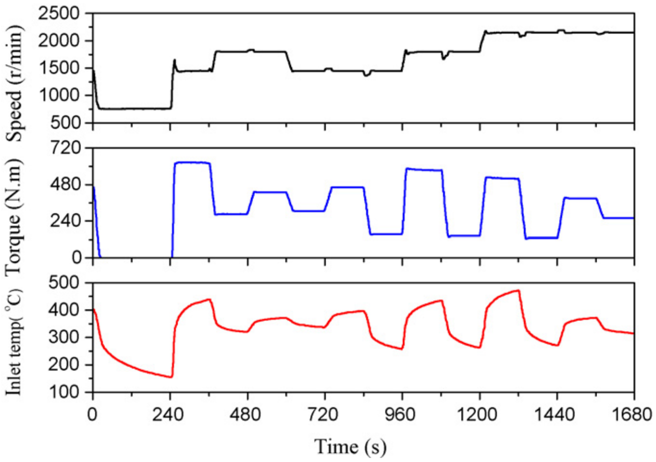

Fig. 9. Inlet temperature, torque, speed in the ESC test mode.

pulse width was set based on the amount of NOx and conversion efficiency. Finally the pulse width was adjusted by a function depending on the voltage of the reductant injector.

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

3.4.2. *ESC test cycle results*

Fig. 9 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 III limit.

To investigate dynamic response performance of the ethanol dosing system, the engine-out emissions and tailpipe emissions during the whole ESC test cycle were measured per second. Fig. 10 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 whole test cycle. However there is almost no NOx conversion in four modes, which were corresponding to the four THC slip peaks. As shown in Fig. 9, 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 Fig. 9, the NOx conversion can quickly get to a high level by this excessive dosing strategy.

Table 5
ESC cycle test results

	NOx (g/kW h)	THC (g/kW h)	CO (g/kW h)
Engine-out	13.06	0.30	0.41
SCR + DOC	4.63	0.34	0.34
Euro III limits	5.0	0.66	2.1

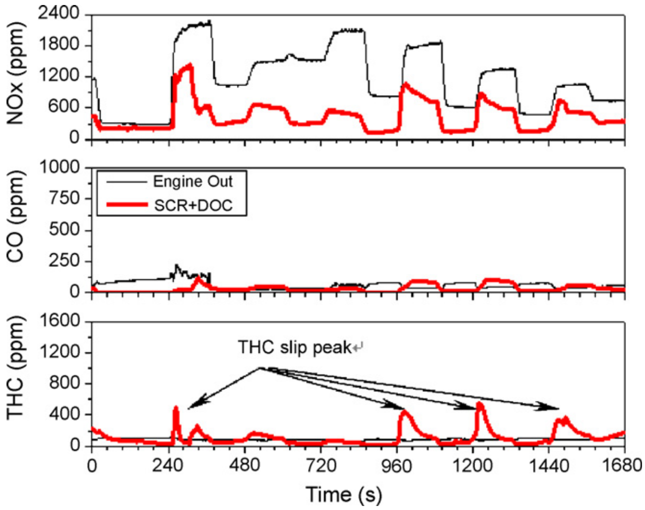

Fig. 10. Engine-out and tailpipe emissions during the ESC test cycle.

4. Conclusions

(1) The NOx conversion efficiency will go up with the increase of the ethanol dosage, but cause the great increase of CO and THC emissions at the same time. As the CO is the by-product of NOx selective reduction reaction, an additional oxidation catalyst to reduce the CO is needed.

(2) Under the condition of fresh catalyst with SV = 30,000 h^{-1}, a high NOx conversion (up to 90%) can be obtained in the range of 350–450 °C, while it is reduced beyond the range. However the NOx conversion was decreased after 30 h aging test. The sulfur absorbed on catalyst surface is a main reason for the decreasing of the catalyst activation.

(3) Under the condition of inlet temperature 400 °C and n_E:n_{NOx} = 1.5, the NOx conversion can maintain above 70% when the space velocity is below 50,000 h^{-1}. However the NOx conversion decreases linearly with the increasing of the space velocity, and under the condition of SV = 80,000 h^{-1}, the NOx conversion decreases to less than 50%.

(4) The Ag/Al_2O_3 catalyst can effectively decrease the SOF of PM, but has no effect on DS. The catalyst can decrease the sulfate slightly when temperature is below 410 °C, but dramatically increase the sulfate when the inlet temperature is at 470 °C. In general, 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 is at 470 °C.

(5) In the application test of the catalyst, an aftertreatment system composed of Ag/Al_2O_3 + Cu/TiO_2 + Pt/TiO_2 catalysts and ethanol dosing control based on the open loop control were designed. The engine emissions based on the ESC test cycle shows that the engine can completely meet EURO III regulations with an original NOx emission of 13.06 g/kW h.

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