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Evaluation of Cu-Based SCR/DPF Technology for Diesel Exhaust Emission Control

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ABSTRACT

Recently, a new technology, termed 2-way SCR/DPF by the authors, has been developed by several catalyst suppliers for diesel exhaust emission control. Unlike a conventional emission control system consisting of an SCR catalyst followed by a catalyzed DPF, a wall-flow filter is coated with SCR catalysts for controlling both NOx and PM emissions in a single catalytic converter, thus reducing the overall system volume and cost. In this work, the potential and limitations of the Cu/Zeolite-based SCR/DPF technology for meeting future emission standards were evaluated on a pick-up truck equipped with a prototype light-duty diesel engine.

INTRODUCTION

The selective catalytic reduction of NOx by urea (urea-SCR) is one of the most promising technologies for diesel engine NOx emission control. Compared to the competing lean NOx reduction technologies such as the NOx adsorber technology (e.g., lean NOx trap), it offers a number of advantages, including excellent NOx reduction efficiency over a wide temperature range and overall lower system cost.

The SCR technology using ammonia as reductant (NH_3-SCR) has been proven effective and used commercially for the removal of NO_x emissions from stationary sources since the 1970s. Because of the challenges associated with storage, handling and transportation of NH_3 on a vehicle, urea is being considered as an NH_3 storage compound in the form of an aqueous urea solution for mobile applications [1]. When the aqueous urea solution is sprayed into a hot exhaust gas stream, urea is decomposed to release NH_3, which is then used to reduce NOx over the downstream SCR catalyst.

A typical aftertreatment system for diesel engines using the SCR technology consists of an oxidation catalyst (DOC), an SCR catalyst, and a catalyzed particulate matter filter (CDPF), which are placed in a specific serial order to achieve a desired level of emission reduction performance: DOC+SCR+CDPF or DOC+CDPF+SCR. The DOC+SCR+CDPF system architecture results in the rapid warm-up of the SCR catalyst and thus the best NOx reduction performance during the cold-start FTP. The exhaust system architecture of DOC+CDPF+SCR [2] results in difficulty controlling the NOx emission during the cold start, especially from the larger engines. However, it is easier to regenerate the filter, which requires a periodic cleaning to remain effective.

Recently, the 2-way SCR/DPF technology has been developed by some catalyst suppliers. Unlike a conventional DPF catalyzed with the usual precious metals such as Pt and Pd, a wall-flow particulate matter (PM) filter is coated with SCR catalysts as shown in Figure 1. Thus, both NOx and PM can be removed in a single catalytic converter, reducing the overall system volume, mass and cost. In addition, both the DPF and NOx reduction functions are precious group metal free, resulting in further substantial cost savings. Compared to the system architectures described above, this technology allows rapid warm-up of the SCR catalyst during the cold-start period (vs. DOC+CDPF+SCR), and lower temperature exposure for the DOC and SCR catalysts during the PM filter regeneration (vs. DOC+SCR+CDPF).

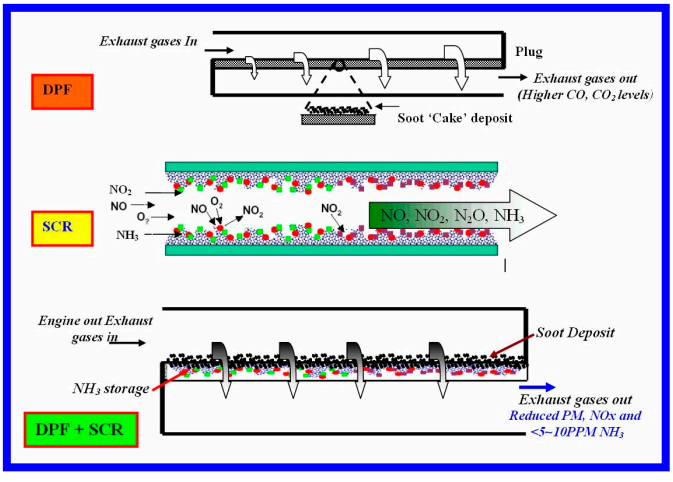

Figure 1. 2-way SCR/DPF Concept (Courtesy of Prof. C.J. Rutland, University of Wisconsin)

In this project, a Cu/Zeolite-based SCR/DPF technology

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prototype light-duty diesel engine for its emission reduction performance during the cold-start FTP and US06 tests. Also examined were NOx reduction efficiency at high temperatures encountered during the filter regeneration by in-cylinder post injections, and the catalyst durability of the system following the regeneration.

EXPERIMENTAL

A Chevy Silverado pick-up truck equipped with a prototype 4.9L 6-cylinder diesel engine was used for this project. As shown in figure 2, the aftertreatment system included a close-coupled DOC (0.85L), an under-floor (U/F) DOC (2.3L), and the 2-way SCR/DPF catalyst. Most of the catalysts used in this study were aged in the oven to simulate low mileage (LM) and high mileage (HM) aging (shown in Table 1), mainly to capture high temperatures encountered during the DPF regeneration mode. For the injection of aqueous urea solution (32.5 wt.% urea), an airless urea dosing system was used. A static mixer was also used to improve the mixing of urea spray in the exhaust. Both the engine and the urea dosing system were controlled using ETAS INCA hardware and software, and all of the control algorithms were developed in-house using the ETAS ASCET rapid prototyping system. Ultra low sulfur diesel fuel (7-15 ppm S; Cetane number = 40-50) was used for the vehicle calibration work and emission tests.

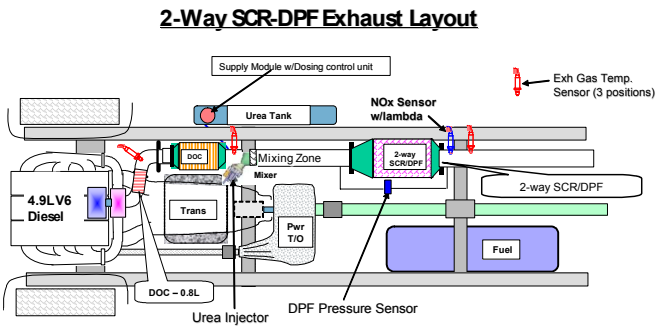

Figure 2. Exhaust system configuration

The exhaust system instrumentation included three temperature sensors for monitoring the exhaust gas temperature, and two NOx sensors for monitoring the NOx concentrations. In addition, K-type chromel-alumel thermocouples were installed at various locations. Figure 3 shows the construction details of the test samples used in this work. For this picture, the DPF substrate had a small section removed to allow examination of the component details. As can be seen in Figure 3, the 2-way SCR/DPF appearance is identical to a standard DPF.

All the emission tests were conducted at the GM Powertrain Emission Laboratories at the Milford Proving Ground. Four emission benches equipped with analyzers for NOx, THC, and CO were used to collect were then used for the engine and emission calibration development. At the tailpipe (TP) location, the dilution and proportional sampling method was used with various analyzers to collect the bag test results to report the tailpipe emissions of all the species, including NOx, THC (CH_4, NMHC), CO, CO_2, PM, NH_3, and N_2O. In addition, the carbon balance technique was used to estimate the fuel economy during the test.

Figure 3. 2-way SCR/DPF hardware

Table 1. Specifications and aging conditions of the U/F DOC and Cu/Zeolite-based 2-way SCR/DPF used in this study

Sample ID	Size	Cell Density	PGM loading	Aging	Aging Condition
U/F DOC					
DOC(1)	2.3L (5"x8"x4")	400	1:0:0/70	low miles	300°C/38h + 500°C/19h on the engine
DOC(2)		400	1:1:0/120	low miles	700°C/3h in the oven*
SCR/DPF					
LM 2-way	8.0L (7.5"x11")	300	N/A	low miles	700°C/4h in the oven*
HM 2-way	8.7L (7.5"x12")	200		high miles	700°C/100h + 750°C/20h in the oven*

*Hydrothermal aging with 10% H_2O in air

FTP COLD START AND US06 PERFORMANCE

As listed in Table 2, when the 8.0L low-mileage-aged Cu/Zeolite 2-way SCR/DPF (LM 2-way) was tested for FTP cold start, ~84% NOx conversion was obtained with just 5 mg/mi NH_3 slip. On the other hand, when the 8.7L high-mileage-aged 2-way SCR/DPF (HM 2-way) was used, ~82% NOx conversion was obtained with 3 mg/mi NH_3 slip. These test results were found to be very encouraging when compared with the NOx conversion performance of a 10L HM-aged Cu/Zeolite SCR catalyst

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HC, CO, NOx, PM, temperatures, etc.) were similar, ~86% NOx conversion was obtained over the HM-aged Cu/Zeolite catalyst with 2 mg/mi NH_3 slip. Therefore, it appears that the NOx reduction efficiency of the 2-way Cu/Zeolite SCR/DPF is comparable with that of a standard flow-through Cu/Zeolite SCR catalyst.

Table 2. Summary of selected emission test results*

Sample ID	EO NOx	TP Emissions						% NOx
		HC	CO	NOx	NH_3	N_2O	PM	
FTP								
HM Cu/Z	.694	.061	.252	.105	.002	.036	.345	86
LM 2-way	.539	.078	.361	.088	.005	.043	N/A	84
HM 2-way	.522	.060	.443	.096	.003	.066	.008	82
US06								
LM 2-way	1.32	.026	2.59	.048	.022	.144	.054	96
HM 2-way	1.50	.089	3.16	.110	.419	.137	.060	93

*All reported in g/mi

In addition, as shown in Figure 4, 67 out of 96 mg/mi tailpipe (TP) NOx occurs with the HM 2-way system during Phase 1 of the FTP test, with 63 mg/mi NOx breakthrough during the Cycle 1 and 2 alone. Thus, with improved engine calibration during the cold-start period, it may be possible to meet the Tier II Bin 5 standards (0.070 g/mi NOx at 120k miles) using the 2-way SCR/DPF technology.

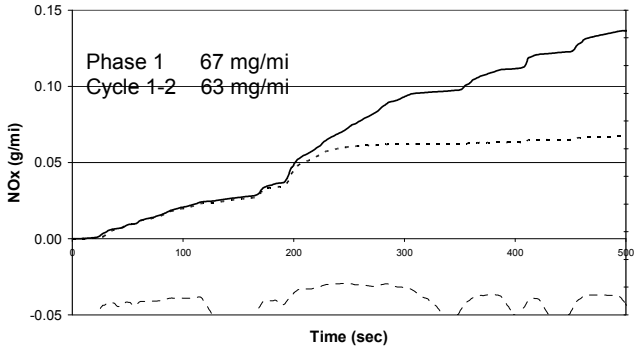

Figure 4. Cumulative NOx emission during Phase 1 of a cold-start FTP test with the HM-aged 2-way system

Solid line: engine-out NOx; Dotted line: tailpipe NOx

US06 PERFORMANCE

Over 90% NOx reduction efficiency was obtained during the US06 tests with the 2-way SCR/DPF technology. As shown in Table 2, ~96% NOx conversion was obtained with just 22 mg/mi NH_3 slip and 144 mg/mi N_2O over the HM 2-way system. The same engine and urea dosing calibrations were used for these tests. Thus, the observed large increase in the ammonia slip from the HM 2-way system can be attributed to the decreased oxidation of NH_3 to N_2 over the Cu catalyst after the aging.

During the US06 tests, the catalyst temperature ranged from 400°C to 550°C for the LM-aged system, and 450°C to 600°C for the HM-aged system. This increase in temperature may be due to the increase in back pressure. For example, the maximum back pressures across the LM and HM 2-way systems, which were observed at 81 mph during the test, were 27 kPa and 55 kPa, respectively. However, the high NOx conversions observed with both systems seem to indicate that the back pressure difference did not influence the NOx reduction efficiency of the 2-way SCR/DPF system significantly.

As mentioned above, the 2-way system was exposed to high temperatures during these tests. Since NH_3 can be selectively oxidized to N_2 over a Cu/Zeolite catalyst at high temperatures (e.g., >350°C), urea dosing rate was increased to compensate for the loss of NH_3 due to its oxidation, and thus to ensure that a sufficient amount of NH_3 was available for the SCR reaction. This overdosing of urea solution resulted in high NOx conversion efficiency without excessive NH_3 slip for the LM 2-way system. However, as indicated by the increased NH_3 slip over the HM 2-way system, urea dosing rate must be adjusted to maximize the NOx reduction and to minimize the NH_3 slip, depending on the degree of catalyst aging.

EFFECTS OF SOOT LOADING ON NO_x REDUCTION EFFICIENCY

In the 2-way SCR/DPF technology, the SCR catalyst materials are washcoated on a wall-flow filter substrate, unlike the conventional flow-through urea-SCR systems. Thus, the effect of soot loading on the NOx reduction efficiency of the SCR catalyst was examined for the FTP and US06 tests.

The NOx reduction efficiency was calculated from the modal engine-out NOx and tailpipe NOx concentrations, while the soot loading on the SCR/DPF system was estimated based on the engine-out PM and the accumulated mileage after a "passive" regeneration of the filter. During this "passive" regeneration, soot was gently removed at 450°C for ~45 min in the absence of EGR and urea injection. The complete removal of soot was assumed, although 3-4 kPa higher ΔP was often observed after each regeneration.

When the NOx reduction efficiency was plotted as a function of soot loading during the FTP Phase 2 tests (shown in Figure 5), it was found that ~95% NOx reduction efficiency was obtained regardless of the soot loadings up to 5 g/L. No correlation was found between

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FTP Phase 3 and US06 tests. Therefore, despite various other factors that may influence the NOx reduction efficiency, it appears that there is no clear effect of soot loading on the NOx reduction efficiency of the 2-way SCR/DPF system, at least up to 5 g/L of soot loading, based on the tests performed to date.

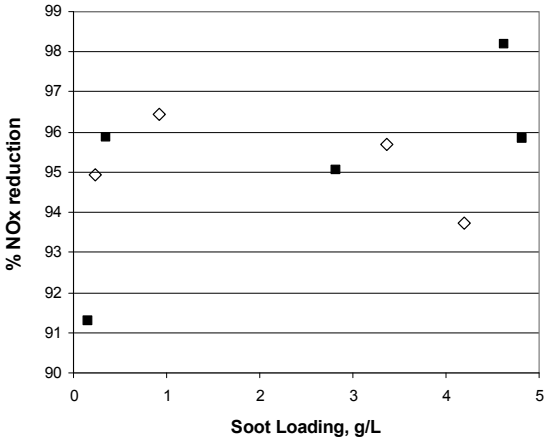

Figure 5. Effect of soot loading on the NOx reduction efficiency during Phase 2 of the FTP tests

Closed square: LM 2-way; Open diamond: HM 2-way

NO_x REDUCTION PERFORMANCE DURING FILTER REGENERATION

FILTER REGENERATION BY IN-CYLINDER POST INJECTIONS

Although there was no evidence that the NOx reduction efficiency of the 2-way SCR/DPF was adversely affected by the level of soot loading, the 2-way system requires a periodic regeneration just like any catalyzed filter to remain effective for PM emission control. The soot removal performance of the 2-way system was examined using the in-cylinder post injection strategy.

If the filter regeneration is not achieved during regular driving by a customer, then the regeneration should be forced. This "active" regeneration is typically accomplished by creating an exotherm over the DOC, which then raises the inlet temperature of a filter (e.g., ~650°C) to achieve faster soot oxidation rate. For the "active" regeneration of the 2-way system, the in-cylinder post injection technique was developed by modifying the existing engine calibration parameters. Calibration parameters, such as temperature settings, post injection fuel quantity, intake throttle position, etc., were adjusted to raise the inlet gas temperature after the first hill of the Cycle 2 during an FTP test. Although large temperature swings (between 500 and 750°C) were observed for the inlet gas temperature, overall, the inlet gas temperature remained above 600°C for ~10 min, and the outlet gas temperature remained above 550°C for 12-15 min during an FTP test.

After the filter was fully cleaned of soot by the "passive" regeneration technique, ~2 g/L soot was loaded on the 120k-aged SCR/DPF system. During the subsequent cold-start FTP test, the filter regeneration was carried out during the Phase 1 and 2. Compared to a previous FTP test conducted with a clean filter, the pressure drop (ΔP) across the 2-way system was high at the beginning of the test, but came down to the same low level at the end of the test, indicating the regeneration of the filter.

NO_x REDUCTION EFFICIENCY & NH_3 OXIDATION DURING FTP COLD START FILTER REGENERATION

The NOx reduction potential of the 2-way SCR/DPF was further examined using the second unit of the HM 2-way part, because the first unit was damaged during the post injection strategy development. As mentioned above, the inlet gas temperature ranged from 500 to 750°C during the FTP cold-start filter regeneration tests. Although the laboratory reactor data suggested over 80% NOx reduction efficiency for Cu/Zeolite catalysts at these temperatures, the NOx reduction efficiency of the HM 2-way system was only ~56%. Due to high engine-out (EO) NOx emissions during the regeneration, this low NOx reduction efficiency resulted in high tailpipe (TP) NOx emissions (e.g., ~1 g/mi). Both the engine-out NOx and the tailpipe NOx emissions can be reduced by improving the engine calibration. However, high tailpipe NOx emissions during filter regeneration may require even higher NOx reduction performance for the 2-way system during the test cycles, when the inventory of NOx emissions is considered.

Interestingly, NOx concentrations increased between the engine and the SCR catalyst inlet during the filter regeneration. Thus, among many factors, the oxidation of ammonia over the mixer and the exhaust pipe, as well as the rear side of the hot DOC was examined by measuring the NOx concentrations at the turbo-out, the outlet of the DOC, and the inlet of the SCR/DPF catalyst.

Table 3. Effect of Ammonia-to-NOx Ratio (ANR) on the TP Emissions during the Phase 2 (all reported in g/mi)

ANR	EO NOx	Add'l NOx btw EO & 2-way	TP NOx	%NOx Conv.	TP NH_3	TP N_2O
1.6	1.630	.492	.716	56	N/A	.182
2	1.614	.534	.703	56	.045	.192
4	1.620	.554	.811	50	.132	.315

As summarized in Table 3, the NOx reduction efficiency remained the same at ~56% regardless of the urea dosing rate (shown as the ammonia-to-NOx ratio) during the Phase 2, where the variance in temperatures among different tests is small. However, a significant amount of NOx was produced from the ammonia oxidation reaction

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dosing rate, it was estimated that only ~5% of NH_3 was oxidized to NOx at these temperatures. Excluding this additional NOx from NH_3 from TP NOx, higher NOx reduction efficiency (84~90%) similar to the reactor test results was obtained. However, the TP NH_3 and N_2O emissions increased with increasing ANR.

Therefore, in view of the oxidation of NH_3 to NOx over the rear side of the hot DOC, the exhaust pipe and the mixer prior to the SCR catalyst, additional refinement in the urea dosing rate must be required to achieve the maximum NOx reduction and the minimum NH_3 slip at higher temperatures.

CATALYST DEACTIVATION BY HIGH TEMPERATURE FILTER REGENERATION

NO_x REDUCTION EFFICIENCY OF SCR/DPF

Since the NOx reduction efficiency of a typical Cu/zeolite catalyst decreases rapidly with increasing temperatures above 550°C, NOx reduction performance of the 2-way SCR/DPF technology was examined during the course of the post injection strategy development. As summarized in Table 4, the NOx reduction efficiency decreased from ~82% to ~76% for the FTP, and from ~93% to ~54% for the US06. The low NOx reduction efficiency observed during the cold-start FTP tests can be attributed to a number of factors, such as inadequate test preparation, HC poisoning due to a misfire or use of excessive EGR, and insufficient NO_2 formation over the DOC, in addition to the deactivation of the DOC and SCR catalysts. On the other hand, the loss of NOx reduction efficiency during the US06 tests conducted using the same engine and emission calibrations can primarily be attributed to the deactivation of the 2-way SCR/DPF system, because its performance at high temperatures is independent of the DOC performance and ammonia storage. Therefore, when the HM 2-way system was replaced by another HM 2-way part, the NOx reduction performance of the 2-way system was recovered for the US06 test, but not for the FTP test (i.e., 54% → 91% and 76% → 71%, respectively).

The durability of the HM 2-way system was further examined by measuring the NOx reduction performance following 5 "active" filter regenerations. Following these 5 filter regenerations via post injections, the U/F DOC(1), which had been exposed to high temperature excursions, was replaced with DOC(2), which contained a more thermally durable formulation. The NOx reduction performance of the HM 2-way system with the LM DOC(2) was then examined for the FTP and US06 tests. As shown in Table 4, low NOx reduction efficiency was observed for both the FTP and US06 tests (i.e., 77% and 76%, respectively).

The low FTP & US06 performance indicates that the current Cu/Zeolite SCR catalyst formulation may not withstand the temperature and air-to-fuel ratio during the 5 regenerations were analyzed. During the 5 regeneration attempts of the HM 2-way(2), which had already been oven-aged at 750°C for 20h, the inlet gas temperature never exceeded 750°C, and both the front and rear bed temperatures remained below 720°C. On the other hand, the tailpipe air-to-fuel (A/F) ratio during the regeneration attempts was found to dip below 20. In particular, the A/F ratio dipped below 15 during one regeneration attempt. The performance degradation of the HM 2-way system may have been caused by the reducing environment at elevated temperatures, not just the high temperatures encountered during the regeneration attempts.

Table 4. Summary of selected emission test results before and after the filter regeneration

Sample ID	EO NOx	TP Emissions (g/mi)						% NOx conv.
		HC	CO	NOx	NH_3	N_2O	PM	
FTP								
HM 2-way(1)*	.493	.060	.443	.096	.003	.066	.008	82
HM 2-way(1)§	.667	.091	.944	.161	.009	.074	.005	76
HM 2-way(2)†	.595	.107	.988	.171	.012	.032	.005	71
HM 2-way(2)‡	.593	.060	.684	.135	.005	.048	N/A	77
US06								
HM 2-way(1)*	1.50	.089	3.155	.110	.419	.137	.060	93
HM 2-way(1)§	1.41	.033	3.295	.654	N/A	.167	.032	54
HM 2-way(2)†	1.42	.047	4.448	.126	.359	.122	.051	91
HM 2-way(2)‡	1.27	.014	.927	.296	N/A	N/A	.000	76

*Baseline of the HM 2-way with DOC(1) before regenerations

§ HM 2-way(1) with DOC(1) during the regeneration strategy development

† HM 2-way(2) before regenerations, but with "damaged" DOC(1)

‡ HM 2-way(2) after 5 regenerations, but with DOC(2)

OXIDATION PERFORMANCE OF DOC

The oxidation performance of the DOC is critical for effective NOx reduction over the downstream SCR catalyst, because HC can poison the active sites for the SCR reaction, and NO_2 can improve the low-temperature SCR reaction kinetics. Thus, the oxidation performance of the DOC was compared before and after the high temperature excursions.

Overall, the oxidation performance for HC, CO, and NO was all improved, following the high temperature

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