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Enhanced Durability of a Cu/Zeolite Based SCR Catalyst

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ABSTRACT

Passenger and light duty diesel vehicles will require up to 90% NOx conversion over the Federal Test Procedure (FTP) to meet future Tier 2 Bin 5 standards. This accomplishment is especially challenging for low exhaust temperature applications that mostly operate in the 200 - 350°C temperature regime. Selective catalytic reduction (SCR) catalysts formulated with Cu/zeolites have shown the potential to deliver this level of performance fresh, but their performance can easily deteriorate over time as a result of high temperature thermal deactivation. These high temperature SCR deactivation modes are unavoidable due to the requirements necessary to actively regenerate diesel particulate filters and purge SCRs from sulfur and hydrocarbon contamination. Careful vehicle temperature control of these events is necessary to prevent unintentional thermal damage but not always possible. As a result, there is a need to develop thermally robust SCR catalysts. Fe/zeolite formulations are known to exhibit superior hydrothermal stability over Cu/zeolite formulations. However, current Fe/zeolite formulations are not very active for NOx conversion in the desired 200 – 350°C temperature regime under conditions having low NO_2/NOx ratios. From previous studies, Cu/zeolite formulations have demonstrated never-to-exceed temperatures up to 775°C. In this work, a laboratory flow reactor was utilized to hydrothermally age and evaluate the latest state-of-the-art Cu/zeolite formulations. Results confirm remarkable high temperature hydrothermal stability up to 950°C while maintaining stable low temperature NOx activity. A broad range of time-at-temperature hydrothermal aging was carried out to clearly define the full durability range. The aging time was varied from 1 hour to 256 hours while the aging temperature was varied from 670°C to 1100°C. The catalyst performance was evaluated under a synthetic exhaust gas mixture commonly known as the "Standard" SCR reaction.

INTRODUCTION

The operating conditions over the Federal Test Procedure (FTP) results in high NOx emissions in the 200 – 350°C temperature range. From current light-duty diesel applications, the future Tier 2 Bin 5 emission standards will require up to 90% reduction in the tailpipe NOx emissions.

Implementation of zeolite based components has been extensively studied for application in gasoline and diesel aftertreatment devices. However, the harsh high exhaust temperatures observed in typical gasoline vehicles have limited their widespread use. On the other hand, the relatively milder diesel exhaust temperatures have encouraged continued development of zeolites as a major component in aftertreatment devices.

One promising diesel aftertreatment technology containing zeolite is the Selective Catalytic Reduction (SCR) of NOx with an ammonia-based reductant such as aqueous urea. As stated in equation (1), NOx reduction is possible due to the high selectivity of the ammonia (NH_3) and nitrogen oxide (NO) reaction to form elemental N_2. In the absence of nitrogen dioxide (NO_2), this reaction is referred to as the "Standard" SCR reaction [1]. Additionally, the SCR reaction containing 50% NO and 50% NO_2 is referred to as the "Fast" SCR reaction (equation 2).

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad \text{"Standard"} \quad (1)$$

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \quad \text{"Fast"} \quad (2)$$

Vanadium, Fe/zeolite, and Cu/zeolite based SCR formulations are very active for the "Standard" SCR reactions. However, vanadium based formulations have been shown to easily deactivate when exposed to temperatures necessary to actively regenerate Diesel particulate filters (DPFs) with oxygen [2]. This cannot be avoided since a DPF is currently required to meet Tier 2 Bin 5 particulate matter (PM) emission standards. Fe/zeolites have been shown to be much more durable to high temperature exposure. However, in the absence of NO_2, Fe/zeolites lack the low temperature (200 - 350°C) NOx activity necessary for high FTP efficiency. In this critical temperature range, Cu/zeolite formulations have been reported to have much lower sensitivity to the NO_2/NOx ratio. As a result, Cu/zeolite formulations have been shown to achieve high NOx conversion at the desired low operating temperatures. Their lack of hydrothermal stability above 775°C has drawn questions

about their long-term in-use durability and robustness to occasional over-temperature events.

Improvements in the thermal durability of Cu/zeolite based SCR formulations has been highly desirable and pursued by many research institutes and catalyst suppliers.

This paper discusses the performance and hydrothermal durability of an enhanced Cu/zeolite based SCR formulation exhibiting durable low temperature NOx activity under a wide matrix of time-at-temperature aging conditions. On key aged samples, surface area measurements and Cu reduction measurements are performed to investigate changes in the zeolite and Cu state, respectively.

EXPERIMENTAL

SAMPLE PREPARATION

A full size monolith washcoated with a state-of-the-art Cu/zeolite based SCR formulation was obtained from a catalyst supplier in 2007. The cordierite-based monolith measured 20.3cm diameter x 15.2cm length with 400 cells per square inch (CPSI) and 4.5 mil wall thickness. The SCR monolith was completely cored and cut into 160 round samples measuring 2.54cm diameter x 2.54cm length. From this, a normal distribution was observed where the 95% confidence interval around the mean mass was determined to be ± 0.4%. Older formulations mentioned in this paper did not necessarily exhibit the same distribution in mass.

HYDROTHERMAL AGING

As configured in Diagram 1, sample cores were hydrothermally aged in flowing gas from an automated flow reactor system. The total flow rate utilized was 6.44 liters/min. The synthetic gas composition consisted of 14% O_2, 5% H_2O, 5% CO_2, and balance N_2. For each aging, three samples measuring 2.54cm diameter x 2.54cm length were placed in a quartz reactor tube and labeled A, B, and C. The three SCR samples were separated by 30mm to ensure well distributed gas flow in all channels. An uncoated cordierite monolith was placed upstream to serve as a gas heat exchanger. The uncoated monolith ensured an isothermal gas temperature across each sample. Samples positioned in location "A" were used for surface area measurements. Samples positioned in location "B" were used for temperature-programmed reduction measurements (TPR). Samples positioned in location "C" were used for the NOx conversion evaluation tests.

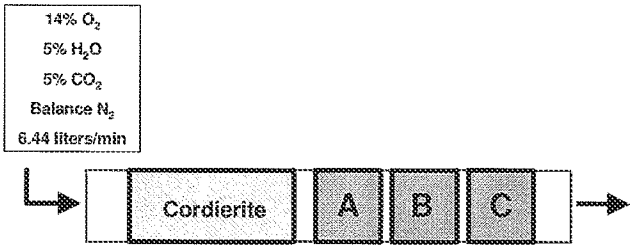

DIAGRAM 1. Sample configuration during hydrothermal aging.

A wide range of time-at-temperature hydrothermal aging was carried out to clearly define the full durability range of a promising Cu/zeolite SCR formulation. The hydrothermal aging duration was varied from 1 hour to 256 hours while the aging temperature was varied from 670℃ to 1100℃. Totaling 1116 aging hours, Table 1 defines the 24 different aging conditions utilized in this study. Special attention was considered to determine the short-term never-to-exceed (NTE) temperature and the long-term SCR durability necessary to withstand the temperature resulting from DPF regeneration events. For a given aging duration, the NTE is defined as the temperature at which the NOx conversion decay accelerates significantly.

Temp. (℃)	Hydrothermal Aging Duration (hours)								
	1	2	4	8	16	32	64	140	256
670							X		
700	X				X	X	X		X
750									
800	X				X	X	X	X	X
850							X		
900	X		X	X	X		X		
950	X	X	X	X					
1000	X								
1100	X								

TABLE 1. Time-at-temperature hydrothermal aging matrix.

LABORATORY CATALYST EVALUATION

Fundamental catalyst activity data were obtained using an automated laboratory-scale flow reactor system. Custom-written LabVIEW based software with National Instruments data acquisition hardware controlled MKS mass flow controllers and Lindberg Mini-Mite tubular furnaces. A computer controlled evaluation protocol was developed and run for each sample to decrease the test-to-test variations commonly observed by manual operation. Table 2 shows the simulated diesel exhaust gas composition flowed through each sample core to study the "Standard" SCR reaction.

Gas Compositon	Concentration
NO (ppm)	350
NO_2 (ppm)	0
NH_3 (ppm)	350
O_2 (%)	14
CO_2 (%)	5
H_2O (%)	5
Balance	N_2

TABLE 2. Simulated gas composition used to study performance for the "Standard" SCR reaction.

For all evaluations, the total gas flow rate was held constant at 6.44 liters/min while the sample size was held constant at 2.54cm diameter x 2.54cm length. As a result, a space velocity equal to 30,000/hr was used in this study. For the typical light-duty diesel vehicle operating over the FTP drive cycle, this space velocity corresponds to a SCR monolith size between 100% - 150% of the engine swept volume.

The SCR inlet gas temperature was maintained with one preheat tubular furnace followed by a second tubular furnace. SCR samples were loaded in quartz tubing and placed in the second tubular furnace. A Thermo Electron Antaris IGS FTIR Gas Analyzer with a heated sample cell was used at the outlet of the reactor to measure NO, NO_2, N_2O, NH_3, CO_2, and H_2O levels. To cover the full exhaust temperatures expected on diesel vehicles, data were taken at SCR inlet gas temperatures from approximately 150°C to 700°C in 25-50°C steps. The computer-controlled evaluation protocol stepped the reaction temperature setting from a high temperature to low temperature for a prescribed duration. At each temperature setting, the duration was chosen so that post SCR gas composition was allowed enough time to completely equilibrate.

The flow reactor used in this study was examined to determine the test-to-test variability of the entire measurement system. Among numerous variables, the FTIR measurement, the thermocouple measurement, and precision of the mass flow controllers may collectively contribute large discrepancies in the data. This may make it difficult to conclude with confidence that one result is statistically different than another result. Repeated evaluation runs were made on a single pre-aged (64hr/670°C) SCR sample to determine the 95% confidence interval. Five evaluation runs were performed over the entire temperature range.

SURFACE AREA MEASUREMENTS

A Micromeritics ASAP 2400 instrument in conjunction with the well-known Brunauer, Emmet, and Teller (BET) equation was employed to determine the surface area of each SCR sample. The BET equation determines the surface area by establishing the relationship between the volume adsorbed at a given partial pressure and the volume adsorbed at monolayer coverage [3].

TEMPERATURE PROGRAMMED REDUCTION (TPR)

The Cu state within zeolite formulations changes during the SCR reaction and after hydrothermal aging. These physical-chemical changes yield different reduction temperatures. The TPR results reveal direct evidence of changing Cu-species in the catalyst and may be correlated to the deactivation of SCR activity after aging.

Temperature-Programmed-Reduction (TPR) was conducted on a Micromeritics AutoChem II 2920 instrument. Part of a catalyst sample (location "B") was sliced off and cut into small pieces, about 3 mm long. These small pieces were then loaded into a quartz reactor for TPR. Typically, 0.5 gram of sample was used in the experiment. The temperature was measured with a thermocouple in the catalyst bed. Prior to TPR, the catalyst sample was pretreated in 10%O_2/He at 600°C for 30 minutes and then cooled down to room temperature in 10%O_2/He. After the pretreatment, the gas flow was changed to 9%H_2/Ar at 20 ml/min. During TPR, the catalyst bed was heated to 600°C at a linearly increasing rate of 10°C/min. The change in H_2 concentration was monitored using Thermal-Conductivity-Detector (TCD). The consumption of H_2 indicated the reduction of oxidized Cu.

RESULTS AND DISCUSSION

FLOW REACTOR VARIABILITY

The variability of the evaluation flow reactor was determined by running a pre-aged SCR sample five times. The steady state "Standard" SCR reaction results for each of the five runs are overlaid in Figure 1. In addition, the 95% confidence interval around the mean

NOx conversion is shown in Figure 2. From Figure 1, the NOx conversion traces are virtually line on line for operating temperatures below 600°C. Above 600°C, the NOx conversion drops slightly after each subsequent evaluation run. For this particular SCR formulation, the explanation for this slight deactivation has to do with the additional aging the sample experiences during high temperature performance evaluations. This trend becomes more apparent with data presented later in this paper. Figure 2 more clearly defines the variability in the overall flow reactor system. The data from Figure 1 was manipulated in Minitab to yield the 95% confidence interval at each evaluation temperature. For evaluation temperatures below 600°C, the 95% confidence interval around the mean NOx conversion was better than ±2%. Due to catalyst deactivation with testing, the higher temperature points showed variability up to ±6%.

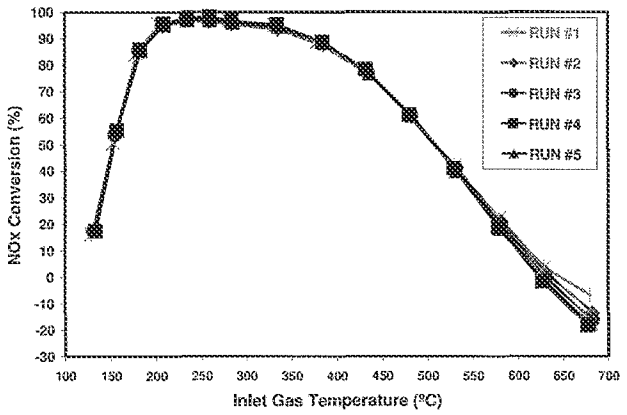

FIGURE 1. NOx conversion results for the STANDARD SCR REACTION. Five consecutive evaluation runs on a single sample aged 64 hours at 670°C.

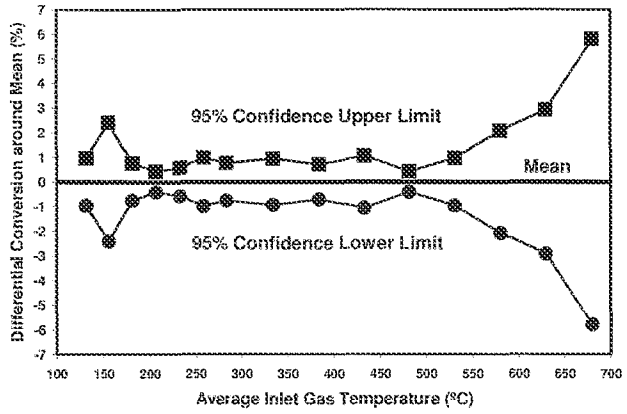

FIGURE 2. Calculated from Figure 1, the differential NOx conversion variability around the mean as determined by the 95% confidence interval.

RECENT SCR DURABILITY IMPROVEMENTS

Since current and future diesel aftertreatment systems contain DPFs, SCR formulations are required to withstand the high temperature process of regenerating soot-loaded particulate filters. A robust engine control strategy that lessens the variability of the actual regeneration temperature is critical to the durability of the SCR. For this study, the target active DPF temperature has been determined to be 670°C. Also, the total cumulative duration for the full vehicle useful life has been determined to be 64 hours. Therefore, the long-term hydrothermal stability of base metal-zeolite SCR catalysts for typical light-duty diesel applications must be able to endure, at minimum, 670°C for 64 hours.

Figure 3 shows the recent progress that has been made in Cu/zeolite SCR development. Many Cu/zeolite formulations have been aged and evaluated between 2005 and 2007. Steady improvements of NOx conversion have been made in the low temperature range (200 – 350°C). For example, at 200°C, the NOx conversion has been enhanced from 70% to 90%. In addition, the 2007 state-of-the-art SCR maintained 90%+ NOx conversion over a much larger temperature range. However, note that the enhanced low temperature activity came with a trade-off in the performance above 400°C.

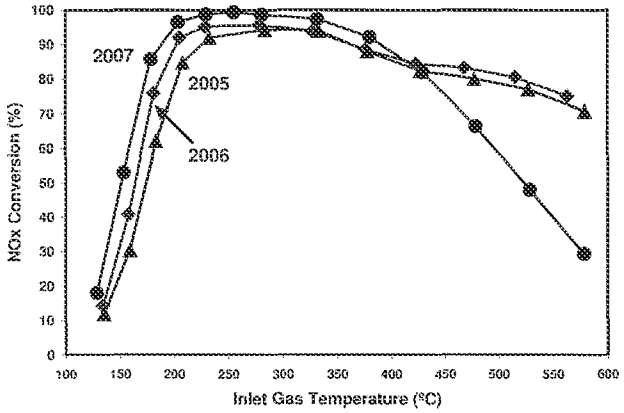

FIGURE 3. NOx conversion results for the STANDARD SCR REACTION. Best in class SCR catalyst formulations from 2005 -- 2007 after hydrothermal aging for 64 hours at 670°C.

As shown in Figure 4, the three SCR formulations generate measurable levels of N_2O as a by-product. The N_2O formation has a bi-modal profile as a function of temperature. The low temperature N_2O formation around 200°C is a result of NH_3 oxidation by NO whereas the high temperature N_2O formation around 525°C is mainly from the oxidation of NH_3 by O_2. The latest SCR formulation generates much less N_2O. At 200°C, the 2007 SCR formulation yielded up to 3 times less N_2O compared to the two older formulations.

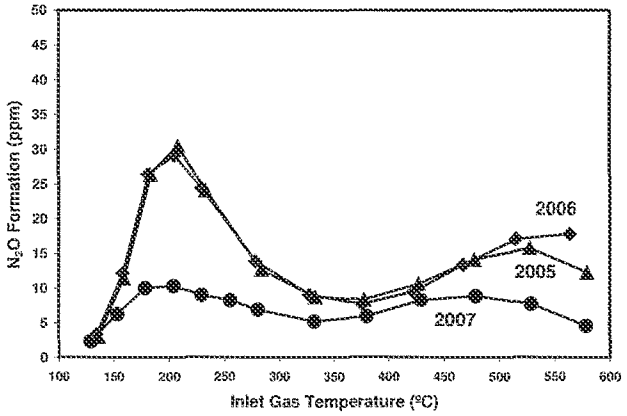

FIGURE 4. N_2O formation results for the STANDARD SCR REACTION in Figure 1. Best in class SCR catalyst formulations from 2005 – 2007 after hydrothermal aging for 64 hours at 670°C.

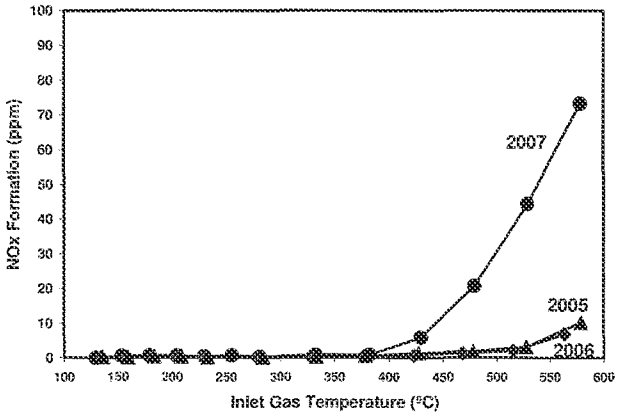

FIGURE 6. NOx formation (ppm) results for the ammonia oxidation reaction in the absence of NOx (FIGURE 5). Best in class SCR catalyst formulations from 2005 – 2007 after hydrothermal aging for 64 hours at 670°C.

Durable low temperature NOx performance is desirable for light-duty diesel applications. However, a considerable amount of NOx is emitted at high temperature during the time when the vehicle undergoes an active DPF regeneration. This added NOx emission must be compensated by additional NOx conversion during low temperature operation. As mentioned previously, the high temperature NOx performance of the 2007 SCR catalyst drops sharply as the temperature increases beyond 400°C (Figure 3). Figure 5 plots the NH_3 oxidation of the three catalysts in the absence of NOx. Ammonia is more strongly oxidized by the 2007 SCR catalyst. In addition, a clear inflection point at 400°C is observed which corresponds to the formation of NOx (Figure 6). As a result, the NOx performance in Figure 3 declines rapidly due to, in part, the remake of NOx from NH_3 oxidation (Figure 6).

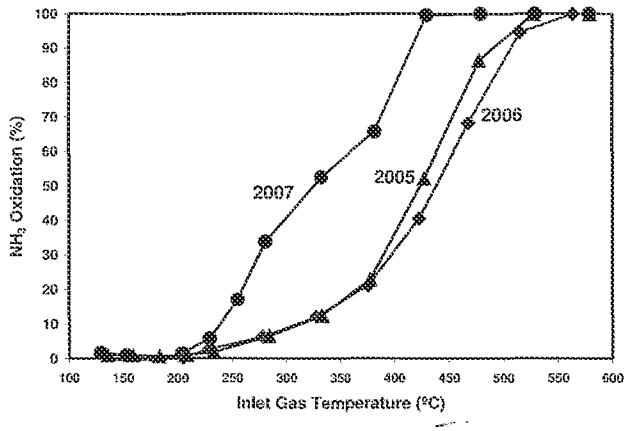

FIGURE 5. NH_3 conversion results for the ammonia oxidation reaction in the absence of NOx. Best in class SCR catalyst formulations from 2005 – 2007 after hydrothermal aging for 64 hours at 670°C.

Unrefined engine exhaust temperature control during DPF regeneration events coupled with inexact temperature measurement may expose SCR catalysts to an occasional unexpected over-temperature. As a result, the SCR formulations are screened with a robustness test protocol consisting of hydrothermal exposure at 900°C for 1 hour. These types of data are used to define the short-term never-to-exceed (NTE) temperature. The NTE testing provides a higher degree of discrimination among similar performing formulations compared to the less severe 64hr/670°C standard aging.

Figure 7 illustrates the remarkable progress that has been made in the past year with the durability of the 2007 Cu/zeolite based SCR formulation. Among the dozens of Cu/zeolite formulations tested in past years, no formulation has been able to withstanding exposure up to 900°C while maintaining stable NOx performance at 200°C. Under the 1 hour/900°C aging condition, the 2007 SCR catalyst retained 90% NOx conversion at 200°C. All older SCR formulations have achieved no better than 20% NOx conversion. The enhanced durability of the 2007 SCR formulations has been mainly attributed to advances in the zeolite type and composition.

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