

Laboratory Study of Soot, Propylene, and Diesel Fuel Impact on Zeolite-Based SCR Filter Catalysts

Giovanni Cavataio, James R. Warner, James W. Girard, Justin Ura, Douglas Dobson
and Christine K. Lambert
Ford Motor Company

Copyright © 2009 SAE International

ABSTRACT

Selective Catalytic Reduction (SCR) catalysts have been designed to reduce NO_x with the assistance of an ammonia-based reductant. Diesel Particulate Filters (DPF) have been designed to trap and eventually oxidize particulate matter (PM). Combining the SCR function within the wall of a high porosity particulate filter substrate has the potential to reduce the overall complexity of the aftertreatment system while maintaining the required NO_x and PM performance. The concept, termed Selective Catalytic Reduction Filter (SCRF) was studied using a synthetic gas bench to determine the NO_x conversion robustness from soot, coke, and hydrocarbon deposition. Soot deposition, coke derived from propylene exposure, and coke derived from diesel fuel exposure negatively affected the NO_x conversion. The type of soot and/or coke responsible for the inhibited NO_x conversion did not contribute to the SCRF backpressure. Reaction gas exposure at 450°C completely regained the NO_x conversion without regenerating the soot and without gaining backpressure relief. Similarly to the soot-loaded experiments, coke generated from propylene exposure negatively affected NO_x conversion for both Cu/zeolite SCRF formulations studied. However, coke generated from diesel fuel vapor impacted one Cu/zeolite SCRF catalyst formulation but not the other.

considered aftertreatment components to meet the upcoming U.S. Heavy-duty NO_x certification requirements. Diesel particulate filters washcoated with or without precious metals have been designed to trap and eventually oxidize particulate matter (PM). Selective catalytic reduction (SCR) catalysts have been designed to reduce NO_x with the assistance of NH₃ generated from urea. To achieve high NO_x and PM reduction efficiency, both of these individual components require a significant amount of brick volume relative to the engine displacement. Combining the SCR function within the wall of a high porosity particulate filter substrate has the potential to reduce the overall complexity of the aftertreatment system while maintaining the required NO_x and PM performance. In such a SCR/DPF combined system, termed Selective Catalyst Reduction Filter (SCRF), uncontrolled regeneration events will result in extreme temperature swings due to the oxidation of particulate matter. The thermal durability improvements of recent Cu/zeolite SCR catalysts have provided confidence toward attaining the required thermal robustness [1]. However, the NO_x activity of zeolite-based SCR formulations has been shown to be poisoned by the various types of hydrocarbon species contained in diesel exhaust [2]. In addition, both Cu/zeolite and Fe/zeolite SCR formulations have been shown to adsorb high levels of diesel fuel that can ultimately generate destructive exotherms up to 1000°C [3].

This paper discusses the NO_x conversion impact of SCRF catalyst formulations that have been preconditioned with laboratory-generated soot, propylene-generated coke, and diesel fuel-generated coke. Initially, the prime SCRFs were hydrothermally aged at 800°C for 64 hours to represent the projected full

INTRODUCTION

Diesel oxidation catalysts, urea selective catalytic reduction catalysts and diesel particulate filters are

useful life due to the likely exotherm resulting from active soot oxidation. Next, the SCRFs were exposed to three different types of preconditioning events before running the NO_x activity evaluations. First, an in-house developed soot generator prepared SCRF samples to investigate the impact of soot-loading [4]. Second, SCRF samples were exposed to a high level of propylene over a wide temperature range. Third, SCRF samples were exposed to diesel fuel vapor at 200°C - 400°C to investigate the NO_x activity inhibition resulting from diesel fuel adsorption and/or coke deposition. After each type of preconditioning, the SCRF catalyst samples were evaluated to determine the impact on NO_x performance.

EXPERIMENTAL

SAMPLE DESCRIPTION

Cordierite-based high porosity diesel particulate filter cores were obtained from a major substrate manufacturer. The laboratory DPF sample cores had a porosity around 65% and a mean pore size around 22 microns. The laboratory DPF core samples measured 2.54cm (1.0") in diameter by 7.62cm (3.0") in length. The SCRF samples had 300 cells per square inch (CPSI) and 12 mil wall thickness. All core samples were skinned and plugged to ensure high efficiency soot accumulation and gas flow through the wall. The plug length on both ends of the DPF measured approximately 0.95cm (3/8"). As a result, the effective wall-flow region of the core was reduced down to 5.72cm (2.25") in length. The latest state-of-the-art Cu/zeolite and Fe/zeolite SCR formulations were washcoated within the walls of the DPF samples. The Cu/zeolite formulations were coded CuSCR#1 and CuSCR#2. The Fe/zeolite formulation was coded FeSCR#1. Some experiments were performed on an uncoated filter monolith to investigate possible side reactions.

HYDROTHERMAL AGING

Cores were hydrothermally aged for the equivalent of 120,000 miles before evaluation in a synthetic gas bench. The amount of time at high temperature required to regenerate the typical DPF system was estimated to be 64 hours with frequent 800°C bed temperature spikes. Table 1 presents the gas composition utilized to hydrothermally age all laboratory SCRF samples studied in this paper. The aging was carried out with a flowing gas composition at 6.44 liters/minute. Relative to static gas aging, the flowing gas aging ensured more direct contact to the washcoat. This allowed for a greater opportunity for real-world deactivation due to a forced wall-flow profile rather than a static ambient condition. In this paper, all the data presented was obtained after pre-

aging each SCRF sample to this 64hr/800°C aging protocol.

Feed Gas Composition	Hydrothermal Aging Composition
O ₂ (%)	14.0
CO ₂ (%)	5.0
H ₂ O (%)	5.0
N ₂	balance
Flow Rate = 6.44 Liters/min	
SCRF Size = 1.0" diameter x 3.0" length	

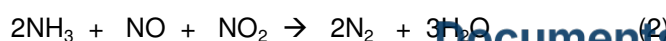
TABLE 1. Feed gas composition utilized to hydrothermally age all SCRF samples for 64hrs/800°C.

LABORATORY CATALYST EVALUATION

Fundamental catalyst activity data were obtained using a laboratory-scale flow reactor system. A computer controlled evaluation protocol was developed to help decrease the test-to-test variations commonly observed by manual operation. The reactor system utilized custom-written LabView software with National Instruments data acquisition hardware. The apparatus precisely controlled the gas composition levels with MKS mass flow controllers and furnace temperatures. Lindberg Mini-Mite tubular furnaces served to attain the target reaction temperatures.

For all evaluations, the total gas flow rate was held constant at 14.49 liters/min while the effective sample size was held constant at 2.54cm (1.0") in diameter by 5.72cm (2.25") in length. As a result, the space velocity equal to 30,000/hr was used in this study. The flow reactor consisted of quartz tubing within two furnaces placed in series. With the use of an inactive silicon carbide (SiC) flow-through monolith, the first furnace served as a gas preheat zone. The SCRF samples were situated in the second furnace. The SCRF bed temperature was measured by a thin K-type thermocouple located approximately 1.27cm (0.5") from the sample inlet. The NH₃ was injected into the main feed stream between the first and second furnaces.

Tables 2 and 3 present the simulated diesel exhaust gas composition flowed through each sample core to study the Standard SCR Reaction and the Fast SCR Reaction. The molar NH₃ to NO_x ratio was held constant at 1.0 to represent the stoichiometry of the well known Standard SCR Reaction and Fast SCR Reaction in Equations 1 and 2, respectively.



Documents

Document Sharing Hub

Feed Gas Composition	STANDARD SCR REACTION
NO (ppm)	350
NO ₂ (ppm)	0
NH ₃ (ppm)	350
O ₂ (%)	14.0
CO ₂ (%)	0.0
H ₂ O (%)	5.0
N ₂	balance

TABLE 2. Feed gas composition utilized to investigate the sample activity for the STANDARD SCR REACTION.

Feed Gas Composition	FAST SCR REACTION
NO (ppm)	175
NO ₂ (ppm)	175
NH ₃ (ppm)	350
O ₂ (%)	14.0
CO ₂ (%)	0.0
H ₂ O (%)	5.0
N ₂	balance

TABLE 3. Feed gas composition utilized to investigate the sample activity for the FAST SCR REACTION.

A MKS FTIR instrument with a heated sample cell was used at the outlet of the reactor to measure NO, NO₂, N₂O, NH₃, CO, and H₂O levels. Since CO₂ can interfere with CO detection, no CO₂ was used in the evaluation so that more sensitive measurements could be made on CO formation. Data were taken under both steady-state temperatures and dynamic temperature tests. For the steady-state measurements, the temperature was varied from 700°C to 125°C in 25-50°C increments in order to cover the normal operating range expected on a diesel vehicle. NO_x conversion was allowed to equilibrate before changing the catalyst temperature to the next level. For the dynamic temperature tests, the SCRf samples were allowed to reach a steady-state with flowing reaction gas conditions at 125°C. Next, the temperature was ramped to 750°C at 5°C/min in most experiments unless otherwise noted. The post-SCR emissions were measured as a function of temperature. The high temperature lean exhaust gas exposure was sufficient enough to completely remove deposited hydrocarbon, coke, and soot from the sample. For contaminated SCRf samples, the ramp test was run several times to determine the impact on NO_x conversion before and after the regeneration.

LABORATORY SOOT LOADING PROCEDURE

Samples having soot loading amounts were performed using a Ford developed soot generator [4]. The reactor can accommodate substrate samples of varying lengths with a diameter of 2.54cm (1 inch), but can be adapted to accommodate samples of other diameters. Generally, the system consists of 1) a locally rich propane flame, 2) a dilution system and 3) a pressure control loop. Propane was provided by a 1.27cm (1/2 inch) O.D. stainless steel tube (burner) that was held concentrically inside of a 25 mm quartz tube. Air was provided through the quartz tube such that the air formed an envelope around the propane flow. The end-cap of the quartz tube contained a glow plug that was used to initially ignite the fuel/air mixture. Following the cap, hot (~90°C) nitrogen (~40 lpm) was used to dilute the sample stream. The soot generator was designed to produce aerosol particles in the range of 40 to 120 nm. Figure 1 shows particle size data taken from the soot generator and a vehicle at three steady state points (hot idle, 40mph, and 70mph). The soot generator's size distribution was reasonably close to the vehicular exhaust particulate matter (PM) size distributions. Additional technical information regarding the development of the PM generator can be located in reference [4].

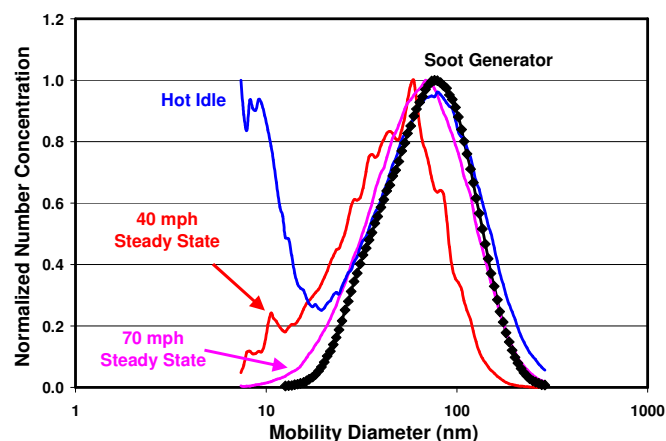


FIGURE 1. Particle size data taken from the soot generator and three steady state points (hot idle, 40mph and 70mph) comparing the soot generator's size distribution to vehicular exhaust PM size distributions.

The soot generator was modified to validate our accelerated loading differences to represent the levels observed on a vehicle. A bypass line, flow controller and a HEPA filter were installed on the reactor. A portion of the reactor flow and generated PM was diverted through the filter to remove PM. The particle-free flow was directed back into the reactor flow so as to maintain the same flow properties as our previous work. This bypass allowed for the control of PM concentration in the gas stream. The overall sample flow rate was maintained at 100 lpm.

40 lpm. The bypass capability was used to elucidate the impact of loading duration on DPF properties during the loading process and its effects on regeneration. Results showed good correlation between vehicle and soot loaded samples [5-6]. For laboratory soot loading of SCRF samples, the duration was held constant to obtain a target 6g/L total soot loading but the actual was variable between sample to sample. The soot loadings ranged from 6g/L to 15g/L.

PROPYLENE EVALUATION AND COKING PROCEDURE

Activity Tests in the Presence of Propylene

Under Standard SCR Reaction conditions, the effect of propylene (C_3H_6) exposure on SCRF NOx performance was studied in a laboratory flow reactor system. The concentration of propylene used was 0ppmC1, 280ppmC1, 1400ppmC1, and 4000ppmC1. The reaction gases in Table 4 were passed over the SCRF samples at 125°C until a steady-state condition was achieved. Next, the activity test was then performed under a dynamic temperature ramp of 5°C/min from 125°C to 750°C. The oxygen level for these tests was chosen to be 2% to represent possible conditions during an active DPF regeneration event.

Feed Gas Composition	STANDARD SCR REACTION with Propylene
C_3H_6 (ppmC1)	0, 280, 1400, 4000
NO (ppm)	350
NO ₂ (ppm)	0
NH ₃ (ppm)	350
O ₂ (%)	2.0
CO ₂ (%)	0.0
H ₂ O (%)	5.0
N ₂	balance

TABLE 4. Feed gas composition utilized to investigate the impact of propylene presence on NOx conversion (STANDARD SCR REACTION with Propylene).

Propylene Coking and Impact on NOx Conversion

To study the potential for depositing coke on the SCRF catalyst, the feed gas composition in Table 4 was exposed over the SCRF samples for 2 hours in duration. The post-SCRF reaction gases were monitored during the coking duration to determine the impact on NOx conversion as a function of time for many different temperatures. In this way, the initial NOx conversion

was compared to steady-state NOx conversion at the end of 2 hours. The propylene concentration chosen for the coking experiments was 4000ppmC1 while the oxygen concentration chosen was 2%. The coking temperature was varied from 125°C to 750°C. Next, at the end of each specific 2 hour coking experiment, the SCRF catalyst was cooled down to 125°C with the reaction gases in Table 2 (Standard SCR Reaction conditions). The impact of the deposited coke on NOx conversion was then determined by a subsequent ramp.

DIESEL FUEL ADSORPTION/COKING PROCEDURE

To study the impact of diesel fuel exposure on SCRF NOx conversion, a bench flow reactor was used to simulate low temperature and high temperature diesel fuel exposure contamination. Figure 2 illustrates the laboratory apparatus utilized for this purpose. The exposure of diesel fuel over the SCRF samples at low temperature represented the possible conditions of an inactive DOC during a cold-start event. The exposure of diesel fuel at high temperatures represented the possible post-DOC hydrocarbon slip conditions during an active SCRF regeneration event. In any event, the SCRF was investigated to determine the robustness to prolonged diesel fuel exposure and the resultant impact on NOx conversion.

The bench flow reactor designed to expose diesel fuel vapor over the SCRF samples utilized two reactor furnaces. Furnace 1 served as a gas preheat and was held constant at a 410°C condition. The inlet gas composition was held constant with 10% O₂, 5% H₂O, 5% CO₂, and balance N₂. The liquid diesel fuel was injected into the gas stream between furnace 1 and furnace 2 by the use of a syringe pump. At this point, the liquid diesel fuel was mixed and vaporized and then carried into furnace 2. Furnace 2 held the SCRF sample at the desired exposure temperature. The diesel fuel exposure temperature over the SCRF samples was varied from 200°C to 500°C. The SCRF core temperature was measured 1/8" before the outlet of the sample by a K-type thermocouple.

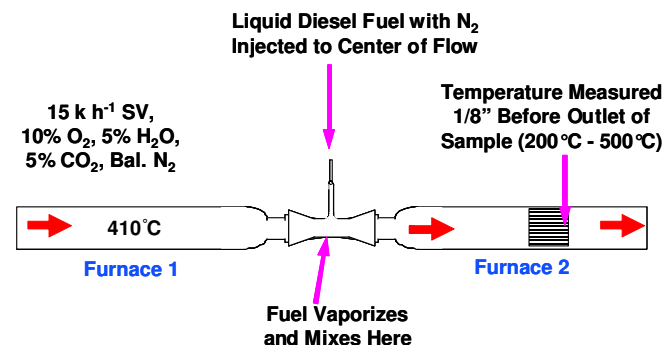


FIGURE 2. Bench flow reactor system designed to expose diesel fuel vapor over SCRF samples.

A diesel fuel flow rate of 10 micro-liters per minute over 6 hours was utilized to expose the SCRF samples to approximately 100 grams of diesel fuel per SCRF liter. The duration ensured a sufficient opportunity for complete saturation and/or coking. Low sulfur U.S. diesel fuel was used with less than 15ppm sulfur content.

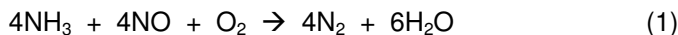
RESULTS AND DISCUSSION

THERMAL DURABILITY OF SCRF CANDIDATES

The long-term hydrothermal stability of base metal-zeolite SCR catalysts for automotive applications was studied to determine impact of cumulative high temperature soot regeneration events. The SCRF candidates were aged at 800°C for 64 hours to represent ~ 120,000 miles on a diesel vehicle. Both the Standard SCR Reaction and the Fast SCR Reaction were studied in the following sections.

STANDARD SCR REACTION

Figures 3A, 3B, and 3C show the steady-state performance of the CuSCR#1, CuSCR#2, and the FeSCR#1 catalyst formulations under the Standard SCR Reaction (Equation 1), respectively. Recall that the samples were pre-aged at 800°C for 64 hours.



Exhaust temperatures for typical light-duty diesel vehicles require aftertreatment devices to function at lower temperatures. At 200°C, the CuSCR#1 formulation achieved 75% NOx conversion while the CuSCR#2 achieved 85% NOx conversion. On the other hand, the FeSCR#1 formulation achieved only 10% NOx conversion.

High temperature activity is required for NOx control during the process of heating the exhaust gas up to regenerate particulate matter that has been trapped on the SCRF. A typical target temperature to achieve an accelerated reaction between soot and O₂ requires the SCRF to reach approximately 650°C. Both Cu-based SCRF catalysts showed a significant drop in efficiency for the desired NH₃ + NOx reaction due to the competing undesirable NH₃ + O₂ reaction. At 650°C, the CuSCR#1 formulation only achieved 10% NOx conversion while the CuSCR#2 achieved 25% NOx conversion. On the other hand, the FeSCR#1 formulation achieved 70% NOx conversion.

For N₂O emissions, CuSCR#1 yielded no more than 10ppm N₂O whereas CuSCR#2 yielded less than about 5ppm. FeSCR#1 generated virtually no N₂O emissions.

Figure 3D shows the interaction of the reaction feed gases flowing in the quartz reactor tube containing only an uncoated filter monolith. The feed gases displayed a reaction as the temperature was increased to 700°C. Apparent NH₃ conversion was first observed at 600°C. At 700°C, 30% NH₃ conversion was achieved with the appearance of about 5ppm NOx. No measurable amount of N₂O was detected.

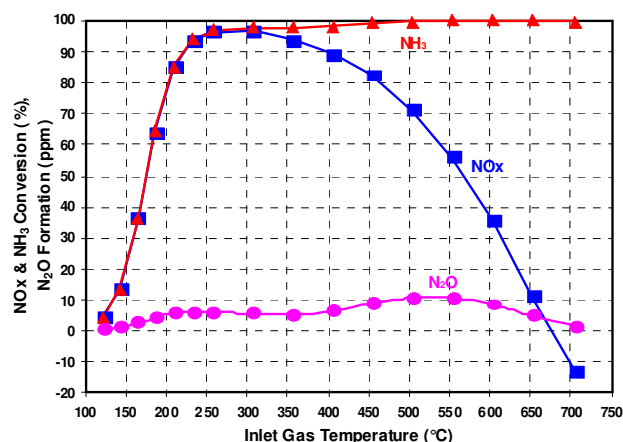


FIGURE 3A. CuSCR#1 steady state activity for the Standard SCR Reaction as a function of inlet gas temperature (°C).

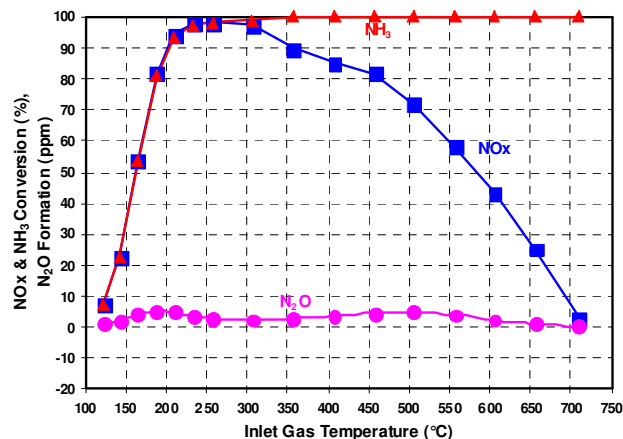


FIGURE 3B. CuSCR#2 steady state activity for the Standard SCR Reaction as a function of inlet gas temperature (°C).

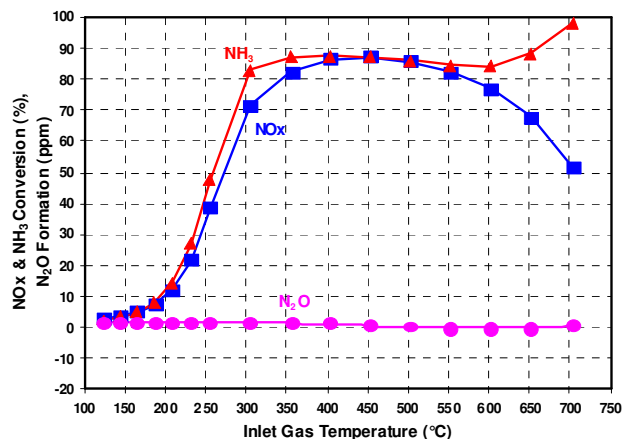


FIGURE 3C. FeSCR#1 steady state activity for the Standard SCR Reaction as a function of inlet gas temperature (°C).

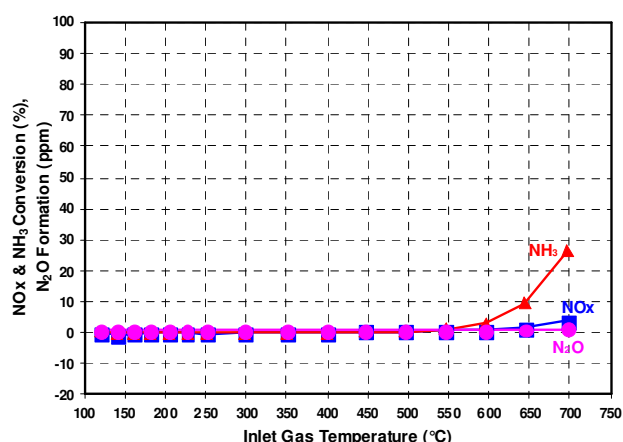
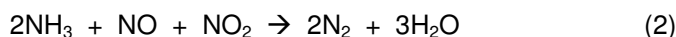


FIGURE 3D. Steady state activity of an uncoated filter monolith for the Standard SCR Reaction as a function of inlet gas temperature (°C).

FAST SCR REACTION

Figures 4A, 4B, and 4C show the steady-state performance of the CuSCR#1, CuSCR#2, and the FeSCR#1 catalyst formulations under the Fast SCR Reaction (Equation 2), respectively.



The NO_x composition in the Fast SCR Reaction experiment followed the stoichiometry in Equation 2 where both the NO composition and the NO₂ composition were fixed at 50% of the total NO_x level. Correspondingly, the NH₃ concentration was chosen to match the Equation 2 stoichiometry at an NH₃ to NO_x ratio equal to 1.0 (i.e. ANR = 1.0).

At 200°C, the CuSCR#1 formulation achieved 92% NO_x conversion while CuSCR#2 achieved 99% NO_x conversion. On the other hand, the FeSCR#1 formulation achieved 90% NO_x conversion compared to 10% for the Standard SCR Reaction.

Compared to the Standard SCR Reaction results, the Fast SCR Reaction improved the NO_x conversion of all three SCR formulations tested. CuSCR#1 improved by 17%, CuSCR#2 improved by 14%, and FeSCR#1 improved by 80%.

However, the Fast SCR Reaction resulted in a decline in the high temperature NO_x conversion. At 650°C, CuSCR#1 shifted from 10% to 5% NO_x conversion whereas CuSCR#2 shifted from 25% to 20% NO_x conversion. Similarly, FeSCR#1 shifted from 70% to 60% NO_x conversion.

All three SCR catalysts generated more N₂O emissions under this NO₂ rich feed gas condition (i.e. Fast SCR Reaction). CuSCR#1 generated a maximum of 20ppm N₂O whereas CuSCR#2 yielded no more than 10ppm. This time, FeSCR#1 generated detectable levels of N₂O in the range of 12ppm.

Under the Fast SCR Reaction conditions, Figure 4D showed the interaction of the reaction feed gases flowing in the quartz reactor tube containing only an uncoated filter monolith. The initial onset of a reaction started at 550°C and accelerated as the temperature increased to 700°C. At 700°C, 65% NH₃ conversion was achieved without the appearance of NO_x. However, up to 12ppm of N₂O was detected.

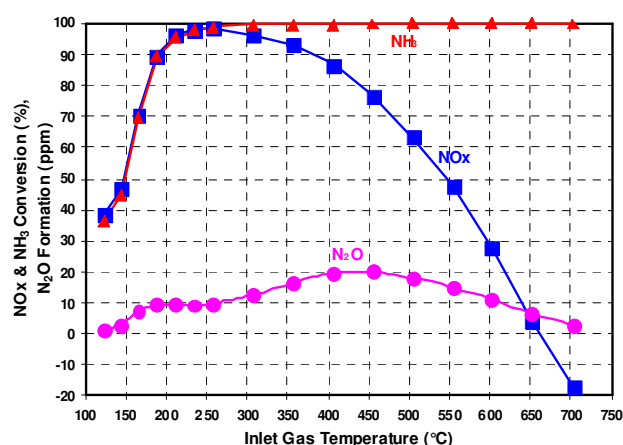


FIGURE 4A. CuSCR#1 steady state activity for the Fast SCR Reaction as a function of inlet gas temperature (°C).

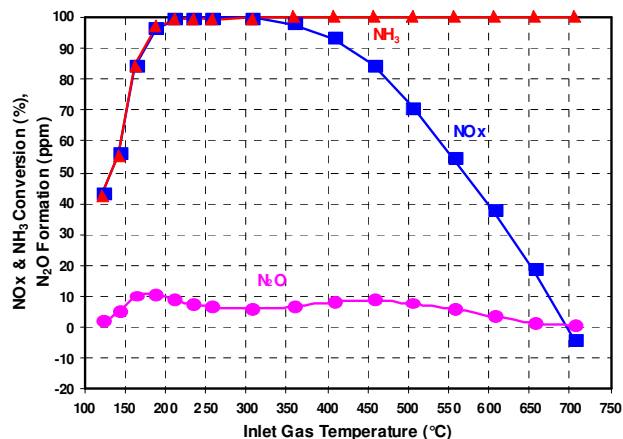


FIGURE 4B. CuSCR#2 steady state activity for the Fast SCR Reaction as a function of inlet gas temperature (°C).

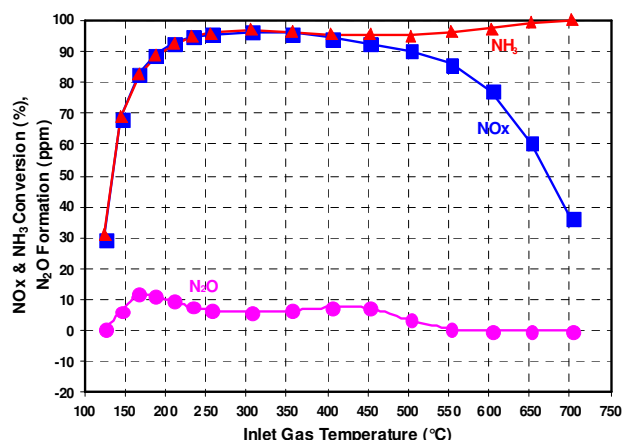


FIGURE 4C. FeSCR#1 steady state activity for the Fast SCR Reaction as a function of inlet gas temperature (°C).

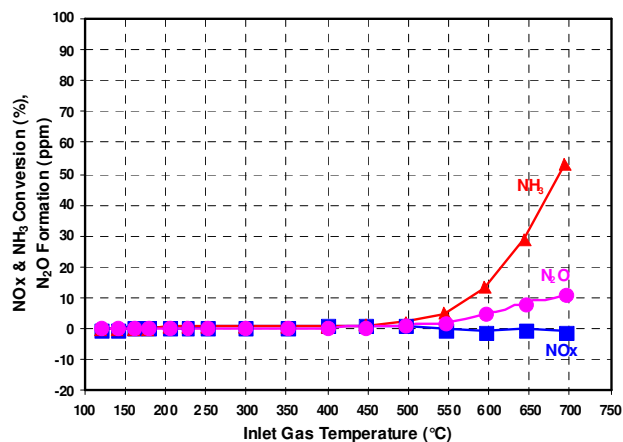


FIGURE 4D. Steady state activity of an uncoated filter monolith for the Fast SCR Reaction as a function of inlet gas temperature (°C).

STEADY-STATE VERSUS TEMPERATURE RAMPING

Up to now, the data presented has been on steady-state activity with saturated levels of NH_3 storage. During vehicle operation, the deposition and oxidation of soot, coke, and hydrocarbons species onto the SCR catalyst will be dynamic and a function of exposure time and temperature. As a result, the steady-state activity in the presence of soot, coke, and/or hydrocarbon species emphasized the long-term performance as compared to the short-term or intermediate impact of these deposits. The transient behavior for NO_x conversion and NH_3 conversion was studied by ramping the temperature at variable rates. The SCR formulation was first exposed to the Standard SCR reaction at 125°C for 1 hour. This conditioning allowed for an initial steady-state performance point at the saturation level of NH_3 coverage. Next, the temperature was increased to 750°C with a variable 1°C/min to 30°C/min ramp rate. The NO_x conversion and NH_3 conversion were monitored as a function of temperature rise. From this, an appropriate ramp rate was chosen for further testing of soot, coke, and hydrocarbon loaded SCR catalysts.

Figures 5A and 5B present the NO_x conversion of the CuSCR#1 and CuSCR#2 SCR formulations with variable ramp rates of 1°C/min, 5°C/min, 10°C/min, 20°C/min, and 30°C/min, respectively. Up to 325°C, the NO_x conversion light-off of both SCR formulations was found to be independent of the ramp rate. From 325°C to 450°C, the higher ramp rate improved the NO_x conversion. For example, at 400°C, the NO_x conversion for the CuSCR#1 formulation increased from 92% to 98% when the ramp rate was changed from 1°C/min to 30°C/min. Similarly, the NO_x conversion for the CuSCR#2 formulation increased from 85% to 98%. Finally, for temperatures above 450°C, both SCR formulations exhibited a 5%-10% NO_x conversion decline as the ramp rate was increased to 30°C/min.

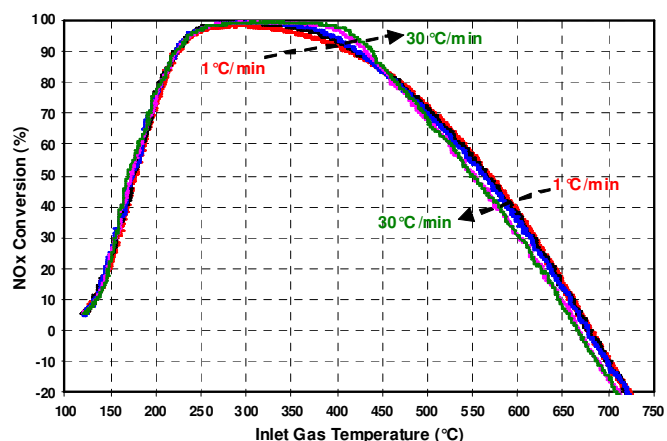


FIGURE 5A. CuSCR#1 NO_x conversion activity for the Standard SCR Reaction when the temperature ramp rate was varied from 1°C/min to 30°C/min.

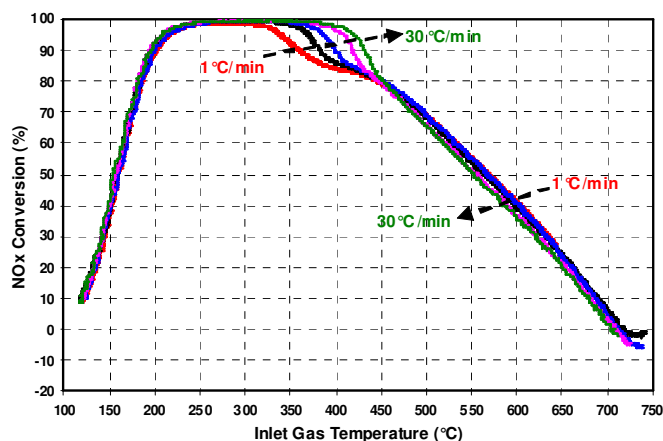


FIGURE 5B. CuSCR#2 NO_x conversion activity for the Standard SCR Reaction when the temperature ramp rate was varied from 1 °C/min to 30 °C/min.

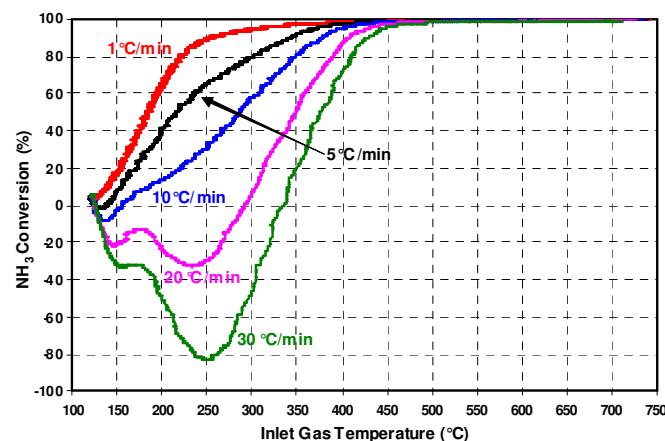


FIGURE 6A. CuSCR#1 NH₃ conversion activity for the Standard SCR Reaction when the temperature ramp rate was varied from 1 °C/min to 30 °C/min.

Figures 6A and 6B show the corresponding NH₃ conversion of the CuSCR#1 and CuSCR#2 SCR formulations as the temperature ramp rate varied from 1 °C/min to 30 °C/min. Recall, before ramping the temperature, the SCR catalyst samples were pre-conditioned to achieve a fully NH₃-saturated state. It is known that the NH₃ storage capacity of zeolite-based SCR formulations decreases as function of temperature. A shift in temperature would off-set this equilibrium. From 125 °C, increasing the ramp rate resulted in an NH₃ release due to the inability of the SCR samples to completely reabsorb the excess NH₃ or react with the feed gas NO_x or O₂. The amount of NH₃ released increased as the ramp rate was changed from 1 °C/min to 30 °C/min. A negative NH₃ conversion signified a release greater than the 350ppm feed gas level. These high levels of NH₃ release occurred below 450 °C for the ramp rates studied. Above 450 °C, the NH₃ conversion approached 100% due to reaction with NO_x and O₂. Interestingly, the dynamic release of NH₃ did not impact the NO_x conversion light-off temperature in the 125 °C – 325 °C temperature range (Figures 5A and 5B).

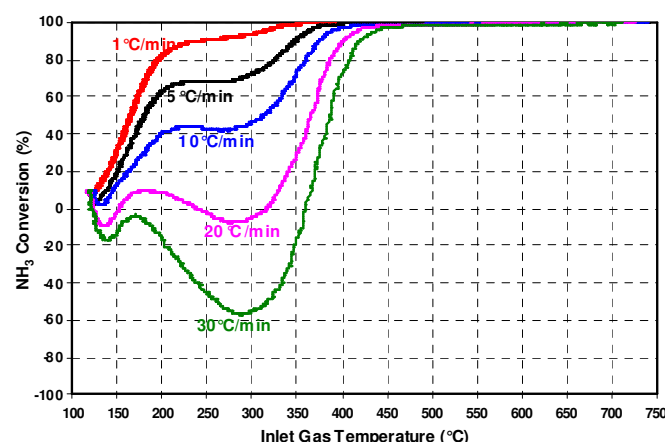


FIGURE 6B. CuSCR#2 NH₃ conversion activity for the Standard SCR Reaction when the temperature ramp rate was varied from 1 °C/min to 30 °C/min.

A comparison of the steady-state NO_x conversion versus the transient 5 °C/min temperature rate data is presented in Figures 7A and 7B. The NO_x conversion profiles for both CuSCR#1 and CuSCR#2 SCR samples showed good agreement within a 5% NO_x conversion margin for most of the temperature range tested. Of particular importance was the NO_x conversion light-off agreement of the steady-state versus the 5 °C/min ramp rate. This becomes apparent in the following sections where the impact of soot, coke, and hydrocarbon will be examined. From these data, the 5 °C/min ramp test was chosen for the following sections to represent the typical short-term NO_x conversion.

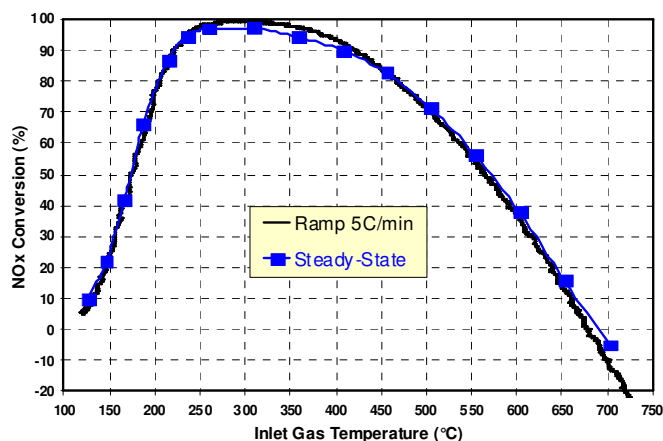


FIGURE 7A. Comparison of the CuSCR#1 SCRf NOx conversion under the steady-state and transient 5°C/min temperature ramp conditions (Standard SCR Reaction).

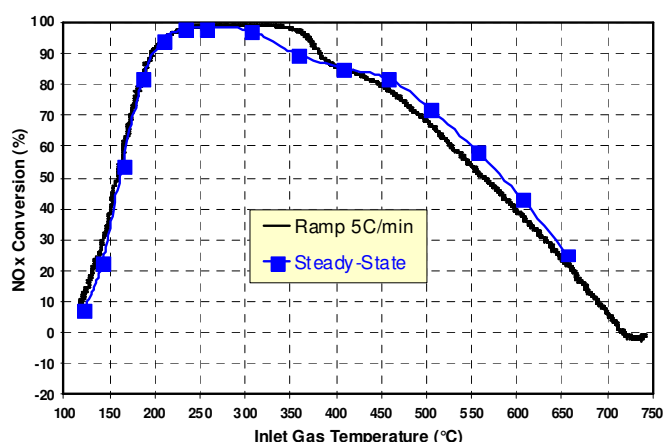


FIGURE 7B. Comparison of the CuSCR#2 SCRf NOx conversion under the steady-state and transient 5°C/min temperature ramp conditions (Standard SCR Reaction).

IMPACT OF SOOT LOADED SCRf CATALYSTS ON THE STANDARD SCR REACTION

Ramp#1 – Soot Loaded SCRf Evaluation

Figures 8A, 8B, 8C, and 8D present the ramp#1 activity profiles of CuSCR#1, CuSCR#2, FeSCR#1, and the uncoated filter monolith, respectively. The figures show the corresponding NOx conversion, NH₃ conversion, N₂O formation, and CO formation as the temperature was ramped at a rate of 5°C/min. All four samples were loaded with soot by the laboratory generator described in the experimental section. Note that the NH₃ conversion lagged behind the NOx conversion due to the disruption in the NH₃ storage capacity during transient events.

Compared to precious metal based catalysts (Pt or Pd), base metals catalysts such as Cu and Fe do not oxidize

soot very efficiently. As a result, Cu and Fe based SCR catalysts generated a significant amount of CO from the partial oxidation of soot.

For all three SCRf catalyst formulations and even the uncoated filter monolith, the peak CO formation occurred at approximately 540°C. Unassisted by the base metal, the CO formation in this temperature region occurred by the oxidation of the bulk soot layer with gas phase O₂. Recall that the SCRf washcoat was coated within the high porosity wall and not in direct contact with all of the soot in the channel. On the other hand, the soot deposition within the SCRf wall was in close contact with the catalyst washcoat. As a result, the SCRf catalyst had an opportunity to assist in the soot oxidation by lowering the light-off temperature (indicated by CO formation).

The catalytically-assisted soot oxidation was clearly shown by the CuSCR#2 formulation in Figure 8B. Figure 8B shows a bi-modal profile for CO formation. Evidence of partial soot oxidation was observed at both 425°C and 540°C. The soot oxidation at 425°C can be attributed to the catalytically-assisted oxidation of soot in the SCRf wall. In contrast, the majority of the soot oxidation in the substrate channel can be attributed to the unassisted oxidation and hence a higher 540°C temperature requirement.

Although less apparent, significant CO formation below 425°C was also observed for the CuSCR#1 formulation (Figure 8A) and the FeSCR#2 formulation (Figure 8C).

Figure 8D shows the activity of the reaction gases over an uncoated filter monolith that was soot-loaded and tested for possible side reactions. A complementary test was shown in Figure 3D where no soot was present. Comparison of Figure 3D to Figure 8D highlights a possible NH₃ interaction during the soot oxidation process. The temperature range where the peak CO formation occurred coincides with 22% NH₃ conversion and no NOx conversion. A possible explanation for this observation has not yet been determined.