

Selective Catalytic Reduction for Treating the NO_x Emissions from Lean-Burn Gasoline Engines: Performance Assessment

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ABSTRACT

Selective catalytic reduction (SCR) with NH₃ provides an attractive alternative to lean NO_x traps for controlling the NO_x emissions from lean-burn gasoline engines. This paper summarizes a laboratory study to assess the effects of temperature, space velocity, and the concentrations of NO, NH₃, and O₂ on the NO_x conversion of an iron/zeolite SCR catalyst. A fresh sample was evaluated on slow temperature ramps with 5% O₂ and 250, 500, or 1000 ppm of NO and NH₃. The NO_x conversion at low temperatures decreased with increasing NO and NH₃ concentrations due to kinetic limitations. Conversely, the conversion at high temperatures increased with increasing NO and NH₃ concentrations because the portion of NH₃ oxidized by O₂ decreased with increasing NO concentration. Thermally aged samples were evaluated at different steady-state temperatures and at different space velocities where the NO concentration was held constant at 250, 500, or 1000 ppm and the NH₃ concentration was controlled at ten levels ranging from 143 to 1085 ppm. The NH₃/NO ratios producing the minimum slip of NH₃+NO_x were approximately 1.0 or higher for most temperatures and NO concentrations when the space velocity was 25K hr⁻¹ or below, allowing high NO_x conversions to be achieved. When the space velocity was 47K hr⁻¹ and higher, kinetic limitations and the need to limit the NH₃ slip resulted in optimum NH₃/NO ratios less than 1.0, which limited the potential NO_x conversion. The NO_x conversion dropped with decreasing O₂ concentration, particularly at low temperatures, and the conversion was very low when the O₂ was removed from the feedgas.

INTRODUCTION

Stratified-charge direct-injection (SCDI) gasoline engines can provide improved fuel economy relative to the stoichiometric port-fuel-injected (PFI) gasoline engine as a result of reduced pumping losses and improved thermodynamics of combustion. However, the exhaust from SCDI engines is lean, and the three-way catalyst (TWC) used for emission control on stoichiometric vehicles cannot provide sufficient NO_x control to satisfy stringent NO_x standards in a lean environment.

The lean NO_x trap (LNT) has been used to control the NO_x emissions on production SCDI engines by

storing the NO_x under lean conditions and reducing the stored NO_x to N₂ during periodic rich purges [1]. Another promising aftertreatment technology that can be used to control the NO_x emissions in lean exhaust is the selective catalytic reduction (SCR) catalyst, where the catalyst promotes the reaction between NO_x and ammonia (NH₃) under lean conditions to produce H₂O and N₂ [2]. Due to the difficulties of working with NH₃ on mobile applications, an aqueous solution of urea [CO(NH₂)₂] can be used to provide the reductant, as urea breaks down into NH₃ in the exhaust system [3]. Compared to the LNT, SCR offers several technical advantages, including a wider temperature window and increased robustness to the feedgas NO_x concentration. With SCR, the NO_x reduction occurs during lean operation, eliminating the need for the rich purges that are required for NO_x traps. This is beneficial for the fuel economy and also eliminates the purge NO_x release, which is the undesired release of NO_x from a LNT during rich purges [4]. This purge NO_x release is especially problematic at high temperatures and is a major impediment to achieving low NO_x emission levels with lean NO_x traps.

SCR offers great potential for treating the NO_x emissions from diesel engines [5, 6, 7], and SCR has already been implemented on diesel-powered trucks in Europe [8]. However, an issue with applying SCR to lean-burn gasoline engines is the potential for hot, rich exhaust conditions during high load operation, as such conditions could degrade the zeolite-based SCR catalysts being developed for mobile applications. It is shown in a companion paper [9] that an iron/zeolite SCR catalyst provided over 90% NO_x conversion at 500°C after aging in primarily rich exhaust at an inlet temperature of 750°C. The same catalyst provided over 90% NO_x conversion at 500°C after aging in primarily stoichiometric exhaust or continuously lean exhaust at an inlet temperature of 800°C, which is a reasonable maximum temperature for underbody catalytic converters on some applications. These data suggested that this Fe SCR catalyst had sufficient durability to be considered for application on lean-burn gasoline engines.

This paper deals with the effect of several operating parameters on the NO_x conversion performance of the Fe SCR catalyst. These parameters include the temperature, the space velocity, and the concentrations of NO, NH₃, and O₂. Temperature ramps were

performed on a fresh sample with 250, 500, or 1000 ppm NO and NH₃. Fresh and thermally aged samples were evaluated at different steady-state temperatures where the NO concentration was held at 250, 500, or 1000 ppm while the NH₃ was controlled at ten levels ranging from 143 to 1085 ppm. A primary objective of this work was to determine the optimum ratio of NH₃ and NO that provided high NO_x conversion while minimizing the NH₃ slip. Different volumes of thermally aged catalysts were evaluated at the different temperatures to assess the effect of space velocity on the optimum NH₃/NO ratio. Finally, temperature ramps were performed on an aged sample with different O₂ levels to assess the effect of oxygen on the NO_x conversion of the Fe SCR catalyst.

EXPERIMENTAL

Catalyst Samples - Several 15.24 cm long cores with a diameter of 1.75 cm were drilled from a cordierite brick (400 cpsi, 0.17 mm wall thickness) that was coated with an iron/zeolite SCR formulation. The 15.24 cm cores were cut with a diamond-blade saw to produce several core samples that were 2.54 cm in length.

Aging - Prior to performance testing, some of the 2.54 cm long cores were aged on a pulse-flame combustion reactor [10]. Here sulfur-free gasoline was combusted with N₂ and O₂ to produce a gas mixture simulating engine exhaust. A heated exhaust gas oxygen sensor (HEGO) downstream of the combustor was used to control the A/F ratio during stoichiometric operation. To simulate the exhaust architecture on a vehicle, each SCR sample was aged downstream of a TWC sample, as shown in Figure 1. Separate ovens were used for the TWC sample and SCR sample; the TWC sample was placed at the outlet of the first furnace, and the SCR sample was placed at the outlet of the second furnace. In all cases, the TWC contained 2.12 g/L Pd/Rh (0/9/1). Since the TWC on a vehicle would normally be smaller than the SCR catalyst, the TWC sample used the same 1.75 cm diameter but was only 1.27 cm in length or half as long as the SCR sample.

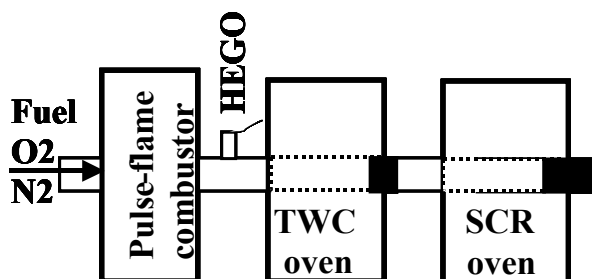


Figure 1. Aging apparatus for TWC and SCR core samples.

Sets of TWC and SCR samples were aged for 34 hours using two different A/F ratio schedules. One schedule involved continuously lean operation. Here the pulse-flame combustion reactor was operated at the

stoichiometric A/F ratio, and full-time secondary air was injected downstream of the control HEGO but upstream of the TWC oven. The inlet temperature to the TWC sample was controlled at 850°C; one SCR sample was aged with an inlet temperature of 750°C, and a second SCR sample was aged with an inlet temperature of 800°C. This schedule will be referred to as the "lean schedule" in this paper.

The second aging schedule utilized a proprietary A/F ratio routine that cycled between lean, rich, and stoichiometric conditions every 60 seconds. The A/F ratio was at stoichiometry for 67% of the time, so this schedule will be referred to as the "stoichiometric schedule" in this paper. The inlet temperature to the TWC sample during the stoichiometric portion of the schedule was controlled at 850°C, and the maximum bed temperature of the TWC was 1000°C. One SCR sample was aged with an inlet temperature of 750°C, and a second SCR sample was aged with an inlet temperature of 800°C.

It is noted that these different A/F ratio schedules were used to assess the effects of the A/F ratio during aging on the durability of the SCR catalyst [9]. In that study, samples were also aged on a "rich schedule", which cycled between lean, rich, and stoichiometric conditions but was at a lambda of 0.92 for 67% of the time. The duration of 34 hours was chosen for all three aging schedules because 34 hours of the rich schedule correlates with 80,000 km of customer use for three-way catalysts in Europe. Also, it is noted that the TWC cores were used only during the aging and were not used during the performance evaluations.

NO_x Conversion Evaluations - A fresh SCR sample was evaluated for NO_x conversion on a flow reactor. The sample was installed into a quartz tube which was placed inside of a furnace with programmable temperature controls. To assess the effects of the NO and NH₃ concentrations on the NO_x conversion, the catalyst was exposed to lean exhaust (5% O₂) containing equal concentrations of NO and NH₃ (250, 500, or 1000 ppm) while the temperature of the furnace was increased slowly from approximately 130°C to 850°C (typically at 3.5 or 4.0°C/min). While the feedgas contained only NO, the emissions were measured as total NO_x (i.e., NO+NO₂). The composition of the exhaust mixture during these temperature ramps is provided in Table I. The total exhaust flow rate was 2.5 L/min, resulting in a space velocity of approximately 25,000 hr⁻¹ for a 2.54 cm long sample.

Table I. Exhaust gas composition during lean temperature ramps for SCR samples.

Component	Concentration
CO ₂	10%
H ₂ O	10%
NO	250, 500, or 1000 ppm
NH ₃	250, 500, or 1000 ppm
O ₂	5%
Bulk N ₂	Balance

The fresh SCR sample was also evaluated at steady-state bed temperatures of approximately 375°C, 550°C, and 750°C. The NO concentration was held constant at 250 ppm while the NH₃ concentration was controlled at 10 different levels, listed in Table II. After a change in the NH₃ concentration, a period of time on the order of 10 to 15 minutes was allowed so the NO_x conversion and NH₃ slip could reach steady-state conditions. This test was also performed with NO concentrations of 500 ppm and 1000 ppm at the three temperatures. For all NO and NH₃ concentrations, the concentrations of the other gas species were approximately the same as those shown in Table I.

Table II. NH₃ concentrations during steady-state temperature test.

Setting	NH ₃ Concentration (ppm)
1	143
2	255
3	365
4	471
5	576
6	678
7	781
8	885
9	986
10	1085

These steady-state tests were also performed on samples aged on the pulse-flame combustion reactor. To provide a more thorough assessment of the effect of temperature on the NO_x conversion and NH₃ slip, the steady-state tests were performed with the three NO concentrations at bed temperatures of 340°C, 377°C, 401°C, 434°C, 530°C, 613°C, and 703°C on a 1.14 cm long sample (space velocity: 55K hr⁻¹) that had been aged 34 hours at 800°C on the lean schedule.

To assess the effect of space velocity on the NO_x conversion and NH₃ slip with different NO and NH₃ concentrations, the steady-state temperature tests were performed at a bed temperature of 355°C on a 2.54 cm long sample (space velocity: 25K hr⁻¹) that had been aged at 800°C on the lean schedule. The tests were also performed on the front 0.76 cm and the front 1.35 cm of the sample, producing space velocities of 83K and 47K hr⁻¹, respectively. Finally, to evaluate a space velocity of 12.5K hr⁻¹, a 2.54 cm sample aged at 750°C on the stoichiometric schedule was placed behind the 2.54 cm sample aged at 800°C on the lean schedule, and the tests were repeated. It is noted that these two samples had similar NO_x performance when evaluated individually. These tests were also performed at bed temperatures of 533°C and 720°C. With this procedure, the NO_x conversion and NH₃ slip were determined as a function of NO concentration (250, 500, and 1000 ppm), NH₃ concentration (143 to 1085 ppm), space velocity (12.5K, 25K, 47K, and 83K hr⁻¹), and catalyst bed temperature (355°C, 533°C, and 720°C).

Finally, to assess the effects of the O₂ concentration on the NO_x performance, several temperature ramps with different O₂ concentrations were performed on a 2.54 cm long sample that had been aged at 750°C on the stoichiometric schedule. The O₂ concentration during the ramps ranged from 8 to 0%. The NO and NH₃ concentrations were held constant at 500 ppm.

For all tests, the exhaust from the reactor was diluted with N₂ in a 10:1 ratio to provide enough flow for all of the analyzers and to reduce the water concentration from 10% to 1%, in order to prevent condensation in unheated sections of tubing or the analyzers. Most of the diluted exhaust was sent directly to the exhaust analyzer bench, which contained a flame ionization detector for measuring the HC, NDIR analyzers for measuring the CO, CO₂, and N₂O, and a chemiluminescence NO_x analyzer for measuring total NO_x (NO+NO₂). The remainder of the diluted exhaust was directed through a second oven containing a platinum catalyst operated at 500°C, which oxidized any NH₃ to NO. This treated exhaust was pumped to a second chemiluminescence NO analyzer. The readings from the NO and NO_x analyzers were subtracted to determine the amount of NH₃ in the diluted exhaust.

RESULTS

Fresh Temperature Ramps – A fresh 2.54 cm long sample of the Fe SCR catalyst was evaluated for NO_x conversion and NH₃ slip with 250, 500, and 1000 ppm NO and NH₃ during slow temperature ramps. Figure 2 displays the NO_x conversion as a function of the catalyst bed temperature for the three tests. Figure 3 shows the measured NH₃ slip from the three tests along with the NH₃ slip calculated from the NO_x conversion and the feedgas level of NH₃, assuming a 1:1 reaction stoichiometry between the NO and NH₃.

Figure 2 shows that the temperature window of the catalyst shifted to higher temperatures and widened as the NO and NH₃ concentrations increased. Below

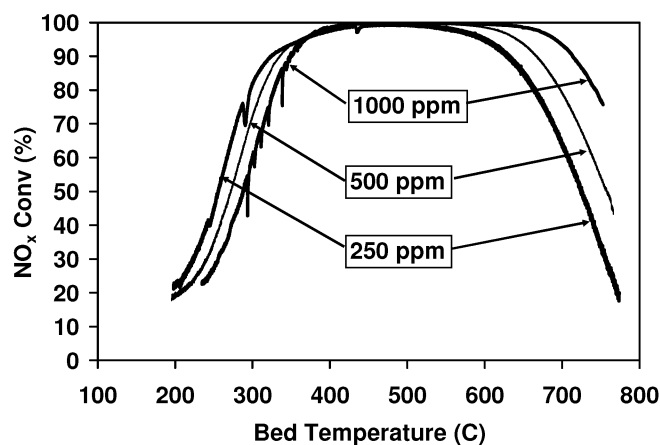


Fig. 2. NO_x conversion for fresh Fe SCR catalyst during slow temperature ramps with 250, 500, or 1000 ppm NO and NH₃ at 25K hr⁻¹. Exhaust included 5% O₂, 10% H₂O, 10% CO₂, balance N₂.

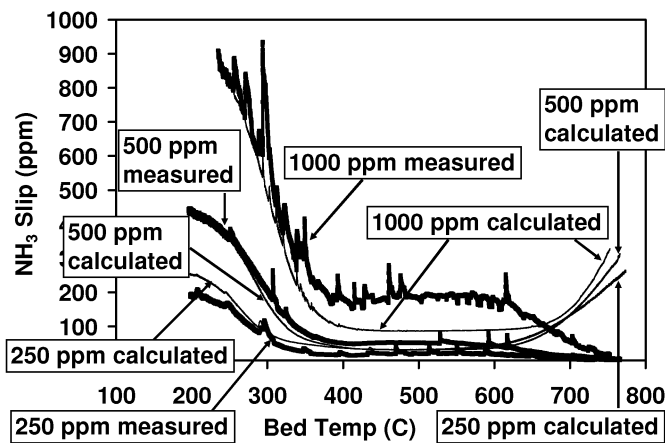


Fig. 3. Measured NH_3 slip (bold lines) for fresh Fe SCR catalyst during slow temperature ramps with 250, 500, or 1000 ppm NO and NH_3 at 25K hr^{-1} . Exhaust included 5% O_2 , 10% H_2O , 10% CO_2 , balance N_2 . Figure also displays NH_3 slip calculated from NO_x conversion and feedgas NH_3 level (thin lines).

350°C, the NO_x conversion at a specified temperature decreased with increasing NO and NH_3 concentrations, attributable to kinetic limitations. Between approximately 400°C and 550°C, the NO_x conversion was essentially constant near 100% for all three concentrations. Above 550°C, the NO_x conversion at a specified temperature increased with increasing NO and NH_3 concentrations.

It was determined that the increase in the NO_x conversion with increasing NO and NH_3 concentrations at high temperatures was due to the competing reaction between NH_3 and O_2 , which consumed some of the NH_3 and thereby decreased the NO_x conversion. To demonstrate, a 2.54 cm long sample aged for 34 hours at 750°C on the stoichiometric schedule was placed in front of another 2.54 cm long sample aged for 34 hours at 800°C on the lean schedule. This 5.08 cm long catalyst was evaluated at 720°C with a constant NH_3 concentration of 255 ppm and NO concentrations of 250, 500, and 1000 ppm. The catalyst was large enough and the temperature high enough that essentially all of the NH_3 was consumed. The NO_x conversions were used to calculate the fraction of NH_3 that reacted with NO; it was assumed that the remainder of the NH_3 was consumed by the reaction between NH_3 and O_2 .

Figure 4 indicates that, as the NO concentration increased, the fraction of NH_3 consumed by NO increased while the fraction of NH_3 consumed by O_2 decreased. Since the NO concentration (250 to 1000 ppm) was much lower than the O_2 concentration (5% or 50,000 ppm) during these tests, this suggested that the $\text{NH}_3 + \text{NO}$ reaction was preferred over the $\text{NH}_3 + \text{O}_2$ reaction. Therefore, when the NO concentration is high, most of the NH_3 consumed at high temperatures is used to reduce NO, and only a small fraction reacts with O_2 . Conversely, when the NO concentration is low, a large fraction of the NH_3 is oxidized by O_2 at high temperatures, leaving less NH_3 to react with NO. This mechanism explains the NO_x conversion results at high temperatures in Figure 2.

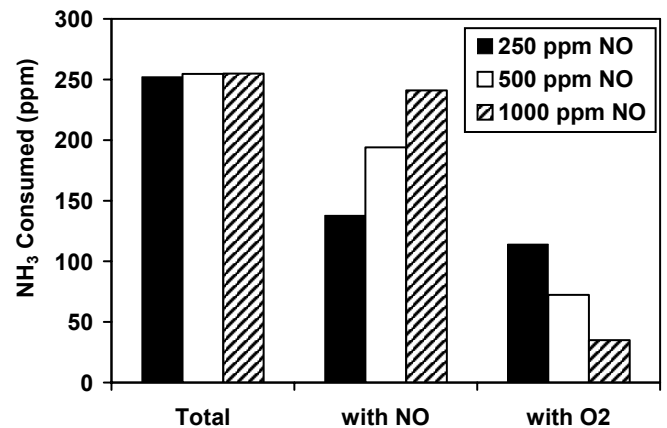


Fig. 4. Total NH_3 consumed, NH_3 consumed by NO, and NH_3 consumed by O_2 at 720°C and $12,500\text{ hr}^{-1}$ for 5.08 cm long Fe SCR catalyst. First 2.58 cm aged 34 hr at 750°C on stoichiometric schedule; second 2.54 cm aged 34 h at 800°C on lean schedule. Evaluated with 255 ppm NH_3 and NO levels of 250, 500, or 1000 ppm. Exhaust also included 5% O_2 , 10% H_2O , 10% CO_2 , balance N_2 .

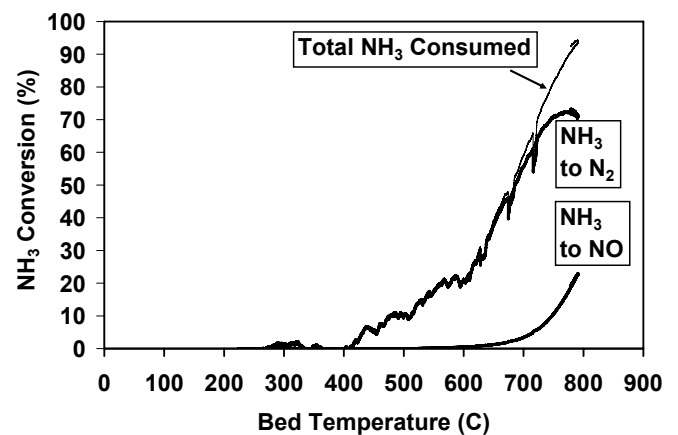


Fig. 5. Conversion of NH_3 to N_2 and NO for fresh Fe SCR catalyst during slow temperature ramp at 25K hr^{-1} with 500 ppm NH_3 but without NO. Exhaust included 5% O_2 , 10% H_2O , 10% CO_2 , balance N_2 .

To further investigate the reaction of NH_3 with O_2 , a fresh sample of the Fe SCR catalyst was evaluated on a temperature ramp with 500 ppm NH_3 but without NO. Figure 5 shows the overall disappearance of NH_3 as well as the portion of NH_3 oxidized to NO. The amount of N_2O produced was negligible, so the oxidation of NH_3 to N_2 at a given temperature was calculated from the difference between the other two curves. In the absence of NO, the catalyst began to oxidize NH_3 to N_2 above 400°C, and above 700°C a significant portion of NH_3 was oxidized to NO.

There was reasonable agreement between the experimental NH_3 slip and the NH_3 slip calculated from the NO_x conversion at temperatures below 600°C in Figure 3, particularly on the tests with 250 and 500 ppm NO and NH_3 . At temperatures above 600°C, the measured NH_3 slip was significantly lower than the calculated slip on all three concentrations. This can be attributed to the reaction