

SCR Catalyst Systems Optimized for Lightoff and Steady-State Performance

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ABSTRACT

A laboratory study was performed to optimize a zoned configuration of an iron (Fe) SCR catalyst and a copper (Cu) SCR catalyst in order to provide high NO_x conversion at lean A/F ratios over a broad range of temperature for diesel and lean-burn gasoline applications. With an optimized space velocity of $8,300 \text{ hr}^{-1}$, a 67% (by volume) Fe section followed by a 33% Cu section provided at least 80% NO_x conversion from approximately 230°C to 640°C when evaluated with 500 ppm NO and NH_3 . To improve the lean lightoff performance of the SCR catalyst system during a cold start, a Cu SCR catalyst that was 1/4 as long as the rear Cu SCR catalyst was placed in front of the Fe SCR catalyst. When evaluated with an excess of NH_3 (NH_3/NO ratio of 2.2), the Cu+Fe+Cu SCR system had significantly improved lightoff performance relative to the Fe+Cu SCR system, although the front Cu SCR catalyst did decrease the NO_x conversion at temperatures above 475°C by oxidizing some of the NH_3 to N_2 or NO.

INTRODUCTION

Selective catalytic reduction (SCR) with ammonia (NH_3) is an effective means for reducing the oxides of nitrogen (NO_x) during lean operation [1]. As a result, SCR is a prime candidate for NO_x control on both diesel and lean-burn gasoline engines. Due to the difficulties of handling ammonia, an aqueous solution of urea [$\text{CO}(\text{NH}_2)_2$] will be used as the source of reductant on mobile applications, as each molecule of urea breaks down into 2 molecules of ammonia in the exhaust system [2]. SCR catalysts with urea injection have already been implemented on heavy-duty diesel trucks in Europe [3], and it is expected that SCR will find wide application on light-duty diesel engines as well. In regards to lean-burn gasoline applications, it was shown

previously that state-of-the-art iron (Fe) and copper (Cu) SCR catalysts are sufficiently durable to be considered for such engines [4].

The other leading catalyst technology for controlling NO_x emissions on lean-burn applications is the lean NO_x trap (LNT), which stores the NO_x during lean operation and reduces the stored NO_x to N_2 during periodic rich purges [5]. Relative to the LNT, SCR provides several advantages, including a wider temperature window and increased robustness to the feedgas NO level [6]. Also, SCR catalysts do not require the rich purges required by lean NO_x traps. This benefits the fuel economy and also eliminates the potential problem of purge NO_x release [7]. Finally, the active materials in SCR catalysts are low cost base metals such as iron and copper instead of the expensive precious metals (i.e., platinum, palladium, and rhodium) used in lean NO_x traps.

Cu SCR catalysts are more effective than Fe SCR catalysts for NO_x control at low temperatures (e.g., $200\text{--}400^\circ\text{C}$), while Fe SCR catalysts are more effective for NO_x control at high temperatures (e.g., $400\text{--}600^\circ\text{C}$) [4, 8]. Therefore, Cu SCR catalysts might be preferred on lean-burn applications that produce low exhaust temperatures a majority of the time, such as light-duty diesel engines. On the other hand, Fe SCR catalysts might be preferred on lean-burn applications where the exhaust temperatures can exceed 400°C over a significant portion of the speed/load range. Such temperatures can occur on naturally-aspirated lean-burn port-fuel-injected (PFI) gasoline engines or naturally-aspirated stratified-charge direct-injection gasoline (SGDI) engines.

Some engines, such as turbocharged lean-burn PFI engines or turbocharged SGDI engines, can produce a wide range of exhaust temperatures, depending on the load condition. At low loads, the turbocharger can act as a heat sink and result in relatively low exhaust temperatures. But when the turbocharger is engaged during heavy load operation, the greater amount of air

and fuel injected into the engine can produce relatively high exhaust temperatures. If lean operation is used over a broad range of speeds and loads to maximize the fuel economy, it would be desirable for the SCR catalyst system to provide effective lean NO_x control over a wide range of temperature. Therefore, zoned combinations of aged Cu and Fe SCR catalysts were investigated on a laboratory reactor to determine the configuration that provided the widest temperature window under steady-state conditions.

Girard previously investigated zoned combinations of Fe SCR catalysts and Cu SCR catalysts for diesel applications [9]. He held the total volume of the SCR catalyst constant and found that a 1/3 Fe + 2/3 Cu SCR catalyst system expanded the temperature window relative to the Cu-only SCR catalyst. However, the lightoff performance of the 1/3 Fe + 2/3 Cu SCR system suffered relative to that of the Cu-only SCR catalyst. Thus, the Cu-only SCR catalyst was recommended for applications where the exhaust temperatures are below 450°C most of the time. The 1/3 Fe + 2/3 Cu SCR system was recommended only for applications where high temperature NO_x conversion is required.

In this study, the total SCR volume and the resulting space velocity were allowed to vary in order to determine the maximum temperature window possible under warmed-up conditions. This emphasis on warmed-up activity would be particularly suitable for lean-burn gasoline applications, where stoichiometric operation and a close-coupled three-way catalyst (TWC) can be used for NO_x control until the underbody SCR catalyst is warmed up and lean operation can be initiated. It was recognized, however, that diesel engines always produce lean exhaust. Such engines require lean NO_x conversion as soon as possible after a cold start. Therefore, modifications to the zoned SCR catalyst system were investigated to improve its lightoff performance while still providing as wide a temperature window as possible during warmed-up operation.

EXPERIMENTAL

Catalyst Samples - Several 15.24 cm long cores with a diameter of 1.75 cm were drilled from cordierite bricks (400 cpsi) coated with either a state-of-the-art Fe/zeolite SCR catalyst or a state-of-the-art Cu/zeolite SCR catalyst. The 15.24 cm cores were cut with a diamond-blade saw to produce core samples that were 2.54 cm long. A small hole was drilled through the axial center of each core so a thermocouple could be inserted into the sample for measuring the catalyst bed temperature.

Aging - Prior to this study, some of the 2.54 cm long Fe SCR samples were aged for 34 hours behind samples of a three-way catalyst (TWC) on a pulse-flame combustion reactor [10], as shown in Figure 1. Details regarding the aging protocol can be found in reference [3]. To briefly summarize, each TWC+SCR set was aged either (1) with full-time lean operation; (2) on a schedule that cycled between stoichiometric, rich, and lean A/F ratios, with 2/3 of the time spent at

stoichiometry; or (3) on a schedule that also cycled between stoichiometric, rich, and lean A/F ratios, with 2/3 of the time spent at a lambda of 0.92. In this paper, these aging conditions will be referred to as "lean" aging, "stoichiometric" aging, or "rich" aging, respectively. For each aging schedule, one Fe SCR sample was aged with an inlet temperatures of 750°C, a second sample was aged at 800°C, and a third sample was aged at 850°C. The duration of 34 hours was used because 34 hours of the rich cycle has been correlated with 80K km of vehicle aging for close-coupled three-way catalysts in Europe.

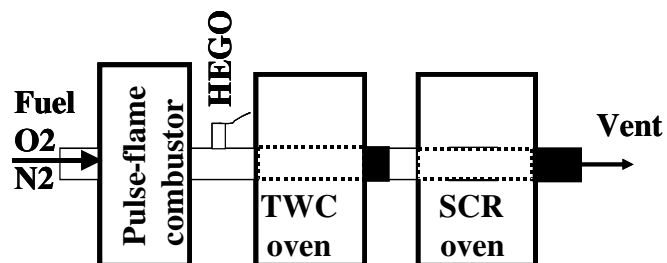


Fig. 1. Aging apparatus.

Samples of the Cu SCR catalyst were also aged downstream of TWC samples using the three A/F ratio schedules. For each aging schedule, one Cu SCR sample was aged with an inlet temperature of 750°C, and a second sample was aged with an inlet temperature of 800°C.

Steady-state NO_x Conversion Performance - Some of these aged Fe SCR and Cu SCR samples were used in this present study to optimize a zoned combination of Fe SCR catalyst and Cu SCR catalyst that provided the widest temperature window under steady-state conditions. The Fe SCR catalysts, Cu SCR catalysts, and zoned combinations of Fe and Cu SCR catalysts were evaluated for NO_x conversion on a flow reactor using lean temperature ramps. The TWC samples that were used during the aging were not used during these performance evaluations. Gaseous NH₃ was used as the source of reductant instead of a liquid urea solution. Each SCR catalyst or combination of catalysts was installed into a quartz tube which was placed inside of a vertical furnace, and a 1.6 mm type K thermocouple was inserted from the rear into the hole that was drilled through the catalyst sample so the bed temperature could be recorded during the ramp, as shown in Figure 2. The catalyst was continually exposed to lean exhaust containing 500 ppm NO and 500 ppm NH₃ while the furnace was ramped slowly (typically at 3.5 to 4.0°C/min) from a low temperature (e.g., 200°C) to a high temperature (e.g., 800°C). Some systems were also evaluated with 250 ppm NO and NH₃ and with 1000 ppm NO and NH₃. 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 listed in Table I.

The standard sample length on this reactor was 2.54 cm or 1.0 inch, and the exhaust flow rate of 2.5 L/min produced a space velocity of approximately 25,000 hr⁻¹. However, the total length of the SCR catalyst

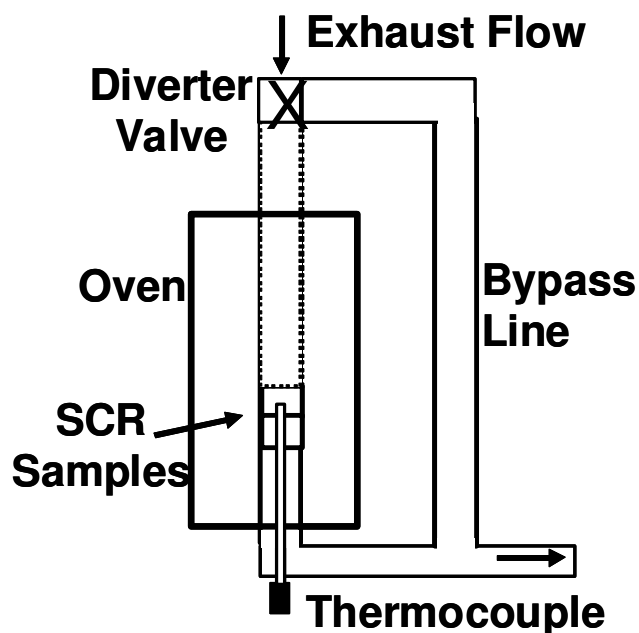


Fig. 2. Experimental apparatus used for temperature ramps and lightoff tests.

Table I. Feedgas composition during lean temperature ramps performed on 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

system was allowed to vary in this study, while the exhaust flow rate was always maintained at 2.5 L/min. Therefore, the resulting space velocity was inversely proportional to the total length of the SCR catalyst system according to

$$\text{Space velocity} = 25,000 \text{ hr}^{-1} / (\text{total length in inches}) \quad (1)$$

Lightoff tests - The performance of the SCR catalyst was also evaluated during lean lightoff tests to simulate cold-start conditions on a vehicle. Here the SCR samples were moved downstream so that they were located just outside of the oven in Figure 2. The vertical furnace was heated to a relatively high temperature (e.g., 800°C), and the bypass line was used to divert the exhaust flow around the furnace and the SCR samples. The feedgas contained 500 ppm NO and NH₃ during

these lightoff tests, and the remainder of the gas concentrations were the same as those listed in Table I. The type K thermocouple was used to measure the catalyst bed temperature. The exhaust flow was directed around the SCR catalyst until its bed temperature was between 100°C and 120°C. To initiate the test, the exhaust gas was directed back through the heated furnace and through the SCR sample. The furnace heated the exhaust which in turn heated the SCR catalyst, and the NO_x conversion and catalyst bed temperature were recorded as a function of time.

For all tests, the 2.5 L/min of exhaust was diluted with 22.5 L/min of N₂ (i.e., 10:1 dilution ratio) to provide sufficient 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 pumped directly to an analyzer bench, which contained a flame ionization detector for measuring HC, NDIR analyzers for measuring CO, CO₂, and N₂O, and a chemiluminescence NO_x analyzer for measuring total NO_x (i.e., NO+NO₂). The remainder of the diluted exhaust was pumped 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 analyzer set up to measure NO. The readings from the two chemiluminescence analyzers were subtracted in order to determine the amount of NH₃ in the diluted exhaust.

RESULTS

During this study, the lengths of the Fe and Cu SCR samples were varied in order to maximize the overall system performance. In this paper, the length of the Fe and Cu SCR catalysts will usually be referred to as a percentage of the standard sample length of 2.54 cm that is normally used on the reactor. Thus, a 2.54 cm Fe SCR sample would be referred to as a 100% sample, while a 5.08 cm Fe SCR catalyst followed by a 2.54 cm Cu SCR catalyst would be referred to as a 200% Fe + 100% Cu system. The 100% length produces a space velocity of approximately 25,000 hr⁻¹. Therefore, the total length of a SCR system can be used to calculate the equivalent space velocity through the use of equation (1).

100% samples of the Fe SCR catalyst and Cu SCR catalyst that had been aged for 34 hours on the lean schedule at 800°C were evaluated for NO_x conversion using lean temperature ramps with 500 ppm NO and NH₃. Then each sample was cut in half, and the front half of the Fe SCR catalyst (i.e., the "inlet" side during aging) was mated with the rear half of the Cu SCR catalyst (i.e., the "outlet" side during aging), and the 50% Fe + 50% Cu SCR system was evaluated. Likewise, the front half of the Cu SCR catalyst was mated with the rear half of the Fe SCR catalyst, and the 50% Cu + 50% Fe SCR system was evaluated. Figure 3 compares the NO_x conversion of the 50% Fe + 50% Cu and 50% Cu + 50% Fe SCR systems with that of the 100% Fe SCR catalyst and the 100% Cu SCR catalyst at a constant space velocity of 25K hr⁻¹. Table II summarizes the minimum