

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

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ABSTRACT

A laboratory study was performed to assess the potential of using selective catalytic reduction (SCR) with NH₃ to treat the NO_x emissions from lean-burn gasoline engines. A primary concern was the potential for hot rich exhaust conditions on the vehicle, as such conditions could degrade the zeolite-based SCR catalysts being developed for automotive applications. Samples of an iron/zeolite formulation were aged for 34 hours behind samples of a three-way catalyst (TWC) on a pulse-flame combustion reactor using different A/F ratio schedules that exposed the catalysts to either continuously lean operation, mostly stoichiometric operation, or mostly rich operation. For each A/F ratio schedule, separate SCR samples were aged with inlet temperatures of 750°C, 800°C, or 850°C. The aged SCR samples were evaluated for NO_x conversion at 25K hr⁻¹ during lean temperature ramps with 500 ppm NO and NH₃. After aging under mostly rich conditions at 750°C inlet, the Fe SCR catalyst provided a NO_x conversion of 94% at 500°C. After aging under mostly stoichiometric or continuously lean conditions at 800°C inlet, which is a reasonable maximum temperature for underfloor converters on some vehicles, the NO_x conversions at 500°C were 93% and 97%, respectively.

Samples of a copper/zeolite formulation were similarly aged with the different A/F ratio schedules at an inlet temperature of 800°C. When evaluated at 350°C, the Cu SCR samples provided peak NO_x conversions of approximately 95%, 100%, and 100% after aging under mostly rich conditions, mostly stoichiometric conditions, and continuously lean conditions, respectively. These results suggested that both SCR formulations have sufficient durability to be considered for potential use in controlling the NO_x emissions from lean-burn gasoline engines.

INTRODUCTION

Lean-burn port-fuel injected (LB-PFI) and stratified-charge direct-injection (SCDI) gasoline engines can provide improved fuel economy relative to the stoichiometric PFI engines used on most vehicles today. This increased fuel economy results from reduced pumping losses and improved thermodynamics of combustion. However, the exhaust from LB-PFI and

SCDI engines contains a surplus of oxygen (O₂). Under these lean conditions, the three-way catalyst (TWC) currently used for emission control on stoichiometric engines cannot provide sufficient reduction of the oxides of nitrogen (NO_x, or NO + NO₂) to satisfy stringent NO_x regulations.

SCDI engines have been used on production vehicles in Japan, Europe, and the U.S. Most of these engines have used a lean NO_x trap (LNT) to control the NO_x emissions under lean conditions. A LNT [1] is essentially a TWC that contains high concentrations of alkaline-earth metals and/or alkali metals, which serve as NO_x storage materials. During lean operation, the NO_x in the exhaust (primarily NO) is oxidized over platinum on the LNT to form NO₂, which reacts with the NO_x storage materials and additional O₂ to form adsorbed NO_x species, such as nitrites or nitrates. As the LNT begins to fill up and the NO_x storage efficiency decreases, the A/F ratio is driven to a rich condition for 2 to 5 seconds. Hydrogen in the rich exhaust promotes the decomposition of the adsorbed NO_x species [2], releasing the NO_x which then reacts with the reductants in the rich exhaust [i.e., hydrogen (H₂), carbon monoxide (CO), and hydrocarbons (HC)] over the precious metal sites to form nitrogen (N₂). Then the A/F ratio returns to the lean condition, and the process repeats.

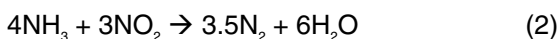
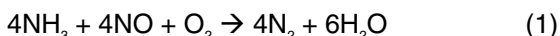
A key characteristic of lean NO_x traps is that they operate with optimal efficiency in a range or "window" of temperature. The NO_x storage performance at low temperatures is limited by incomplete purging and low rates of NO oxidation, while the high temperature NO_x performance is limited by the decreasing stability of the adsorbed NO_x species [3]. As a result, the effective temperature window of the LNT is typically between 300°C and 500°C.

NO_x traps are typically large in volume and utilize high concentrations of platinum group metal (PGM) in order to ensure good lean NO_x performance for the life of the vehicle. Consequently, the traps can be relatively expensive. Other issues with NO_x traps include

- (1) the need for the rich purges, which negates some of the fuel economy benefit of lean operation;
 - (2) the undesired release of NO_x from the LNT during the rich purges, particularly at high temperatures [4];
 - (3) the need for desulfations at high temperatures [5].
- SO₂ in the exhaust (from the combustion of sulfur in the fuel and oil) reacts with the NO_x storage sites to form

sulfates. These sulfates are very stable and prevent those sites from storing NO_x . To recover the NO_x storage capability of those sites, the sulfates must be removed periodically by exposing the LNT to hot rich conditions for several minutes. Similar to the rich purges, these rich desulfations reduce the fuel economy of the vehicle. Also, care must be taken to minimize the production of hydrogen sulfide (H_2S) during the desulfations, as H_2S has a highly offensive odor.

An alternative approach to treating the NO_x emissions under lean conditions is Selective Catalytic Reduction, or SCR [6]. Here a catalyst is used to promote the reaction of NO_x with ammonia (NH_3) under lean conditions to produce N_2 and H_2O . NH_3 can react with pure NO , pure NO_2 , or a mixture of NO and NO_2 according to the following reactions [7]:



This last reaction is referred to as the "fast SCR reaction" and is significantly faster than the reduction of pure NO or pure NO_2 . This can improve the NO_x conversion of the SCR catalyst at low temperatures. Similar to lean NO_x traps, SCR catalysts are most effective in a range or window of temperature.

The NH_3 can be either generated in the exhaust or supplied from an external source. NH_3 can be generated under rich conditions by reacting NO_x and fuel (or H_2) over a platinum-containing catalyst upstream of the SCR, such as a TWC or a diesel oxidation catalyst (DOC). Below 400°C , the NH_3 generated on the platinum catalyst can be stored on the SCR and used to reduce NO_x during a subsequent lean period. Alternatively, the NH_3 can be injected from an external source on the vehicle. Since NH_3 can be difficult to handle, an aqueous solution of urea [$\text{CO}(\text{NH}_2)_2$] is being considered for mobile applications, as a molecule of urea breaks down into 2 molecules of NH_3 in the exhaust [8].

The SCR catalyst that has traditionally been used to treat NO_x from stationary sources consists of vanadium (V) and tungsten (W) on titania (Ti) [6]. SCR catalysts with improved thermal durability are being developed for diesel exhaust systems equipped with periodically regenerating particulate traps. These catalysts use either iron (Fe) or copper (Cu) in a zeolite framework. Such technology provides good potential for controlling the NO_x emissions from diesel engines [9, 10, 11].

Relative to a LNT, SCR technology offers several advantages. There is no need for the rich purges, since the NO_x reduction is performed under lean conditions. This is beneficial for the fuel economy of the vehicle and also eliminates the issue of purge NO_x release. Also, the temperature window of the SCR is much broader than that of a LNT, thereby expanding the range of engine speeds and loads where lean operation can be used to improve the fuel economy. Since SCR catalysts use base metals instead of precious metals, they are significantly lower in cost than a lean NO_x trap (although

there are other costs associated with SCR that will be mentioned shortly). SCR catalysts are also more robust to the feedgas NO_x concentration than lean NO_x traps.

Another feature of SCR catalysts is that they can store large quantities of NH_3 at low temperatures. Analogous to the role of the oxygen storage component in three-way catalysts, this stored NH_3 can serve as a buffer during NO_x transients. The stored NH_3 can supplement the injected NH_3 (i.e., urea) when the NO concentration increases rapidly to high levels, such as during rapid accelerations. In contrast, excess NH_3 can be stored on the SCR catalyst when the NO concentration drops rapidly to low levels, such as during rapid decelerations.

However, there are several issues associated with SCR, some of which are generic to lean-burn gasoline engines and diesel engines. As previously mentioned, the reducing agent (NH_3) has to be generated in the exhaust or supplied from an external source. The generation of NH_3 by an upstream platinum catalyst during rich operation decreases the fuel economy of the vehicle. In addition, the concept of storing this NH_3 on the SCR catalyst would not be effective during heavy load operation on the vehicle, as the NH_3 storage capacity of the SCR catalyst drops to low levels at temperatures above 400°C [3].

The alternative approach of supplying the reductant from an external source requires another tank on the vehicle for the urea solution. This may be more feasible for large vehicles such as trucks. Indeed, SCR catalysts based on the V/W/Ti formulation are currently being used with urea injection to treat the NO_x emissions from heavy-duty diesel trucks in Europe [12]. However, the need for the urea tank can be more of a challenge for small cars, where space is often limited. Also, the urea injection system can be expensive. An infrastructure for the urea solution will be required that will allow customers to refill their urea tanks when necessary. Such an infrastructure is underway in Europe, and there have been discussions in the U.S. regarding this issue. In addition, customers will need to be educated on the need to keep their urea tanks filled.

There are still other technical challenges that are generic to diesel and gasoline engines. The urea solution can freeze in cold climates, requiring an external heater and/or insulation. Exhaust mixing vanes may be needed to ensure good mixing of the liquid urea solution with the exhaust gas. Under cold exhaust conditions, the urea may have difficulty completely decomposing into NH_3 [13].

In summary, there are several technical and socio-political challenges associated with SCR. However, the technology potentially offers significant NO_x conversion performance and economic benefits relative to a LNT. This is particularly true for large engines, where large and expensive NO_x traps would be required to treat the NO_x emissions during lean operation. Therefore, a program was initiated to investigate SCR technology as an alternative to lean NO_x traps for treating the NO_x emissions from lean-burn gasoline engines.

In addition to the generic issues listed above, there are additional challenges with SCR that are particular to gasoline engines. The exhaust temperatures are

generally higher on a gasoline engine relative to a diesel engine and can easily exceed 400°C, even in the underfloor location on a vehicle. As mentioned earlier, the NH₃ storage capacity of the SCR catalyst is quite low at these high temperatures [3]. Under such conditions, the urea solution will need to be injected to precisely match the flux of NO_x from the engine. This can be a significant challenge for the urea injection control system during transient driving conditions.

Another challenge is that the NO_x concentrations are typically higher in gasoline exhaust than in diesel exhaust. This can require customers to refill their urea tanks more frequently.

An even greater concern is the likelihood for hot, rich exhaust conditions during heavy load operation on gasoline vehicles, such as during trailer tow. Such conditions could potentially degrade the zeolite-based SCR catalysts being considered for mobile applications, which would essentially eliminate the possibility of applying SCR technology to gasoline vehicles. Therefore, a laboratory investigation was launched to investigate the effects of aging temperature and A/F ratio on the NO_x performance of SCR catalysts. A leading iron/zeolite SCR catalyst (i.e., Fe SCR) and a leading copper/zeolite SCR catalyst (i.e., Cu SCR) were used for this assessment.

EXPERIMENTAL

Catalyst Samples - Several 15.24 cm long cores with a diameter of 1.75 cm were extracted from a cordierite brick (62 cells per square cm, 0.15 mm wall thickness) that was coated with a leading Fe/zeolite SCR formulation. The cores were cut with a diamond-blade saw to produce several core samples that were 2.54 cm in length.

Aging - To simulate the exhaust architecture on a vehicle during aging, each Fe SCR sample was aged downstream of a TWC sample on a pulse-flame combustion reactor [14], as shown in Figure 1. Here gasoline was combusted with a mixture of N₂ and O₂ to produce a gas mixture that simulated engine exhaust. A heated exhaust gas oxygen sensor (HEGO) downstream of the combustor was used to control the A/F ratio during stoichiometric operation. Separate ovens were used for the TWC and SCR samples; the TWC sample was placed at the outlet of the first oven, and the SCR sample was placed at the outlet of the second oven. In all cases, the TWC contained 2.12 g/L Pd/Rh (0/9/1).

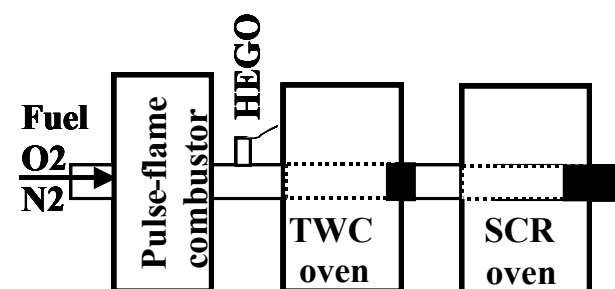


Figure 1. Aging apparatus for TWC and SCR core samples.

Since the TWC on a vehicle would typically be smaller than the SCR catalyst, the TWC core samples used the same 1.75 cm diameter but were only 1.27 cm in length or half as long as the SCR core samples.

To investigate the sensitivity of the Fe SCR catalyst to the A/F ratio and temperature during aging, separate sets of TWC and SCR samples were aged with different A/F ratio schedules and with different inlet temperatures to the SCR. One aging schedule was a proprietary schedule that cycled between stoichiometric, rich, and lean conditions. The catalyst was exposed to rich exhaust (lambda of 0.92) for 67% of the time, so this schedule will be referred to as the "rich schedule" in this paper. It has been found that 34 hrs of this aging schedule correlates with 80,000 km of customer use for three-way catalysts in Europe. Therefore, 34 hrs was used for all of the A/F ratio schedules. The maximum temperature of the TWC was 1040°C. Separate SCR samples were aged on this schedule at inlet temperatures of 650°C, 750°C, 800°C, and 850°C.

The second aging schedule utilized another proprietary A/F ratio routine that also cycled between lean, rich, and stoichiometric conditions. However, the A/F ratio was at stoichiometry for 67% of the time with this schedule, so it will be referred to as the "stoichiometric schedule" in this paper. The inlet temperature to the TWC during the stoichiometric portion was 850°C, and the maximum bed temperature of the TWC was 1000°C. Separate SCR samples were aged on the stoichiometric schedule at inlet temperatures of 750°C, 800°C, and 850°C.

The third aging schedule involved continuously lean operation. Here the pulse-flame combustion reactor was operated continuously at the stoichiometric A/F ratio, and full-time secondary air was injected downstream of the control HEGO but upstream of the TWC oven. This schedule will be referred to as the "lean schedule" in this paper. The inlet temperature to the TWC sample was controlled at 850°C. Separate SCR samples were aged on the lean schedule at inlet temperatures of 750°C, 800°C, and 850°C.

Core samples from a leading Cu/zeolite SCR catalyst were produced in a similar fashion and aged behind samples of a TWC on the pulse flame combustion reactor using the three A/F ratio schedules. The Cu SCR samples were aged with an inlet temperature of 800°C.

NO_x Conversion Performance - The aged SCR samples were evaluated for NO_x conversion on a flow reactor; the TWC samples were not used during the evaluations. Gaseous NH₃ was used as the source of reductant instead of a liquid urea solution. Each SCR sample was installed into a quartz tube which was placed inside of a furnace with programmable temperature controls. The catalyst was continually exposed to lean exhaust containing 500 ppm NO and 500 ppm NH₃ at a space velocity of 25K hr⁻¹ while the temperature of the furnace was ramped slowly (typically at 3.5°C/min) from approximately 150°C to 800°C. 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 1. For some samples, temperature ramps were