

The Poisoning and Desulfation Characteristics of Iron and Copper SCR Catalysts

Joseph R. Theis
Ford Motor Company

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ABSTRACT

A laboratory study was performed to assess the effects of SO₂ poisoning on the NO_x conversion of iron (Fe) and copper (Cu) SCR catalysts. Thermally aged samples of the catalysts were poisoned with SO₂ under lean conditions. At various times during the poisonings, the samples were evaluated for NO_x conversion with NO and NH₃ using lean temperature ramps. The low temperature NO_x conversions of both catalysts decreased by 10 to 20% after 1 to 4 hours of poisoning but were stable with continued exposure to the SO₂. The poisoned Cu SCR catalyst could be desulfated repeatedly with 5 minutes of lean operation at 600°C. Initially, the poisoned Fe SCR catalyst required 5 minutes of lean operation at 750°C to recover its maximum NO_x conversion. However, after multiple poisonings and desulfations, the low temperature NO_x conversion of the catalyst exhibited significantly less sensitivity to the SO₂, although the final NO_x conversion following the 750°C desulfation also decreased slightly with the repeated poisonings and desulfations. This decrease in SO₂ sensitivity for the Fe SCR catalyst could potentially eliminate the need to desulfate this catalyst.

INTRODUCTION

Selective catalytic reduction (SCR) with ammonia (NH₃) is becoming the preferred method for treating the NO_x emissions from diesel engines, as SCR catalysts can use NH₃ to reduce NO_x during lean operation [1]. The active materials in SCR catalysts are low cost base metals such as iron (Fe), copper (Cu), or vanadium (V). Due to the difficulties of handling ammonia, an aqueous solution of urea [CO(NH₂)₂] will be used as the source of NH₃ on mobile applications, as 1 molecule of urea breaks down into 2 molecules of ammonia in the exhaust system. SCR is also under consideration for treating the

NO_x emissions from lean-burn gasoline engines. Even though the aging temperatures are considerably higher on gasoline engines than on diesel engines, it was shown previously that state-of-the-art SCR catalysts are sufficiently durable to be considered for such engines [2].

The other catalyst technology for controlling NO_x emissions from lean-burn engines is the lean NO_x trap (LNT). These catalysts contain relatively high concentrations of precious metal [e.g., platinum (Pt), palladium (Pd), and/or rhodium (Rh)]. They also contain high concentrations of alkaline-earth materials (e.g., barium) and/or alkali metals (e.g., potassium), which react with the NO_x under lean conditions to form adsorbed NO_x species, such as nitrates [3]. When the LNT begins to saturate with adsorbed NO_x, the A/F ratio is driven to a rich condition for 2 to 5 seconds. The nitrates decompose under the rich conditions, releasing the NO_x which then reacts with the reductants in the exhaust over the precious metal sites to produce N₂. This purges the LNT so it can store NO_x again during the next lean period. Relative to SCR catalysts, lean NO_x traps are more sensitive to temperature as well as the NO_x concentration in the exhaust [4]. In addition, the rich purges required by NO_x traps decrease the overall fuel economy of the vehicle. Finally, because of the relatively high loadings of precious metal, lean NO_x traps are considerably higher in cost than SCR catalysts.

Another major concern with lean NO_x traps is their sensitivity to sulfur poisoning [5]. Sulfur in the fuel and/or oil forms sulfur dioxide (SO₂) in the combustion chamber, and this SO₂ can react with the NO_x storage materials to form sulfates. These sulfates are very stable and effectively poison the NO_x storage sites, rendering them unable to store NO_x. Figure 1 shows the NO_x storage efficiency of 3 degreened NO_x traps as a function of time when exposed to 9 ppm SO₂ at 400°C using a 60 second lean/60 second rich cycle. The NO_x storage efficiency (averaged over the 60 second lean

periods) continued to drop with increasing time of exposure to the SO₂.

To recover the NO_x storage efficiency, the LNT must be desulfated periodically. The desulfation of a poisoned LNT requires several minutes of rich operation at temperatures of approximately 725°C [5]. Therefore, the engine software must be capable of generating these high exhaust temperatures, even when the vehicle is used primarily for low load operation. However, the extended hot, rich desulfations decrease the overall fuel economy of the engine. Also, care must be taken to avoid the production of hydrogen sulfide (H₂S) during the rich desulfation, as H₂S has a highly offensive odor. This is typically accomplished by oscillating the A/F ratio between a lean condition and a rich condition during the desulfation.

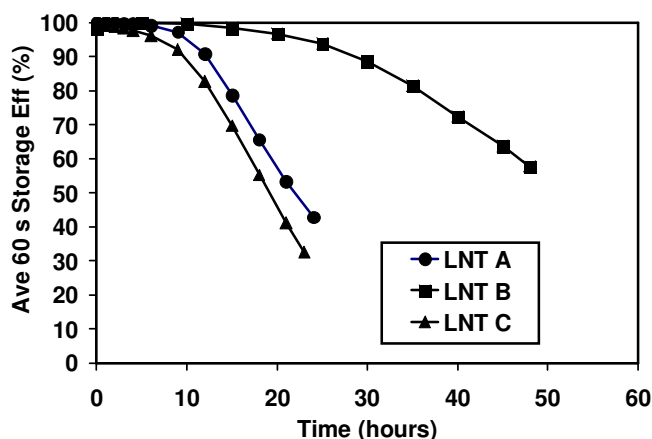


Fig. 1. NO_x storage efficiency for three lean NO_x traps exposed to 9 ppm SO₂ at 400°C. Samples degreened 10 minutes at 600°C. Storage efficiencies averaged over lean periods of a 60 second lean/60 second rich cycle.

Some SCR catalysts also demonstrate some sensitivity to sulfur poisoning. Schmiege [6] subjected Cu/zeolite, Fe/zeolite, and vanadium-based SCR catalysts to 28 ppm SO₂ at 225°C until the catalysts had been exposed to 10 g S/liter. The vanadium-based SCR was essentially insensitive to the sulfur, while the conversion of the Fe/zeolite catalyst dropped by only 2 to 6%, depending on the NO/NO₂ ratio. But the conversion of the Cu/zeolite SCR catalyst dropped by 17% when NO₂ was 25% of the total NO_x, with much of the decrease occurring during the early stages of the poisoning. When the NO₂ was 75% of the total NO_x, the decrease in conversion was even higher at 35%. But when the NO₂ was 50% of the total NO_x, the decrease was only 3%. This agreed with the results of Lambert [7], who showed that a base metal/zeolite SCR formulation exposed to SO₃ for the equivalent of 120K miles performed nearly as well as a sample aged to the equivalent of 4K miles when evaluated between approximately 160 and 530°C with a 50/50 mix of NO and NO₂.

Cheng [8] also investigated Cu/zeolite and Fe/zeolite SCR catalysts for their sensitivity to sulfur poisoning. She found that the effect of sulfur changed with the thermal aging condition of some SCR catalysts, while it remained essentially the same for other SCR

catalysts. For one Cu/zeolite SCR catalyst, the effect of SO₂ on the low temperature NO_x conversion was larger on a part aged 64 hours (i.e., 100K mile equivalent) than for a sample aged 2 hrs (i.e., 4K mile equivalent), while for another Cu/zeolite catalyst, the effect of SO₂ was about the same for both aging conditions. For a Fe/zeolite SCR formulation, the effect of SO₂ was about the same for both aging conditions, while for another Fe/zeolite formulation the effect of SO₂ on the sample aged 64 hours was larger than the effect on the sample aged 2 hrs. In general, the effect of SO₂ was larger on the Cu SCR catalysts than on the Fe SCR catalysts, in agreement with the results of Schmiege [6].

This study also assessed the effects of SO₂ on the NO_x performance of state-of-the-art Cu/zeolite and Fe/zeolite SCR catalysts after the catalysts were aged at high temperatures. The aged catalysts were exposed to SO₂ under lean conditions for several hours and periodically evaluated the NO_x conversion during lean temperature ramps while supplying NO and NH₃. Studies were also performed to determine the time and temperature necessary to desulfate the poisoned SCR catalysts and recover their NO_x conversion performance. Multiple poisonings and desulfations were performed on each sample to simulate the repeated poisonings and desulfations that will occur on vehicles.

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 a sample so a thermocouple could be inserted through the hole for measuring either the inlet temperature or the catalyst bed temperature.

Thermal Aging - Prior to this study, samples of the Fe and Cu SCR catalysts were aged for 34 hours downstream of a three-way catalyst (TWC) on a pulse-flame combustion reactor [9], as shown in Figure 2. Details regarding the aging protocol can be found in reference [2]. Some samples were aged with full-time lean operation, while other samples were aged on a schedule that 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 and "rich" aging, respectively. The duration of 34 hours was used because 34 hours of

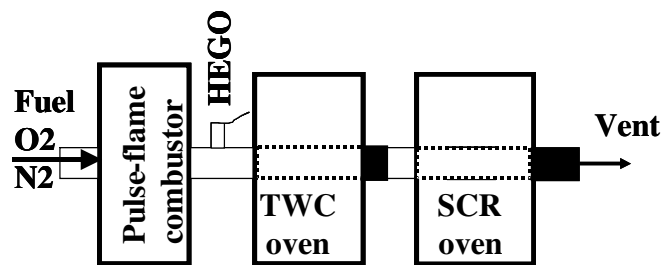


Fig. 2. Apparatus for aging SCR catalyst samples.

the rich cycle has been correlated with 80K km of vehicle aging for close-coupled three-way catalysts in Europe.

The poisoning and desulfation work described in this paper was performed on a Fe SCR sample that was aged on the rich schedule with an inlet temperature of 650°C; corresponding work was performed on a Cu SCR sample that was aged on the lean schedule at 800°C. While the aging conditions were different, these samples were selected because they provided high NO_x conversion over a broad range of temperature prior to the SO₂ poisonings. In particular, the conversions of the samples at low temperatures were relatively high. During the poisonings, the drop in low temperature conversion was used to indicate the extent of sulfur poisoning, and the recovery in low temperature conversion following the desulfations was used to indicate the extent of sulfur removal from the catalyst.

Sulfur Poisoning – For the sulfur poisonings, the SCR catalyst was inserted into a quartz tube which was placed inside of a programmable furnace. It is noted that the TWC samples used during the thermal aging in Figure 2 were not used during the poisoning and desulfation work. The catalyst was heated to an inlet temperature of 400°C and exposed to a continuously lean exhaust stream containing 9 ppm SO₂, 5% O₂, 500 ppm NO, 10% CO₂ and H₂O, and the balance N₂. The total poisoning time was typically 8 hours, and the exhaust flow was 3.0 L/min, resulting in a space velocity of approximately 30,000 hr⁻¹. A SO₂ level of 9 ppm represents a relatively high level of sulfur in the fuel (approximately 280 ppm for an engine operating with an A/F ratio of 30:1), and one hour of the poisoning schedule exposed the catalyst to approximately 0.36 g/liter of sulfur.

After 1, 2, 4, and 8 hours of SO₂ poisoning, the SCR sample was removed from the poisoning reactor and installed into another flow reactor that was set up for evaluating the lean NO_x conversion of the SCR catalyst. The performance was assessed using lean temperature ramps at 25,000 hr⁻¹ with 500 ppm NO and NH₃ along with 5% O₂, 10% CO₂ and H₂O, and the balance N₂. The ramp rate was typically 3.5 to 4.0°C per minute, and the maximum bed temperature during the ramp was limited to 400°C (i.e., the poisoning temperature) to avoid removing some of the sulfur from the SCR catalyst. To ensure that the sample was not partially desulfated during the performance evaluation, the NO_x conversion was also assessed as the temperature ramped down from 400°C. The SCR sample was then reinstalled into the poisoning reactor, and this poisoning and evaluation sequence was continued until the total poisoning time of 8 hours was achieved.

Desulfations – Once the 8 hours of SO₂ poisoning were achieved and the final performance evaluation was completed, a desulfation study was performed. Here the poisoned catalyst was exposed to several 5-minute periods at increasing temperatures. While lean NO_x traps require high temperature rich conditions to recover their maximum NO_x performance, these SCR samples were desulfated with lean exhaust using the same gas concentrations used during the performance evaluations (i.e., 500 ppm NO and NH₃, 5% O₂, 10% CO₂ and H₂O, balance H₂). After each 5 minute desulfation period, the

SCR catalyst was cooled and evaluated for lean NO_x conversion performance at a specified temperature using 500 ppm NO and NH₃ at 25K hr⁻¹. For the Cu SCR catalyst, the desulfation temperatures ranged from 450°C to 800°C, and the evaluation temperature was 250°C. For the Fe SCR catalyst, the desulfation temperatures ranged from 500°C to 800°C. Since the Fe SCR catalyst requires higher temperatures than the Cu SCR catalyst to achieve high conversion levels [2, 10], the performance of the Fe SCR catalyst was evaluated after each desulfation period at 350°C.

On the reactor used for performance assessments and desulfations, the 2.5 L/min of exhaust was diluted with 22.5 L/min of N₂ (i.e., 10:1 dilution ratio) in order to provide enough flow for the different analyzers. This also reduced 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 (FID) 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 heated to 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 to calculate the amount of NH₃ in the diluted exhaust.

RESULTS

Poisoning of Cu SCR Catalyst– The Cu SCR sample that had been aged for 34 hours on the lean schedule at 800°C was poisoned for 8 hours at 400 C with 9 ppm SO₂. The NO_x conversion performance was assessed using lean temperature ramps with 500 ppm NO and NH₃ at various times during the poisoning, typically after 1, 2, 4, and 8 hours. The conversion was assessed as the temperature ramped up and as the temperature ramped back down. Initially, the maximum temperature during the ramp was allowed to reach as high as 540°C. However, it was observed that the conversion at low temperatures could be higher during the temperature ramp down than it was during the temperature ramp up.

To demonstrate, Figure 3 shows the NO_x conversion of the thermally aged Cu SCR catalyst before it was poisoned (ramp performed with increasing temperature) and during the temperature ramps up and down after it was poisoned with 9 ppm SO₂ for 6 hours. The NH₃ slip is also shown before the poisoning and during the ramp up after the poisoning (the NH₃ slip is not shown during the ramp down because the catalyst stored some of the NH₃ as the temperature decreased due to the increasing NH₃ storage capacity). Relative to the conversion before the poisoning, the NO_x conversion during the ramp up was significantly lower after the 6 hours of poisoning, and the NH₃ slip was also significantly higher. However, the NO_x conversion at temperatures below 400°C was higher during the ramp down than it was during the ramp up. Since the sulfur