

Deactivation of Accelerated Engine-Aged and Field-Aged Fe-Zeolite SCR Catalysts and the Role of the Diesel Oxidation Catalyst

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Introduction

Fe-zeolite SCR catalysts have been identified as a promising candidate for NO_x abatement in heavy-duty diesel engines due to their good durability and high activity [1,2]. While the catalysts are durable, the high temperatures that the catalysts can incur during the regeneration of the diesel particulate filter (DPF) can lead to degradation and lost performance. Typical aging techniques to evaluate the durability of the catalyst employ steam, SO₂ and high temperatures in a controlled furnace; however, this approach only hydro-thermally ages the SCR catalyst and does not expose the catalyst to key transients that occur during actual operation. On-board emissions control systems employ a diesel oxidation catalyst (DOC) upstream of the SCR and a DPF positioned either upstream or downstream. In addition to oxidizing NO to NO₂, the DOC helps to achieve the high temperature necessary for oxidizing the soot in the DPF. To more accurately capture the conditions that occur on-board, the present study implements an accelerated thermal aging protocol on a diesel aftertreatment system consisting of a DOC, an Fe-zeolite SCR catalyst and a DPF. The objectives of this study are two-fold: (i) to assess the validity of the implemented accelerated thermal aging protocol in replicating the aging conditions observed in the field-aged catalysts, and (ii) to identify deactivation mechanisms associated with performance losses.

Materials and Methods

Fresh Fe-zeolite SCR catalysts coated on a 400 cpsi cordierite substrate, provided by Catalytic Solutions, Inc., are used for accelerated aging. Additionally, field-aged SCR catalysts of similar formulation obtained from a high-mileage bus fleet are cut into three different sections: front, middle, and rear. A bench-mounted naturally-aspirated direct injection (NA/DI) Hatz single-cylinder diesel engine fitted with an exhaust aftertreatment system, consisting of an upstream DOC, an Fe-zeolite SCR catalyst and a downstream DPF, is used to perform accelerated aging. The rapid aging utilizes the high temperature exhaust gases obtained during the DPF regeneration cycles where excess fuel is periodically introduced to initiate an exotherm over the DOC. Cyclic aging is performed at SCR inlet temperatures of 650, 750 and 850°C for up to 50 cycles. Cored samples of 2.2 cm diameter and 7.6 cm long from front and rear sections of fresh, field-aged and accelerated engine-aged SCR catalysts are evaluated for NO_x performance in a bench-flow reactor using simulated diesel exhaust gases consisting of 5% CO₂, 5% H₂O, 14% O₂, 350 ppm NO_x, 350 ppm NH₃, balance N₂ at a GHSV of 30,000 h⁻¹ over a temperature range of 200–600°C. Surface characterization techniques such as EPMA, SEM-EDS, XRD and BET are used to characterize material changes induced by thermal aging for both field-aged and engine-aged SCR catalysts.

Results and Discussion

Evidence of thermal aging is apparent on all of the aged catalysts, especially when applying the accelerated engine-aging technique above 750°C. However, while the rear SCR

section maintains the same general NO_x performance curve as the fresh catalyst, the front section demonstrates a significantly different performance curve as evidenced in Figure 1a. When evaluating above 300°C, the NO_x conversion drops significantly and is only about 20% for each aging condition. This severely degraded performance is also observed in the field-aged samples. Figure 1b shows the NO_x conversion from the accelerated engine-aging technique at 750°C along with the field-aged results. Both the rear and front sections show a strong similarity, indicating that the accelerated aging protocol used in this study accurately replicates key on-board conditions.

To understand the observed performance changes, a thorough materials characterization was performed. The degradation in the rear section appears to be due to the loss of the zeolite structure as evidenced by surface area losses, Al₂O₃ formation, and increased Fe₂O₃ formation. SEM images also reveal cracking and delamination of the washcoat for the samples aged at 750 and 850°C, as well as the field-aged catalysts. However, the samples aged at 650°C have pristine washcoat images, unaffected surface area and XRD patterns very similar to that of the fresh sample. This indicates that the drastic difference in NO_x performance between the front and rear sections must be attributed to another mechanism. A recent study by Jen et al. [3] reports similar behavior and attributes the deactivation mechanism to trace levels of platinum originating from the upstream DOC. They theorize that Pt-O is vaporized during the exotherm and subsequently deposited on the cooler SCR catalyst. This Pt level is too small to detect with XRF, but will cause a loss in performance above 300°C due to the direct oxidation of NH₃ over the Pt site.

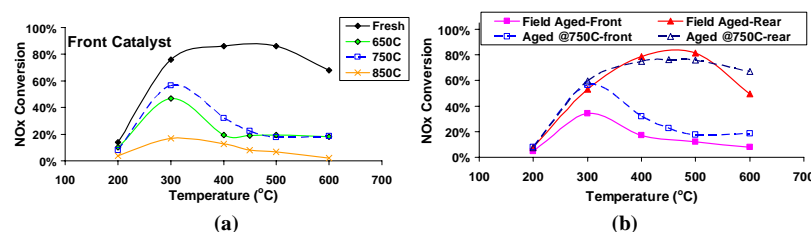


Figure 1. (a) NO_x performance of the fresh and front sections of the accelerated engine-aged Fe-zeolite SCR catalysts. (b) Performance of accelerated engine-aged catalysts at 750°C for 50 aging cycles closely replicates front section of field-aged catalyst. Evaluation conditions: GHSV = 30k hr⁻¹, NH₃:NO_x = 1.0, NO₂/NO_x = 0.0.

Significance

This work shows the implemented accelerated thermal aging protocol is successful in replicating behavior in field-aged catalysts and offers further evidence of the role of DOC-originating Pt on the severe deactivation of the front section of a SCR catalysts.

References

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