

# Sulfur Tolerance and DeSOx Studies on Diesel SCR Catalysts

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## ABSTRACT

Base metal/zeolite catalysts, particularly containing copper and iron, are among the leading candidates for treatment of NO<sub>x</sub> emissions for diesel applications. Even with the use of ultra low sulfur fuel, sulfur poisoning is still a durability issue for base metal/zeolite SCR catalysts. In this study, the impact of sulfur poisoning on SCR activity and the stored sulfur removal effectiveness were investigated on several Cu and Fe/zeolite SCR catalysts after different thermal aging. The impact of sulfur was more significant on the Cu than on Fe/zeolite SCR catalysts for the NO<sub>x</sub> activity. It was found that the sensitivity of thermal aging status to the sulfur poisoning impact was different. The impact of sulfur on NO<sub>x</sub> activity changed with thermal aging on some catalysts, while it remained relatively the same for other catalysts. The most thermally durable SCR catalyst was not necessarily the most durable to sulfur poisoning. These results suggested that each base metal/zeolite SCR catalyst has its own characteristic response to sulfur poisoning. Control of sulfur poisoning and strategy for deSO<sub>x</sub> might be different depending on the formulation as well as thermal aging status. This study provides a better estimate of the durability of SCR catalysts as well as the strategy of deSO<sub>x</sub> for diesel engine aftertreatment.

## INTRODUCTION

Urea-based Selective Catalytic Reduction (SCR) has the potential to meet U.S. Diesel Tier 2 Bin 5 emission standards for NO<sub>x</sub> in 2010 (1-4). Base metal/zeolite catalysts, particularly copper and iron zeolite SCR catalysts are among the leading candidates for treatment of NO<sub>x</sub> emissions for North American diesel applications because of their high de-NO<sub>x</sub> activity and superior thermal durability (4-5). It is known that these base metal/zeolite SCR catalysts are sensitive to sulfur poisoning and exhibit this susceptibility (3-6). It is further known that these catalysts can be regenerated by decomposing the sulfates (deSO<sub>x</sub>) at high temperatures in lean condition. Low sulfur fuel is required to achieve robust low temperature SCR activity typical of light load driving. In addition to fuel sulfur, the sulfur content within engine oil also makes its way to the aftertreatment system. Even with the use of ultra low sulfur fuel (diesel fuel containing less than 15ppm sulfur) that is expected in the U.S.,

sulfur poisoning is still a durability issue for base metal/zeolite SCR catalysts.

Although the deactivation of SCR catalysts due to sulfur poisoning is not a major deactivation mode, it directly impacts the overall SCR performance as long as sulfur exists in the exhaust system. The sulfur tolerance should be considered equally in SCR catalyst selection for engine applications. While the phenomena of sulfur poisoning is well known, some details, such as the impact of sulfur poisoning on SCR activity and the stored sulfur removal effectiveness in a long term vehicle application, have not been understood. In this study, several Cu and Fe/zeolite SCR catalysts that have potential to be applied on diesel vehicles for aftertreatment were thermally aged at different aging times. The impacts of sulfur poisoning as well as the effectiveness of a temperature programmed desulfation (deSO<sub>x</sub>) were studied on these different thermally aged catalysts. The purpose of this study was to provide insight into the durability of SCR catalysts due to sulfur poisoning in diesel engine applications. A way to investigate the sulfur tolerance on base metal/zeolite SCR catalysts for vehicle applications is presented to provide a better estimate of the durability of SCR catalysts as well as a strategy of SCR deSO<sub>x</sub>.

## EXPERIMENTAL

### DIESEL SCR CATALYSTS, TESTING PROCEDURES, AND CONDITIONS

The SCR catalysts used in this study were fully formulated monolith copper/zeolite and iron/zeolite selected from several catalyst suppliers. A brief summary is given in Table 1. Further details of the formulations are proprietary.

Each catalyst was aged and tested in the following order. First, two catalyst samples from each SCR formulation were hydrothermally aged with 14% O<sub>2</sub>, 5% CO<sub>2</sub>, 4.5% H<sub>2</sub>O, and N<sub>2</sub> balance, at 670°C for 2 hours and 64 hours respectively, based on the amount of time at high temperature equivalent to 4K and 120k mi due to a regenerating Diesel Particulate Filter (DPF). The NO<sub>x</sub> performance was measured on each sample right after the thermal aging and is called Test1 in the following

section. Then, the sample was sulfated for 16 hours as described below. The SCR activity of the sulfated sample was measured and called Test2. The last NO<sub>x</sub> activity measurement on each sample in the series, called Test3, was conducted after a temperature sulfur removal process.

Table 1. Summary of base metal/zeolite catalysts

| Catalyst Name | Description |
|---------------|-------------|
| CatA          | Cu/zeolite  |
| CatB          | Cu/zeolite  |
| CatC          | Fe/zeolite  |
| CatD          | Fe/zeolite  |

The catalyst monolith core samples were in size 1" diameter by 1" long in this study, and were aged and tested using a laboratory flow reactor at a space velocity of 30,000 hr<sup>-1</sup>. The steady state NO<sub>x</sub> activity of samples were measured from 170°C to 500°C in 30-50°C steps in the flow reactor connected to an FTIR instrument from MIDAC Corporation with a heated sample cell system for gas analysis. The SCR evaluation was stopped at 500°C so as not to decompose any sulfates on the catalyst surface that were generated during the sulfur aging. Simulated diesel exhaust gas was flowed through the sample core with a composition as shown in Table 2 for the steady state SCR activity measurements.

Table 2. Composition of simulated diesel exhaust gas for SCR activity measurements.

| Component        | Concentration |
|------------------|---------------|
| O <sub>2</sub>   | 14%           |
| H <sub>2</sub> O | 4.5%          |
| CO <sub>2</sub>  | 5%            |
| NO <sub>x</sub>  | 350 ppm       |
| NH <sub>3</sub>  | 350 ppm       |
| N <sub>2</sub>   | Balance       |

## SULFUR POISONING AND REGENERATION

A laboratory sulfur aging process was developed for this study. The sample was exposed to 112ppm SO<sub>2</sub> in the gas mixture as shown in Table 3 at 250°C for 16 hours. The total sulfur throughput corresponded to 77 g/L of SCR catalyst or 200,000 miles sulfur-equivalent miles

(assuming 15ppm S fuel). To remove sulfur from the SCR catalysts, the sulfated samples were first heated and stabilized in the reactor at 150°C in 14% O<sub>2</sub>, 5% CO<sub>2</sub>, and 4.5% H<sub>2</sub>O in balance N<sub>2</sub>. Then, the stored sulfur was removed by heating the catalyst in the same gas from 150°C to 650°C at a rate of 10°C/min. The released sulfur components during the temperature programmed deSO<sub>x</sub> were measured using V&F Instruments Inc. mass spectrometry.

Table 3. Gas composition over SCR samples during sulfation at 250°C.

| Component        | Concentration |
|------------------|---------------|
| SO <sub>2</sub>  | 112 ppm       |
| O <sub>2</sub>   | 14 %          |
| H <sub>2</sub> O | 4.5 %         |
| CO <sub>2</sub>  | 5 %           |
| N <sub>2</sub>   | Balance       |

## RESULTS AND DISCUSSION

### THERMAL DURABILITY – 4K VS 120K MI AGING

The impact of thermal aging at two aging times, 2h and 64h (4K and 120K mi aging), was evaluated for each catalyst. The steady state NO<sub>x</sub> conversions for Cu/zeolite SCR catalysts, CatA and CatB, are shown in Figure 1. CatA deteriorated more than CatB after 64h thermal aging, although their NO<sub>x</sub> activities were very close after 2h thermal aging. The same comparison on Fe/zeolite catalysts, CatC and CatD, is shown in Figure 2. CatD had less deterioration after 64h aging and had better overall NO<sub>x</sub> activity comparing to CatC. Thermal durability was different even among the same type of base metal/zeolite SCR catalysts.

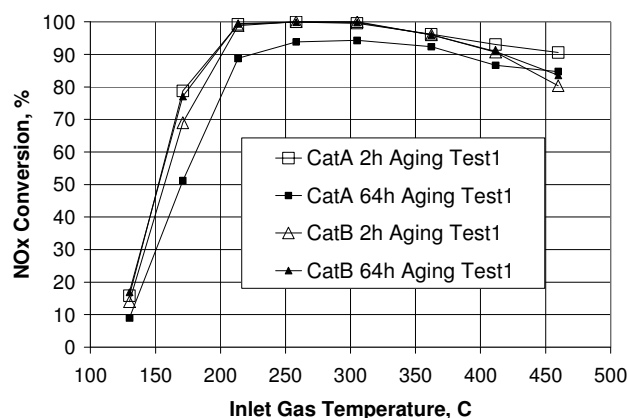


Figure 1. Steady state NO<sub>x</sub> conversions for Cu/zeolite SCR catalysts, CatA and CatB, after aging at 671°C for 2h and 64h.