

## The Different Impacts of SO<sub>2</sub> and SO<sub>3</sub> on Cu/Zeolite SCR Catalysts

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### Introduction

Cu/zeolite catalysts that have high de-NO<sub>x</sub> activity and superior thermal durability are among the leading candidates for treatment of NO<sub>x</sub> emissions for diesel applications. It is known that the SCR performance of sulfur poisoned Cu/zeolite SCR catalysts is significantly reduced, although the catalysts can be regenerated by decomposing the sulfates (deSO<sub>x</sub>) at high temperatures in lean condition (1). Most studies on sulfur poisoning of Cu/zeolite SCR catalysts have been based on SO<sub>2</sub> as the poisoning agent (1-5). Insofar as diesel oxidation catalysts (DOCs) will be employed upstream of SCR catalysts for most applications, it is likely that a portion of the SO<sub>2</sub> will be oxidized into SO<sub>3</sub>. Thus, although the issue of SO<sub>2</sub> vs. SO<sub>3</sub> impacts on base metal/zeolite SCR catalysts has not been raised to date, it is important to investigate the relative poisoning effects of these species.

### Materials and Methods

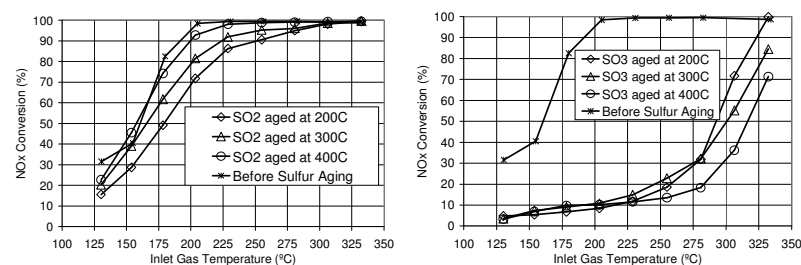
Cu/zeolite SCR catalysts were exposed to 40ppm SO<sub>2</sub> or SO<sub>3</sub> in the gas mixture with 14% O<sub>2</sub>, 5% CO<sub>2</sub>, 4.5% H<sub>2</sub>O, and N<sub>2</sub> balance at 200°C, 300°C, and 400°C for 1.5 hours. To remove the sulfur (deSO<sub>x</sub>), the catalysts were heated to 770°C in 14% O<sub>2</sub>, 5% CO<sub>2</sub>, 4.5% H<sub>2</sub>O, and N<sub>2</sub> balance. The NO<sub>x</sub> performance was measured before and after the sulfur poisoning, and after the deSO<sub>x</sub>. The steady state NO<sub>x</sub> activity was measured from 130°C to 340°C in a flow reactor. The sulfur poisoned Cu/zeolite SCR catalysts were also characterized by several analytical tools, such as x-ray photoelectron spectroscopy (XPS), to investigate the difference in surface species remaining on the samples after poisoning by SO<sub>2</sub> and SO<sub>3</sub>.

### Results and Discussion

The NO<sub>x</sub> activity for Cu/zeolite SCR catalysts before and after sulfur poisoning by SO<sub>2</sub> and SO<sub>3</sub> at 200°C, 300°C, and 400°C is shown in Figure 1. The NO<sub>x</sub> activity decreased up to 33% for the samples poisoned by SO<sub>2</sub>; however, it was significantly decreased for all the samples after being exposed to 40ppm SO<sub>3</sub> for 1.5 hours regardless the exposure temperature. The low temperature (T < 250°C) NO<sub>x</sub> activities were almost lost, but activity begins to recover above 250°C. There is not much available in the literature to explain the SO<sub>3</sub> poisoning mechanism on Cu/zeolite SCR catalysts. Ramachandran et al. (2) observed that V-ZSM-5 catalysts exhibit stable activity for NO reduction in the presence of H<sub>2</sub>O and SO<sub>2</sub> but rapidly deactivate in the presence of 10ppm SO<sub>3</sub>. These authors attributed the possible SO<sub>3</sub> deactivation to the formation of ammonium (bi)sulfate when both NH<sub>3</sub> and SO<sub>3</sub> are present. However, there was no NH<sub>3</sub> during the aging in this study and, therefore, it is not likely that ammonium (bi)sulfate were formed. Other kinds of sulfur compounds may be formed and impact the active sites for NO<sub>x</sub> SCR reaction but, fortunately, these compounds can apparently be removed or decomposed at elevated temperatures in the deSO<sub>x</sub> process used here.

SO<sub>2</sub> was the main sulfur compound released during the deSO<sub>x</sub> of samples aged with SO<sub>2</sub> and SO<sub>3</sub>. However, the amounts of SO<sub>2</sub> released from the SO<sub>3</sub>-aged catalysts during the

deSO<sub>x</sub> were 5 to 15 times higher than those from the SO<sub>2</sub>-aged samples. In addition, the NH<sub>3</sub> also interacted with the sulfur compounds formed on the SO<sub>3</sub>-aged Cu/zeolite SCR catalysts before the deSO<sub>x</sub>. The temperatures of SO<sub>2</sub> peak and the amounts of released SO<sub>2</sub> during the deSO<sub>x</sub> were very similar among the samples without NH<sub>3</sub> exposure regardless of the SO<sub>3</sub> aging temperatures. However, the deSO<sub>x</sub> profiles changed significantly after being exposed to NH<sub>3</sub> before the deSO<sub>x</sub>. The amounts of released SO<sub>2</sub> were about 1.5 to 4.5 times higher for the samples being exposed to NH<sub>3</sub> before the deSO<sub>x</sub>. Furthermore, the temperatures of the released SO<sub>2</sub> peak were all shifted to some extent. These results indicate that sulfur compounds might be reformed due to the interaction between NH<sub>3</sub> and stored sulfur. Surface analysis results using XPS also demonstrate that a larger amount of sulfur species are retained in the form of sulfate (SO<sub>4</sub><sup>2-</sup>) when SO<sub>3</sub> was introduced compared to samples sulfated with SO<sub>2</sub>, a result clearly consistent with the lower deNO<sub>x</sub> activity for the former sample.



**Figure 1.** Steady state NO<sub>x</sub> conversions for Cu/zeolite SCR catalysts before and after SO<sub>2</sub> (left) and SO<sub>3</sub> (right) aging at 200°C, 300°C, and 400°C.

### Conclusions

The results of this study, based on deNO<sub>x</sub> activity and characterization measurements, suggest that the active sites of Cu/zeolite SCR catalysts involved in the storage and removal of sulfur react with SO<sub>2</sub> and SO<sub>3</sub> in very different ways. The sulfation of Cu/ZSM-5 with SO<sub>3</sub> results in significantly more severe deactivation than with SO<sub>2</sub>, suggesting that the effects of the oxidation catalyst upstream of the SCR catalyst must be considered when designing the after-treatment system.

### References

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