Chemical deSOx: A low temperature desulfation method for zeolite-based SCR catalysts

Ashok Kumar*, Michael A. Smith, Krishna Kamasamudram, Neal W. Currier, Aleksey Yezerets

Corporate Research and Technology, Cummins Inc

1900 McKinley Ave, Columbus IN 47201

*kumar.a@cummins.com

Introduction

Cu-exchanged small-pore zeolite catalysts, belonging to the structural family of chabazite (CHA), have achieved substantial commercial importance in the recent years as the materials of choice for selective catalytic reduction (SCR) of oxides of nitrogen with ammonia in diesel exhaust. This was achieved because of their unparallel NOx conversion ability at low temperatures and hydrothermal stability at elevated temperatures. Nonetheless, the NOx conversion activity of these catalysts is not immune to sulfur oxide species. Sulfur oxides (SO_2 and SO_3, commonly referred to as SOx) are ubiquitous in the exhaust gases and are detrimental to SCR catalyst performance. Despite drastic reduction of sulfur content in diesel fuels, for example by the introduction of ultra-low sulfur diesel (ULSD), sulfur poisoning remains one of the most significant factors impacting the performance of various catalysts in diesel exhaust after-treatment systems.

In order to maintain the high NOx conversion to meet stringent emission requirements, Cu-zeolite SCR catalyst is periodically exposed to high temperatures, in excess of 550°C, which can be detrimental to the health of the SCR catalyst, other PGM-based aftertreatment components and also results in a fuel penalty. In this presentation a newly discovered method of sulfur removal at relatively low temperatures from Cu-zeolite SCR catalyst, by modulating the feed gas conditions, will be described.

Materials and Methods

Commercial Cu-CHA SCR catalysts, supported on 300 cpsi cordierite substrate of dimensions 1" diameter and 3" length, were used in this study. Two specialized bench scale reactors, one for loading controlled amount of sulfur on SCR catalyst and a second reactor for catalyst performance measurements as a function of progressive desulfation and quantification of sulfur on the catalyst, were used in this study [1]. Sulfur loading reactor uses an oxidation catalyst to oxidize SO_2 in the humid environment to expose downstream SCR catalyst to a mixture of SO_2, SO_3, and H_2SO_4. The ratio of SO_3/SOx was controlled using the temperature of the oxidation catalyst.

Bench flow reactor was used to evaluate several facets of catalyst behavior including oxidation, NH_3 storage, and NOx conversion ability in sulfur free, fully sulfated, and progressively desulfated states of the catalyst. The amount of sulfur stored on the catalyst was estimated by measuring cumulative amounts of SO_2 and H_2SO_4 released during temperature programmed desorption (TPD) up to 1000°C. The accuracy in sulfur measurement was verified with ICP-OES and combustion method and found to be in agreement [1].

Results and Discussion

Cu-CHA offer higher NOx conversion at low temperatures as compared to SCR alternatives like Fe-zeolite and V-based SCR catalysts. However, presence of sulfur selectively decreases its low temperature performance. Exposing Cu-zeolite catalysts to high temperature can partially recover the performance, but in order to fully rejuvenate the catalytic performance, temperature approximately 700C is needed. A newly discovered low temperature desulfation method, herein referred as chemical deSOx, is found to be effective for removal of sulfur and for the recovery of NOx conversion.

Chemical deSOx can be accomplished by modulating the exhaust flow and its components at temperatures as low as 350°C. As shown in Figure 1 example, greater than 90% of the stored sulfur can be removed from the SCR catalyst and NOx conversion can be fully recovered by chemical deSOx around 500°C. Such an extent of sulfur removal by conventional heat treatment methods would have required >700°C.

In this work, underlying mechanism of chemical deSOx, explored by various probe reactions and characterization techniques, will be discussed.

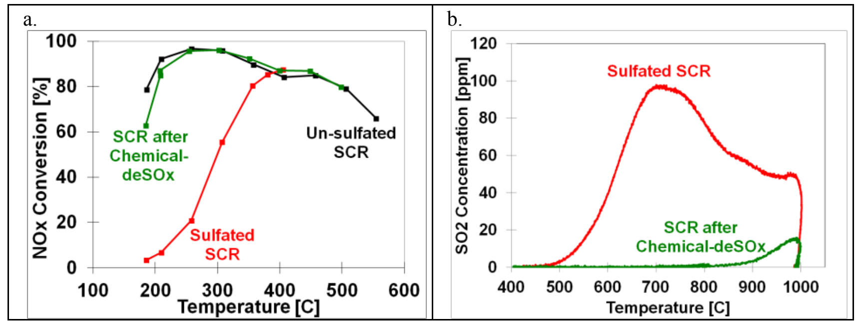

Figure 1. Effect of chemical deSOx on performance of NOx conversion during SCR reaction (a) and evolution of sulfur after sulfation and chemical deSOx treatment (b)

Significance

Greenhouse gas regulations demand higher fuel economy out of the diesel engines and that translates into lower exhaust temperatures. With the lowering of the exhaust temperatures, there is a need to develop strategies to remove sulfur from the aftertreatment catalyst at low temperatures or design catalysts which are less sensitive to sulfur as lower levels of sulfur in fuel as compared to ULSD are not economically feasible. The chemical deSOx method developed by us achieves this goal.

References

1. Kumar A., Smith M.A., Kamasamudram K., Currier N.W., An H., and Yezerets A., Catalysis Today (2014), http://dx.doi.org/10.1016/j.cattod.2013.12.038
2. Kamasamudram K., Currier N.W., Szailer T., and Yezerets A., SAE Technical Paper 2010-01-1182