

# Fundamentals of $\text{NH}_3$ -SCR and $\text{SO}_x$ chemistry over copper zeolite for the control of $\text{NO}_x$ and greenhouse gas ( $\text{N}_2\text{O}$ ) emissions

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## Abstract

The release of  $\text{N}_2\text{O}$  over Cu-zeolite was investigated due to the critical contribution it makes to the atmosphere as one of the greenhouse gases (GHGs). An exhaust after-treatment system (EATS) for heavy-duty vehicles that uses Cu/SSZ-13 as the selective catalyst reduction (SCR) catalyst experiences not only a variety of flow, temperature and chemical conditions but is also exposed to various resulting contaminants. Among these, sulfur has been the focus of studies due to its critical deactivation of DeNO<sub>x</sub> performance, even at low concentration levels. Adsorption/desorption of sulfur species over Cu/SSZ-13 is connected closely to the lifetime of the SCR catalyst. The task of unravelling the synergistic effect of sulfur has on the formation of  $\text{N}_2\text{O}$  during the  $\text{NH}_3$ -SCR of  $\text{NO}_x$ , while also reflecting realistic application conditions, is challenging. The ambition here is to gain a comprehensive understanding of the formation of  $\text{N}_2\text{O}$  in the presence of sulfur species during the  $\text{NH}_3$ -SCR of  $\text{NO}_x$  at low temperature for  $\text{NO}_x$  emissions control.

Model catalysts were prepared to investigate a variety of copper species and ammonium nitrate (AN) within the CHA cage. It was found that the CHA structure promotes surface nitrate species in  $\text{NO}_2$ -rich conditions, and an environment with strong polarity within the CHA cage was proposed as a feasible reason for the largest formation of ammonium nitrate compared to the MFI and BEA structures with medium and large pore/cage sizes. In addition, zeolite acidity was more a viable reason as to why ammonium nitrate is thermally stable in Cu/CHA compared to Cu/MFI and Cu/BEA than the pore-confinement effect, which has been used to explain the thermal stability of AN over Cu/zeolites. The IR signature of the ammonium nitrate was also obtained; it is believed that ammonium nitrate exists mainly by interacting with copper ions to form copper-ammonium nitrate within the CHA cage.

Copper species and the adsorption of sulfur oxides ( $\text{SO}_2/\text{SO}_3$ ) were investigated and their synergistic effects on the formation of  $\text{N}_2\text{O}$  assessed. The  $\text{SO}_3$ -poisoning effect was highlighted which, from an experimental aspect, is very challenging. We found two different states of sulfur species.  $\text{SO}_2$  and  $\text{SO}_3$  interaction with copper-monomers ( $\text{Z}_1\text{CuOH}$  and  $\text{Z}_2\text{Cu}$ ) and copper-dimer ( $\text{Z}_2\text{Cu}_2\text{O}_2$ ) are possible. Sulfated Cu-dimer is lower in energy compared to its copper-monomers counterparts.  $\text{SO}_3$  interacts with both  $\text{Z}_1\text{CuOH}$  and  $\text{Z}_2\text{Cu}$  but  $\text{SO}_2$  mainly interacts with  $\text{Z}_1\text{CuOH}$ .  $\text{SO}_3$ -poisoning only causes copper-(bi)sulfate ( $\text{ZCuHSO}_4$ ), whereas  $\text{SO}_2$ -poisoning can cause both copper- (bi)sulfite ( $\text{ZCuHSO}_3$ ) and (bi)sulfate ( $\text{ZCuHSO}_4$ ). Taken together, our results well demonstrate why the  $\text{SO}_3$  exposure results in more critical chemical poisoning (irreversible deactivation) compared to the  $\text{SO}_2$  exposure to Cu/CHA. Finally, synergistical effect of sulfur, copper, and Brønsted sites were found for  $\text{N}_2\text{O}$  formation under  $\text{NO}_2$ -rich condition. Consequently, we found that sulfur promotes  $\text{N}_2\text{O}$  intermediate formation but increasing Brønsted site density increases  $\text{N}_2$  selectivity, thereby, reducing  $\text{N}_2\text{O}$  formation from Cu/CHA.

**Keywords:**  $\text{N}_2\text{O}$ , AN,  $\text{SO}_2$ ,  $\text{SO}_3$ , Cu/SSZ-13,  $\text{NH}_3$ -SCR, DeNO<sub>x</sub>, EATS.