

Fundamentals of NH_3 -SCR and SO_x chemistry over copper zeolite for the control of NO_x and greenhouse gas (N_2O) emissions

Joonsoo Han

Department of Chemistry and Chemical Engineering
Chalmers University of Technology, Gothenburg 2024

Abstract

The release of N_2O 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_x 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 N_2O during the NH_3 -SCR of NO_x , while also reflecting realistic application conditions, is challenging. The ambition here is to gain a comprehensive understanding of the formation of N_2O in the presence of sulfur species during the NH_3 -SCR of NO_x at low temperature for 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 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 (SO_2/SO_3) were investigated and their synergistic effects on the formation of N_2O assessed. The SO_3 -poisoning effect was highlighted which, from an experimental aspect, is very challenging. We found two different states of sulfur species. SO_2 and SO_3 interaction with copper-monomers (Z_1CuOH and Z_2Cu) 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. SO_3 interacts with both Z_1CuOH and Z_2Cu but SO_2 mainly interacts with Z_1CuOH . SO_3 -poisoning only causes copper-(bi)sulfate (ZCuHSO_4), whereas SO_2 -poisoning can cause both copper-(bi)sulfite (ZCuHSO_3) and (bi)sulfate (ZCuHSO_4). Taken together, our results well demonstrate why the SO_3 exposure results in more critical chemical poisoning (irreversible deactivation) compared to the SO_2 exposure to Cu/CHA. Finally, synergistical effect of sulfur, copper, and Brønsted sites were found for N_2O formation under NO_2 -rich condition. Consequently, we found that sulfur promotes N_2O intermediate formation but increasing Brønsted site density increases N_2 selectivity, thereby, reducing N_2O formation from Cu/CHA.

Keywords: N_2O , AN, SO_2 , SO_3 , Cu/SSZ-13, NH_3 -SCR, DeNO_x, EATS.