

Impact of NO₂ on Sulfur Poisoning of Cu-SSZ-13 Catalysts

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Significance and Relevance

Selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) using Cu-CHA is commercially used to reduce NO_x emissions from diesel engine exhaust. Even with its commercial success, sulfur poisoning is a known degradation mechanism for Cu-CHA SCR catalysis. Here, we show how exposure to NO₂ affects sulfur species that form on Cu-SSZ-13, and that sulfation affects the formation of ammonium nitrate and copper nitrate during NO₂ exposure. The extent of NO₂ exposure changes the distribution of sulfur species on the catalyst surface, with long NO₂ exposure times leading to more challenging desulfation. The insights from this research can help design desulfation strategies.

Preferred and 2nd choice for the topic: Automotive and stationary emission control, fundamental advances in understanding catalysis

Preferred presentation: Oral only / Oral preferred

Introduction and Motivations

Selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) using Cu-SSZ-13 is commercially used to reduce NO_x emissions from diesel engine exhaust. Among several reactions that occur over the SCR catalyst, the most discussed include the standard and fast SCR reactions, with the latter dependent on NO₂: 2NH₃ + NO + NO₂ \rightarrow 2N₂ + 3H₂O. It is generally known that Cu-SSZ-13 is vulnerable to sulfur deactivation by SO₂, SO₃, and H₂SO₄ present in the exhaust. Though sulfur poisoning during standard SCR reaction conditions is relatively well-studied,¹ key questions remain about the impact of sulfur on the fast SCR process. Here, we studied how SO₂ affects the interaction between NO₂ and Cu-SSZ-13 and how NO₂ affects the interaction between SO₂ and Cu-SSZ-13.

Materials and Methods

A monolith-supported Cu-SSZ-13 catalyst with 600 cells per square inch (cpsi) was provided by Cummins Inc. The catalyst samples were formed to 2.9 cm in length, 45 cells and 0.89 g in weight. The total flow was 1400 sccm, corresponding to a gas space velocity of 60000 h⁻¹. Catalysts were pretreated with 10% O₂, 7% H₂O and balance N₂ for 4 h at 550 °C before use. SO₂ exposure included 30 ppm SO₂ for 21 h at 400 °C, followed by pretreatment with 10% O₂ and balance N₂ also at 400 °C. For the set of experiments described in this abstract, the sample was cooled to 200 °C and then exposed either to (i) NO₂, (ii) NH₃, then NO₂, or (iii) NO+NH₃, then NO₂, all typically followed by temperature programmed desorption (TPD) from 200 to 900 °C with a 10 °C/min heating rate. Other NO₂-focused experiments were run and the results of those will be presented also.

Results and Discussion

After SO_2 exposure, ZCuSO₄ forms from ZCuOH.¹ Our results show that exposing the sample to NO_2 after this sulfur exposure leads to less NO_2 reacted with Cu, and the TPD confirms that less nitrate was formed relative to a sample that had not been exposed to SO_2 . Our results also demonstrate that when exposing the ZCuSO₄ to NH_3 or $NO+NH_3$, $(NH_4)_2SO_4$ forms, E1.

 $\begin{array}{ccc} 2NH_3 + ZCuSO_4 + 2H_2O \rightarrow (NH_4)_2SO_4 + ZCuOH & E1 \\ \\ \text{When the sample is then exposed to NO_2, we show that the following reactions occur,}^2 \\ 2ZCuOH + 3NO_2 \rightarrow 2ZCuNO_3 + NO + H_2O & E2 \\ 2NO_2 + 2NH_3 \rightarrow NH_4NO_3 + N_2 + H_2O & E3 \\ \\ \text{The ZCuNO_3 from E2 and (NH_4)_2SO_4 from E1 can react through a series of reactions summed up by E4 \\ 2ZCuNO_3 + 2(NH_4)_2SO_4 + 3NO_2 \rightarrow 2ZCuSO_4 + 4NH_4NO_3 + 0.5N_2 & E4 \\ \end{array}$



Finally, NH_4NO_3 decomposes to N_2O and H_2O according to the following equation

 $NH_4NO_3 \rightarrow N_2O + 2H_2O$ E5 Our results suggest that these reactions occur sequentially/simultaneously, and to show that, here we use an example where we varied NO_2 exposure times after a SO_2 then $NO+NH_3$ exposure, and then performed a TPD experiment. Figure 1A and B show that with 0.5 h and 1 h NO₂ exposure, the NO₂ concentration did not reach 300 ppm. For these NO₂ exposures, NO₂ was still reacting - we conclude that (NH₄)₂SO₄ was still present, so the nitrate formed via E2 was still reacting with (NH₄)₂SO₄ (E4), therefore the NO_2 is still being consumed in reforming a nitrate. With the 2 h NO_2 exposure, the inlet 300 ppm concentration was reached, Fig 1C, because 2 h was enough to consume all the $(NH_4)_2SO_4$ via E4, allowing the build up and saturation of Cu nitrates. Following this logic, with the shorter NO_2 exposure times, there should be no ZCuNO₃, since the NO₂/nitrate was reacting with the (NH₄)₂SO₄, but there should be CuSO₄ and NH₄NO₃ from E3 and E4, and the residual (NH₄)₂SO₄. First, the absence of NO₂ during the TPD (Fig 1D and E) supports the absence of ZCuNO₃. With the nitrates/NO₂ reacting with the $(NH_4)_2SO_4$, the $(NH_4)_2SO_4$ should decrease, and CuSO₄ should increase with NO₂ exposure time, which aligns with the TPD results in the bottom panel of Figure 1, where the low-temperature SO₂ peak originates from (NH₄)₂SO₄ and the higher-temperature release is from CuSO₄.³ If with the 2 h NO₂ exposure, the $(NH_4)_2SO_4$ is consumed and the NH_4NO_3 has had time to decompose (E5), there should be no N₂O or low temperature SO₂ release in Fig 1F, which is indeed the case. Only ZCuNO₃ and CuSO₄ should be present, which is why we see NO_2 and the high temperature SO_2 peaks. These results all show that initially ZCuNO₃ forms from ZCuOH and reacts with (NH₄)₂SO₄. Once (NH₄)₂SO₄ is depleted, only ZCuNO₃ persists which ultimately decomposes during TPD.



Figure 1. Top panel - NO₂ profiles, and bottom panel - corresponding TPD profiles after SO₂, then NO+NH₃ followed by NO₂ exposures, for different NO₂ exposure periods on Cu-SSZ-13 at 200 °C.

Our study shows that Cu and ammonium nitrate formation are impacted by SO_2 exposure, and Cu and ammonium sulfate formation are impacted by NO_2 exposure. This has implications for desulfation strategies and SCR design.

References

- 1. K. Mandal, P. Rani, Y.-R. Chen, A. Wijerathne, K. Nam, K. Meena, D.A. Kiani, R. Daya, W.S. Epling, C. Paolucci, *Applied Catalysis B: Environment and Energy* **2024**, *358*, 124361.
- 2. C. Liu, G. Malta, H. Kubota, T. Toyao, Z. Maeno, K.J. Shimizu, *Journal of Physical Chemistry C* **2021**, *125*, 21975–21987.
- 3. A. Wang, L. Olsson, Chemical Engineering Journal 2020, 395, 125048

Acknowledgements

The authors acknowledge the financial support provided by Cummins Inc.