

NH₃-SCR over Cu-CHA from first principles

¹Competence Centre for Catalysis and Department of Physics, Chalmers University of Technology, Göteborg, Sweden *ghj@chalmers.se

Significance and Relevance

The results provide atomic-level understanding of the hierarchy of effects that determine the NH_3 -SCR activity over Cu-exchanged chabazite catalysts at low- and high-temperatures. The low-temperature activity is determined by pairing of mobile $Cu(NH_3)_2^+$ complexes and blocking of the active sites by NH_3 , whereas the high-temperature activity is limited by NH_3 -blocking of single framework-bound Cu species. The first-principles based kinetic model describes accurately the non-monotonic temperature dependence of the activity.

Introduction and Motivations

 NO_x emission control continues to be a major challenge in lean-burn engine exhaust after treatment due to increasingly stricter legislations. The leading technology for NOx reduction to N_2 and H_2O in oxygen excess is selective catalytic reduction using ammonia as the reducing agent (NH_3 -SCR). A stateof-the-art catalyst for NH_3 -SCR is chabazite zeolite functionalized with Cu (Cu-CHA). Cu-CHA has high activity and selectivity for NH_3 -SCR over a wide temperature range and is, moreover, hydrothermally stable at high temperatures.

The conversion of NOx over Cu-CHA under standard SCR conditions shows a nonmonotonic trend with respect to temperature, with a minimum at about 350 °C. This minimum results in the, so-called, "seagull" profile and indicates that different reaction mechanisms dominate at low and high temperatures. An additional indication that the reaction mechanism changes with temperature is different initial exponential increases of the conversion in the low- and high-temperature regimes. The temperature dependence of the nonselective N_2O formation during the NH_3 -SCR is yet another indication that the NH_3 -SCR reaction follows different mechanisms at low and high temperatures.

Understanding the dominating reaction mechanisms for NH_3 -SCR over Cu-CHA provides a handle to further improve the performance.

Materials and Methods

First-Principles Calculations. Spin-polarized DFT calculations are performed with the Vienna Abinitio simulation package. The gradient-corrected Perdew–Burke–Ernzerhof functional, augmented with a Hubbard-U term and van der Waals corrections, is used to describe exchange–correlation effects. Mean-field microkinetic modeling and kinetic Monte Carlo simulations are used to explore the consequences of the first-principles reaction landscapes and facilitate comparison to experiments.

Results and Discussion

Figure 1 shows the proposed reaction cycle at low and high temperatures. The low temperature mechanisms proceeds over a pair of mobile $Cu(NH_3)_2^+$ complexes. The reaction can proceed only when two $Cu(NH_3)_2^+$ complexes are in the same CHA-cage. O_2 adsorbs over the two complexes forming a peroxo-complex, $[Cu_2(NH_3)_4O_2]^{2+}$. NO and NH₃ couple over the peroxo-complex forming the intermediates H₂NNO and HONO, which diffuse to Bronsted acid sites where they decompose into N₂ and H₂O with low barriers [1]. H₂NNO has been suggested to decompose also over a $[Cu_2(NH_3)_4OOH]^{2+}$ complex generating N₂O and H₂O [2]. The reaction can be hindered by NH₃ adsorption onto the Cucations when being in a Cu(II) oxidation state. The kinetic analysis [3] shows that the NH₃-blocking determines the light-off temperature. Taking the pairing of $Cu(NH_3)_2^+$ complexes into account by kinetic Monte-Carlo simulations [4] shows that the turn-over frequency is determined by the stability



of the paired $Cu(NH_3)_2^+$ complexes together with the relative stability of NO and NH_3 adsorption onto the peroxo-complex.

The low- and high-temperature mechanisms are linked via the decomposition of the $Cu(NH_3)_2^+$ complexes forming framework-bound $CuNH_3^+$ species [5]. The desorption of NH_3 forming framework bound Cu^+ is found to be limiting the high-temperature mechanism. The non-monotonic NO-conversion profile is, thus, found to originate from i) the low coverage of the peroxo-complex and ii) NH_3 -blocking of the high-temperature mechanism.



Figure 1. The proposed DFT-based reaction paths at low (left) and high (right) temperatures.

References

- 1. L. Chen, T.V.W. Janssens, P.N.R. Vennestrøm, J. Jansson, M. Skoglundh, H. Grönbeck, ACS *Catalysis* **2020**, *10*, 5646.
- 2. Y. Feng, T.V.W. Janssens, P.N.R. Vennestrøm, J. Jansson, M. Skoglundh, H. Grönbeck, *J. Phys. Chem. C* **2021**, *125*, 4595.
- 3. Y. Feng, X. Wang, T.V.W. Janssens, P.N.R. Vennestrøm, J. Jansson, M. Skoglundh, H. Grönbeck *ACS Catalysis* **2021**, *11*, 14395.
- 4. Y. Feng and H. Grönbeck, ChemPhysChem 2024, 25, e202400558.
- 5. Y. Feng, T.V.W. Janssens, P.N.R. Vennestrøm, J. Jansson, M. Skoglundh, H. Grönbeck, J. Phys. Chem. C 2024, 128, 6689.

Acknowledgements

Financial support from the Swedish Energy Agency (47110-1). The Competence Centre for Catalysis (KCK) is hosted by Chalmers University of Technology and financially supported by the Swedish Energy Agency (52689-1) and the member companies Johnson Matthey, Perstorp, Powercell, Preem, Scania CV, Umicore and Volvo Group. The calculations were performed at PDC (Stockholm) through a NAISS grant.