



## Water Inhibition of NH<sub>3</sub>-SCR over Cu-CHA: Measurements and DFT-based kinetic modeling

Shivangi Singh,<sup>a,b</sup> Yingxin Feng<sup>a</sup>, Ton V. W. Janssens<sup>b</sup>, and Henrik Grönbeck<sup>a</sup>

<sup>a</sup>Department of Physics and Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

<sup>b</sup>Umicore Denmark ApS, DK-2970 Hørsholm, Denmark

### Significance and Relevance

Understanding the interaction between water and zeolite catalysts is vital not only for diesel exhaust treatment but also extends to exhaust systems for hydrogen combustion in internal combustion engines (ICEs), where water vapor is present in large amounts. Water is measured to significantly impact ammonia-selective catalytic reduction (NH<sub>3</sub>-SCR) over Cu-CHA. Atomic-level understanding is provided by a DFT-based kinetic model.

*Preferred and 2<sup>nd</sup> choice for the topic:*

*Automotive and stationary emissions control*

*Preferred presentation: Oral preferred or Short Oral*

### Introduction and Motivations

Cu-exchanged chabazite (Cu-CHA) is a widely applied catalyst for selective catalytic reduction of nitrogen oxides in oxygen excess.[1] However, the potential application of Cu-CHA in hydrogen-fueled internal combustion engines (H<sub>2</sub>-ICEs) presents new challenges due to the high partial pressures of water vapor produced during hydrogen combustion.[2]

Herein, we present flow reactor measurements to study the NH<sub>3</sub>-SCR rate over Cu-CHA with H<sub>2</sub>O partial pressures in the range from 2% to 25%. The measurements are corroborated with Density Functional Theory (DFT) calculations and DFT-based microkinetic modeling to understand the atomic-level mechanisms for the H<sub>2</sub>O inhibition of the NH<sub>3</sub>-SCR reaction.

### Materials and Methods

A Cu-CHA catalyst (Si/Al = 6.7, 3.2 wt% Cu) was prepared via Cu-nitrate impregnation and calcination (600 °C, 2 h). For SCR measurements, 4 mg catalyst (150–300 μm) mixed with 76 mg SiC was degreened (10% O<sub>2</sub>, 500 °C, 30 min) and exposed to 500 ppm NO, 600 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, and 2–25% H<sub>2</sub>O in N<sub>2</sub> at 200 °C, at the flow rate of 18 NL/h.

Density functional theory (DFT) calculations were performed using the Vienna Ab-Initio Simulation Package (VASP). Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional with Hubbard- U and van der Waals corrections was applied using a plane wave basis with the kinetic energy cutoff at 480 eV. The chabazite structure is described with a periodic rhombohedral unit cell, which contains 12 tetrahedral Si-sites. We use the experimentally determined lattice parameters which are fixed during the structural optimizations.

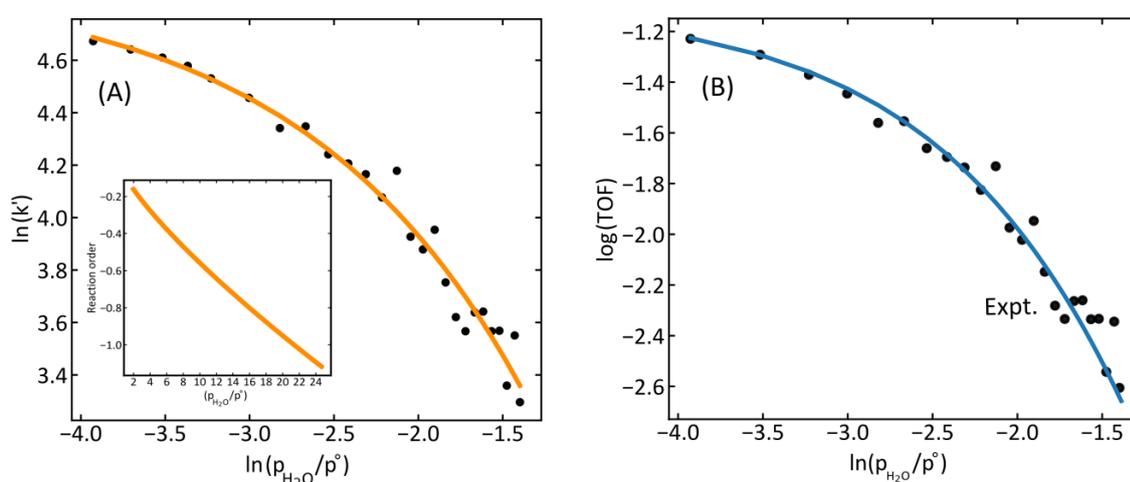
### Results and Discussion

The effect of water on the NO<sub>x</sub> conversion is studied under dry and wet conditions (5% water). We find that water reduced the conversion in the temperature range of 160°C to 260°C. Measuring the NO<sub>x</sub> conversion for pressures in the range from 0% to 25% at 200°C supports this trend, with a reduction in NO<sub>x</sub> conversion for water pressures higher than 2%. The NO<sub>x</sub> conversion is used to calculate the reaction order with respect to water, we find a change in the reaction order in water from -0.16 at 2% water to -1.11 at 25% water. The measured reaction order for water follows the simple equation:  $-3.23 \cdot \exp(0.76 \cdot \ln(p(\text{H}_2\text{O})))$  as shown figure 1 (A).

Density functional theory (DFT) calculations are performed to explore the mechanism for water inhibition. The calculations investigate water adsorption on key intermediates in a previously

suggested reaction cycle [3,4]. O<sub>2</sub> is at low temperatures activated by adsorption on a pair of NH<sub>3</sub>-solvated Cu<sup>+</sup> species [Cu<sup>+</sup>(NH<sub>3</sub>)<sub>2</sub>] forming a Cu-peroxo species, [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup>. NH<sub>3</sub> and NO couple twice over the Cu-peroxo species, resulting in the formation of two H<sub>2</sub>NNO and a [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>OHOH]<sup>2+</sup> complex. Previous simulations indicate that [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup> and [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>OHOH]<sup>2+</sup> together with [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>5</sub>O<sub>2</sub>]<sup>2+</sup> are the most abundant intermediates at temperatures around 200°C [3,4]. The present DFT calculations show that H<sub>2</sub>O adsorption competes with NO adsorption on the Cu-sites on [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup> and [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>OHOH]<sup>2+</sup>.

By accounting for H<sub>2</sub>O adsorption in the DFT-based microkinetic model [4], we are able to reproduce the experimentally measured reaction orders, which supports the inhibitory effect of H<sub>2</sub>O. The simulated TOF aligns well with experimental data when slight adjustments have been done to the H<sub>2</sub>O entropy of adsorption as well as a weak partial pressure-dependent term in the H<sub>2</sub>O Gibbs free energy of adsorption is introduced as shown in Figure 1(B).



**Figure 1:** (A) Natural logarithm of the rate constant  $\ln(k')$  as a function of the natural logarithm of partial pressures of water and (B) Logarithm of simulated TOF as a function of logarithm of the partial pressures of water.

## References

- [1] A.M. Beale et al., *Chem. Soc. Rev.*, **2015**, *44*, 7371-7405.
- [2] C.M. White et al., *Int. J. Hydrogen Energy*, **2006**, *31*, 1292-1305.
- [3] L. Chen et al., *ACS Catal.*, **2020**, *10*, 5646-5656.
- [4] Y. Feng et al., *ACS Catal.*, **2021**, *11*, 14395-14407.

## Acknowledgements

We acknowledge support from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement no. 955839 (CHASS). The calculations have been performed at PDC (Stockholm) and NSC (Linköping) through a NAISS grant (2022/3-14). 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, Perstorps, Powercell, Preem, Scania CV, Umicore and Volvo Group.