



## H<sub>2</sub>O-assisted Oxidation Half-Cycle of Low Temperature NH<sub>3</sub>-SCR over Cu-CHA

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### Significance and Relevance

The detailed mechanistic investigation of the role of H<sub>2</sub>O in the oxidation half-cycle (OHC) of NH<sub>3</sub>-SCR is here exploited with DFT calculations. We show that H<sub>2</sub>O preferentially dissociates over dimeric Cu(I) species to form H<sub>2</sub>O<sub>2</sub>, a strong oxidant that completes the oxidation of a second pair of Cu(I) moieties in adjacent CHA cages. Such results describe the reaction mechanism of OHC under wet conditions and clarify the active role of H<sub>2</sub>O involved in the kinetically-relevant step of the reaction. These interpretations are therefore fundamental in describing at an atomistic level the catalytic phenomena occurring in the redox chemistry of NH<sub>3</sub>-SCR.

*Preferred and 2<sup>nd</sup> choice for the topic: Automotive and stationary emission control, Fundamental Advances in understanding Catalysis*

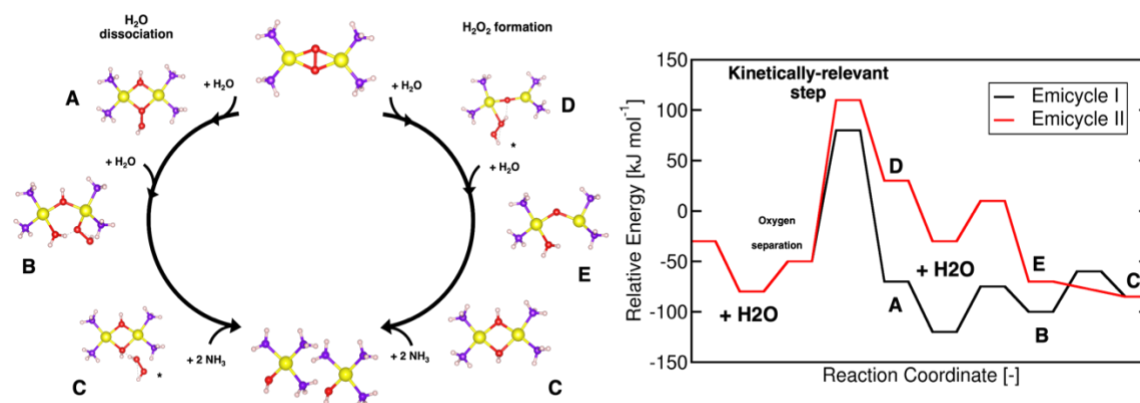
*Preferred presentation: Oral preferred or Short Oral*

### Introduction and Motivations

Copper-exchanged chabazite (CHA) zeolites are the state-of-the-art catalysts for the abatement of nitrogen oxides (NO<sub>x</sub>) in vehicles exhausts via selective catalytic reduction (SCR) of NO by NH<sub>3</sub><sup>1</sup>. In particular, the detailed reaction chemistry that regulates the Low-Temperature (LT) Standard SCR mechanism has attracted extensive research interest in the last years, specifically targeting the relevant role of water in the overall redox chemistry<sup>2</sup>. The scientific community agrees on the redox nature of the global SCR reaction  $4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$ , consisting in a reduction half cycle (RHC), where Cu active sites change their oxidation state from Cu(II) to Cu(I), and the subsequent oxidation half cycle (OHC), where Cu(I) is reoxidized. For the RHC, there is converging evidence that Cu(II) is reduced by NO and NH<sub>3</sub> to form linear Cu(I)(NH<sub>3</sub>)<sub>2</sub> complexes, which are weakly bound to the zeolite and able to diffuse in adjacent CHA cages. On the other side, a detailed Cu-oxidation pathway is unclear, and additional investigation is required to describe a kinetically consistent oxidation scheme. Experimental evidence combined with theoretical calculations show that the presence of water vapor in the feed stream produce a promoting effect that accelerate the rate of the OHC step<sup>3</sup>. These conclusions also reveal that OHC proceed with a NO-silent mechanism, thus suggesting the sole presence of H<sub>2</sub>O and O<sub>2</sub> that take part in the total oxidation of Cu(I) moieties. The aim of this work is to provide a detailed description of the oxidation half cycle mechanism by means of theoretical calculations, in order to demonstrate the active role of H<sub>2</sub>O in oxidizing Cu(I) moieties and provide fundamental insights of the elementary steps involved in the oxidation emicycle. These results will assess the OHC catalytic cycle under wet conditions at a molecular level, thus paving the way towards a complete understanding of the redox chemistry involved in the NH<sub>3</sub>-selective catalytic reduction of NO<sub>x</sub>.

### Materials and Methods

A hexagonal, 36T-sites unit cell is adopted to describe the crystal structure of Cu-CHA. Density Functional Theory (DFT) calculations that include dispersive forces (Grimme D<sub>3</sub>) are performed within the generalized gradient approximation (GGA-PBE) functional for the electron exchange and correlation, plane-wave basis-set and norm-conserving pseudopotentials. Brillouin zone samplings are restricted to the  $\Gamma$ -point. All the transition states structures are identified using the climbing-image nudge elastic band methodology (CI-NEB) and vibrational frequency calculations were performed by using a finite-difference approximation of the Hessian matrix implemented in Atomic Simulation Environment (ASE). Molecules in gas phase are assumed ideal.



**Figure 1:** a)  $\text{H}_2\text{O}$  dissociation and  $\text{H}_2\text{O}_2$  formation mechanisms. b) Minimum Energy Path of OHC.

## Results and Discussion

The oxidation half-cycle of  $\text{NH}_3$ -SCR is studied under wet conditions by adding physisorbed, mobile  $\text{H}_2\text{O}$  species in the cage of Cu-CHA. The zero-energy level adopted for the construction of the catalytic cycles corresponds to two  $\text{Cu}(\text{NH}_3)_2^+$  complexes within the same cage of CHA and reactants in gas phase conditions. According to our result,  $\text{O}_2$  chemisorption on the Cu(I) dimers is exergonic by  $-30$  kJ/mol, in accordance with available literature<sup>4</sup>. Based on the analysis of the potential energy paths, we find two parallel oxidation cycles, which shares the  $\text{O}_2$  activation, i.e. i) the  $\text{H}_2\text{O}$ -dissociation mechanism into  $\text{OH}^-$  and  $\text{H}^+$  and ii) the direct  $\text{H}_2\text{O}_2$  formation pathway, shown in Fig.1 (a). Considering the  $\text{H}_2\text{O}$ -dissociation mechanism, black curve in Fig.1 (b),  $\text{H}_2\text{O}$  dissociates over Cu moieties to form a reacting intermediate (species A) where  $\text{OH}^-$  and  $\text{H}^+$  ions breaks the oxygen bridge between the Cu moieties with a large electronic barrier of 150 kJ/mol. Then, a second  $\text{H}_2\text{O}$  molecule chemisorbs over one of the two available Cu forming structure B. The energy diagram shows that  $\text{H}^+$  transfer from the chemisorbed  $\text{H}_2\text{O}$  to form  $\text{H}_2\text{O}_2$  and structure C has an intrinsic energetic barrier of 40 kJ/mol.

The second mechanism studied consists in the direct  $\text{H}_2\text{O}_2$  formation over Cu moieties by breaking the oxygen bridge between the two copper moieties (structure D), red curve in Fig.1 (b). The energetic barrier for this step is found to be 200 kJ/mol, larger than the previous mechanism. Moreover, this step is energetically endergonic, with a reaction energy of  $+90$  kJ/mol, resulting in a much unstable structure. Once  $\text{H}_2\text{O}_2$  detaches from the Cu moiety, a second  $\text{H}_2\text{O}$  molecule chemisorbs (structure E), a  $\text{H}^+$  is transferred to the second free oxygen atom with an electronic barrier of 50 kJ/mol, finally forming structure C, which is shared between the two proposed mechanisms. The formed  $\text{H}_2\text{O}_2$  molecule, which is a strong oxidant species, diffuses in an adjacent CHA cage and activates an additional pair of  $\text{Cu}(\text{NH}_3)_2^+$  moieties with an energy barrier of 55 kJ/mol. Our results reveal that the  $\text{H}_2\text{O}$  dissociation mechanism is energetically more favorable than the  $\text{H}_2\text{O}_2$  formation pathway. Moreover, the apparent activation energy obtained for the  $\text{H}_2\text{O}$ -dissociation path is equal to 82 kJ/mol, in excellent agreement with experimental measurements (71-79 kJ/mol<sup>3</sup>). With this study we highlight the relevant contribution of  $\text{H}_2\text{O}$  in the kinetically-relevant step of OHC, elucidating the fundamental insights into the mechanism of the Cu oxidation of  $\text{NH}_3$ -SCR. These results thus pave the way towards additional computational study of the complex catalytic phenomena involved in  $\text{NH}_3$ -SCR at atomistic levels of detail.

## References

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