

# Oxidative half-cycle of SCR NO<sub>x</sub> on single and dual copper sites of CuSSZ-13 catalyst via NO<sub>2</sub>, nitrates and nitrites formation – spectroscopic and thermodynamic DFT background for reaction networks

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### Significance and Relevance

The mechanistic pathways of Cu redox changes in SSZ-13 zeolite during NO SCR were investigated based on the evolution of the selective NO oxidation cycle. Combined use of *ab initio* thermodynamics (DFT model), spectroscopy (EPR, IR), and catalytic tests (temperature-programmed using isotopically labeled <sup>18</sup>O<sub>2</sub>) revealed three principal routes of NO<sub>2</sub> production. Direct NO reaction with O<sub>2</sub> includes the HONO pathway, the metal-redox pathway, and the ligand-redox pathway. They involve the comproportionation of surface nitrate adducts with NO, and versatile HONO behavior as a key factor.

*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

 $NH_3$ -SCR is generally factored into the reduction half-cycle (RHC) with the participation of  $NH_3$  and NO, and the oxidation half-cycle (OHC), where NO and  $O_2$  are involved.<sup>1,2</sup> The mechanism of RHC has been addressed in several articles, and a consensus has been achieved about its main features.<sup>3</sup> The OHC stage is examined less intensively, and its mechanism at medium and high temperatures is still debated.<sup>4</sup> In this contribution, we aimed to provide a thermodynamic feasibility study for interpreting the complex network of the NO selective catalytic oxidation (NO-SCO) reactions by unraveling meaningful pathways of  $NO_x$  generation, its reactivity, and evolution under NO oxidation conditions.

### Materials

Two types of CuSSZ-13 zeolites that differ in the Si/Al ratio, the Al sites' distribution, and the copper loading method were examined. The sample prepared by impregnation of NH<sub>4</sub>SSZ-13 with a solution of CuCl<sub>2</sub> is labeled i-CuSSZ-13 (Si/Al = 7.9 with 70% of the Al atoms as singles, total Cu content 780 µmol/g), and that prepared by one-pot synthesis as o-CuSSZ-13 (Si/Al = 3.4, total Cu content 590 µmol/g). Detailed descriptions of the synthesis protocols and characterization results of these samples have been provided in our previous articles,<sup>5,6</sup> including quantification of all types of active sites of copper: Cu<sup>2+</sup> (330 and 140 µmol/g), Cu<sup>2+</sup>-OH<sup>-</sup> (30 and 255 µmol/g), and Cu<sup>2+</sup>-O<sup>2-</sup>-Cu<sup>2+</sup> (220 µmol/g and undetermined amount) for o-CuSSZ-13 and i-CuSSZ-13, respectively. The latter sample contained 325 µmol/g nano-CuO/Cu-oxo species in total, while the concentration of Brønsted sites was equal to 600 µmol/g (o-CuSSZ-13) and 160 µmol/g (i-CuSSZ-13). Furthermore, from analysis of the EPR parameters of divalent copper in o-CuSSZ-13, 80% occupies 6MR, whereas 20% - 8MR sites. In the case of o-CuSSZ-13, the occupancies are equal to 54 and 46 %, respectively.

### **Results and Discussion**

Molecular DFT modeling coupled with first principles thermodynamic (FPT), spectroscopic (EPR/IR), and catalytic investigations into a complex network of reactions involved in the interaction of NO and  $O_2$  with a comprehensive variety of active centers (Cu<sup>2+</sup>, Cu<sup>+</sup>, Cu<sup>2+</sup>-OH<sup>-</sup>, Cu<sup>2+</sup>-O<sup>2-</sup>-Cu<sup>2+</sup>, Cu<sup>2+</sup>-O<sub>2</sub><sup>2-</sup>-Cu<sup>2+</sup> and segregated CuO) of the CuSSZ-13 zeolites were carried out. The structure, electronic, and magnetic properties of various adducts with the reactants were ascertained with DFT calculations. In contrast, their thermal stability and reactivity were assessed using the 2D thermodynamic diagrams,  $\Delta G(p,T)$ , constructed for a wide range of experimental conditions. The course of selective catalytic oxidation of NO (NO-SCO) with <sup>16</sup>O<sub>2</sub> or <sup>18</sup>O<sub>2</sub> was examined by temperature-programmed surface reaction (TPSR),



using two types of CuSSZ-13 catalysts of controlled copper speciation. Corroborative IR and EPR measurements revealed multiple molecular pathways of NO and O<sub>2</sub> interaction with the single (Cu<sup>2+</sup>, Cu<sup>+</sup>, Cu<sup>2+</sup>-OH<sup>-</sup>), and dual (Cu<sup>2+</sup>-O<sup>2-</sup>-Cu<sup>2+</sup>, Cu<sup>2+</sup>-O<sub>2</sub><sup>2-</sup>-Cu<sup>2+</sup>) copper centers of the 6MR and 8MR topology, and with segregated CuO. The progress of the investigated reactions was evaluated using the calculated FPT thermodynamic profiles. The temperature behavior and reactivity of the critical intermediates (NO, HONO, nitrate, and nitrite) and their dynamic transformations into NO<sub>2</sub> were elucidated. The established complex reaction network was successfully used to clarify the temperature dependence of the experimental NO-SCO profiles, also providing a mechanistic background for interpreting the nature of the oxidative half-cycle of the selective catalytic reduction of NO over Cu-SSZ-13 catalysts. The unraveled redox reactions were classified into metal (cationic) redox, ligand (anionic) redox, and HONO redox cycles, where comproportionation of surface nitrate adducts with NO plays a crucial role. The  $Cu^{2+}OH^{-}$  species were identified as versatile active centers for NO<sub>2</sub> formation via the HONO pathway. Elusive HONO intermediates allow for chemical communication between the individual redox cycles. Depending on the actual reaction conditions, HONO can act as a reduction agent for Cu<sup>2+</sup> with the electroprotic formation of NO<sub>2</sub>, a source of nitrites upon deprotonation, or as an oxidant of Cu<sup>+</sup> with the formation of H<sub>2</sub>O and NO. The significant difference in the Cu<sup>2+</sup> cations' reactivity in the 6MR and 8MR rings is apparent at the metal redox pathway, where  $Cu^{2+}/6MR$  are spectators and  $Cu^{2+}/8MR$  are active species. Dimeric copper centers with the bridging oxo and peroxo moieties can produce a variety of nitrates and nitrites via ligand redox mechanisms. In addition, we found that segregated CuO nanocrystals contributed to NO oxidation only at high temperatures (T > 400 °C), leading to the isotopic scrambling of <sup>18</sup>O-labeled oxygen and nitric oxide.

The obtained results allowed us to establish a comprehensive network of reactions involved in the NO oxidation and the temperature windows of their occurrence. We provided an interpretation of temperature-programmed desorption and surface reaction profiles of NO oxidation based on copper speciation within CuSSZ-13 zeolite (Figure 1).



**Figure 1** Thermodynamic range of the investigated NO<sub>2</sub> formation pathways on mononuclear copper centers in 8MR and 6MR sites (left-hand side panel). Temperature-programmed NO<sub>2</sub> formation reaction profiles for dimeric copper centers (right-hand side panel).

### References

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