A Theoretical Study on NOx Selective Catalytic Reduction on single Cu-sites and Brønsted acid sites in Cu-SSZ-13

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ABSTRACT: The mechanism for Cu-SSZ-13 catalyzed Selective Catalytic Reduction (SCR) of NO_x with NH_3 is investigated for single Cu-sites. Barriers are determined for all elementary steps and are calculated with high accuracy using DLPNO-CCSD(T) single point calculations on large 46T cluster models derived from periodic density functional theory (DFT) calculations. For standard SCR, NO oxidation to NO_2 is necessary, which requires barriers above 250 kJ/mol on single Cu sites, indicating that they are not catalytically active for this process. Contrary, for fast SCR, barriers are below 150 kJ/mol, indicating that single Cu sites are active. Most of the elementary reactions, such as the required N-N bond formation between NO and NH_3 take place on the single Cu sites. After N-N bond formation, which yields H_2NNO, however, the intermediate is most easily decomposed into N_2 and H_2O on a Brønsted acid site.

INTRODUCTION

NO_x exhaust gases, products of the oxidation of nitrogen during the combustion of fuels at high temperatures, are still one of the major contributors to local air pollution, hence their emission is being strictly controlled.[1-2] One successful strategy of reducing NO_x emissions is through their selective reduction by ammonia to N_2 over heterogeneous catalysts such as transition-metal exchanged zeolites and transition-metal oxide.[3-24] Copper-exchanged zeolites, and in particular Cu-SSZ-13, have been commercialized as they are highly active and also stable at a broad range of temperatures.[4-6, 8, 11, 25] For that reason, the selective catalytic reduction (SCR) of ammonia over Cu-SSZ-13 has been the subject of many experimental[4-8, 10-11, 14-15, 25-33] and theoretical studies.[7-8, 10, 14-15, 32, 34-36] These studies led to the establishment of equations 1-3 for the reduction of NO and NO_2 to N_2.

$$4NH_3+4NO+O_2 \rightarrow 4N_2+6H_2O \qquad (1)$$

$$2NH_3+NO+NO_2 \rightarrow 2N_2+3H_2O \qquad (2)$$

$$2NH_3+3NO+O_2 \rightarrow 2N_2+3H_2O+NO_2 \qquad (3)$$
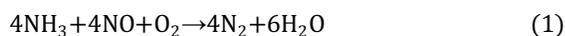
The so-called "Standard SCR"[3, 8, 37] is given by Equation 1. Additionally, if NO_2 is present in the exhaust gases, nitrogen can also be formed via Equation 2. This reaction is also called "Fast SCR" since its efficiency, above 473 K, is at least 10 times higher than that of the "Standard SCR".[8, 38-39] NO_2 can be formed through the so-called "NO activation cycle" shown in Equation 3. During the standard SCR, there is no excess of NO_2 and as the fast cycle depends crucially on the availability of NO_2, the standard SCR is limited by the rate of NO_2 formation. One of the most detailed computational studies of the reaction mechanism of the standard and fast-SCR has been reported by Janssens et al.,[8] who proposed a consistent reaction scheme for Cu-SSZ-13. However, most of the elementary reaction steps put forward have not been investigated in detail with respect to the actual reaction barriers of the elementary reactions. Recently, Grönbeck and co-workers presented a detailed DFT-investigation, including Cu-dimers and Brønsted acid sites as active site motifs.[34] In addition, ammonia-SCR has so far only been investigated using density functional theory (DFT), where in addition to GGA, also DFT+U[34] and hybrid functionals[10, 14, 40] have been employed. We recently found that calculations at the generalized gradient approximation (GGA) level of theory are problematic for the description of ammonia-SCR in Cu-SSZ-13 leading to errors of adsorption energies and reaction energetics of about 50 kJ/mol when compared to CCSD(T) calculations.[41]

In this work we investigate both, the standard and fast-SCR over single-site Cu-SSZ-13 and H-SSZ-13 using a hierarchical cluster model that allows us to obtain highly accurate reaction energies and barriers using ab initio methods.

RESULTS AND DISCUSSION

We investigate SCR on Cu-SSZ-13, focusing on the reactivity introduced by isolated Al-substitution of Si-atoms. In our computational models, we employ a unit cell containing 36 tetrahedral atoms out of which one is substituted by Al, giving a Si/Al-ratio of 35. When the introduced charge is balanced by Cu^+, this leads to isolated, Cu-monomers as active sites (see Fig. 1a and Fig. 1b). It is also known that some of the Al-substituted sites remain charge-balanced with a proton as Brønsted acid sites (BAS).

We will study both cases separately, with only one of these active sites per unit cell.

All zeolite structures were fully optimized using dispersion-corrected DFT, specifically PBE-D3 with periodic boundary conditions (PBC). Due to the known limitations of DFT calculations at the generalized gradient approximation level of theory, ab initio calculations were additionally performed. Inspired by the work of Sauer and coworkers[42-46] we have cut nonperiodic, large 46T cluster models (including 46 tetrahedral atoms) on which we performed additional calculations (see Fig. 1c).[42-51] The corrected energies were computed as:

$$E_{CCSD(T)}^{PBC} = E_{PBE-D3}^{PBC} + E_{DLPNO-CCSD(T)}^{46T} - E_{PBE-D3}^{46T} \qquad (4)$$

Where E_{PBE-D3}^{PBC} is the DFT energy obtained for the periodic model and $E_{DLPNO-CCSD(T)}^{46T}$ and E_{PBE-D3}^{46T} are the energies obtained for the 46T model with DLPNO-CCSD(T) and PBE-D3, respectively. Gibbs free energies were computed based on the harmonic oscillator approximation and, for gas phase species, using additionally the rigid-rotator free translator approximation. All reported Gibbs free energies are at 473 K and 1 bar reference pressure.

a)

H-SSZ-13   Cu-SSZ-13

b)

Periodic model

H-SSZ-13   NH$_3$-Cu-SSZ-13

c)

T46 cluster model

H-SSZ-13   NH$_3$-Cu-SSZ-13
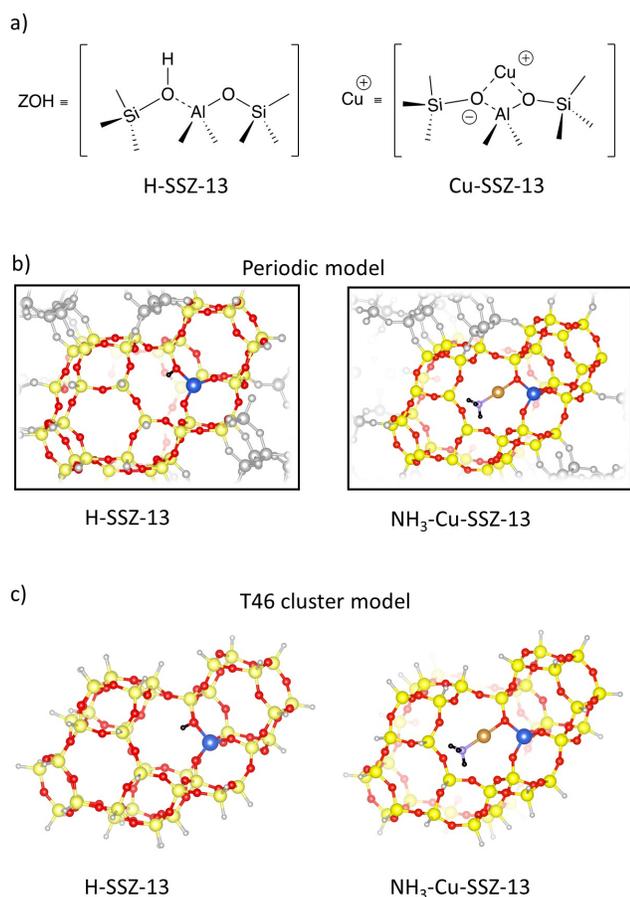
Figure 1. a) Representation of H-SSZ-13 and the Cu-SSZ-13 resonance structures. Illustration of b) the periodic model and c) the 46T cluster model for the H-SSZ-13 and Cu-SSZ-13 zeolite. Color scheme: Cu – Brown; Al – Blue; O – Red; Si – Yellow; N – Purple; H – Black; Periodic/Cluster termination – Gray.

We have investigated the mechanism of the fast SCR cycle on H/Cu-SSZ-13 starting from the mechanistic proposal

Janssens et al.[8] The most favorable investigated path is depicted in Fig. 2a.

Before discussing the elementary steps in detail, we will first focus on particularly stable intermediates that are likely resting states of the catalytic cycle. The stability is discussed based on Gibbs free energies at 200 °C and 1 bar reference pressure. Starting from a copper site with ammonia (structure 1, according to Figure 2a) as illustrated in Fig. 1, several stable structures can be formed through adsorption. While the clean Cu atom in oxidation state 1 is most stable when located in the six-membered ring by 39 kJ/mol, when bound to adsorbates it is located in the 8-membered ring as shown in Figure 1b, which is in agreement with previous work.[8, 52-54] We nevertheless computed the free energy for structure 5 from Fig. 2a for Cu in the 8- rather than the 6-membered ring, since we do not need to consider potential barriers for rearrangement of Cu between the two positions and because the difference in stability is eventually unimportant as both structures are high-energy intermediates. We find that both NO$_2$ and NH$_3$ adsorb strongly with adsorption free energies of -75 and -105 kJ/mol respectively. The co-adsorption of NO$_2$ and NH$_3$ is also only slightly less favorable (-100 kJ/mol). Adsorption of other potential adsorbates is significantly weaker (H$_2$O: -45 kJ/mol; NO: -14 kJ/mol; O$_2$: 3 kJ/mol; N$_2$: -18 kJ/mol; H$_2$NNO: -39 kJ/mol and HNO$_2$: -29 kJ/mol). The adsorption of multiple ammonia molecules leading to Cu(NH$_3$)$_n^+$ complexes[8, 10, 55-56] was also investigated. We note that upon adsorption of two or more ammonia molecules the formed copper complex detaches from the zeolite framework and is mobile.[10, 15, 40, 57-59] We find free energies of -114 and -111 kJ/mol for two and three NH$_3$ adsorbed molecules, respectively (see Table S2). We thus find that adsorption of a second molecule of NH$_3$ is only 9 kJ/mol more stable. We note that Paolucci et al. have computed Cu(NH$_3$)$_2^+$ to be more than 30 kJ/mol more stable than Cu(NH$_3$)$_1^+$ in terms of free energy at 200 °C.[40] With an increasing number of NH$_3$-ligands, the Cu(NH$_3$)$_n^+$ complex is exceedingly weakly bound to the zeolite framework and thus becomes mobile at elevated temperatures.[15, 26, 34, 40, 60-61] This situation is poorly described by the harmonic approximation, which can to some extend be circumvented using MD simulations or approximations to the entropies of weakly bound adsorbates.[34] Here, we will focus on the reactivity of Cu with only a single NH$_3$ adsorbed and the free energy profile in Fig. 2b) is referenced to that.

The computed Gibbs free energies employing DLPNO-CCSD(T) are compared with DFT results in Table S1. In agreement with previous work,[41] we find large deviations for PBE-D3, in some cases more than 50 kJ/mol. We also compare with HSE-06-TSvdw results of Paolucci and co-workers,[40] which are in most cases in very good agreement with DLPNO-CCSD(T), with deviations below 15 kJ/mol. Larger differences are observed for the mobile species Cu(NH$_3$)$_2^+$ and Cu(NH$_3$)$_3^+$, where the free energies computed by Paolucci and co-workers are lower by up to 40 kJ/mol. This can at least partially be attributed to the harmonic approximation applied to the motion of the nuclei in this work.

The formation of N$_2$ and H$_2$O from NO, NO$_2$ and NH$_3$ in the fast SCR-cycle requires three types of reactions: 1) transferring H from N to O, 2) N-O bond cleavage and 3) N-N bond formation. These steps can in principle occur in

different order and the path depicted in Fig. 2a is the most favorable of those that we have studied.

Starting in cycle II with Cu-NH$_3$ (structure 1), co-adsorption of NO$_2$ and a hydrogen transfer leads to an adsorbed amide (NH$_2$) plus nitrous acid (HNO$_2$), which is desorbed and released into the gas phase. This hydrogen-transfer oxidizes Cu from oxidation state +1 to +2 and is also computed to be the step with the highest barrier (143 kJ/mol) of the fast SCR. We note that nitrous acid has also been considered in previous theoretical and experimental studies but is hard to detect in reaction conditions as it is a reactive intermediate.[11, 15, 34, 60, 62-68] Before discussing the fate of nitrous acid, we will continue with Cu-NH$_2$ (structure 3, cycle II in Fig. 2a). Co-adsorption of NO results in spontaneous N-N bond formation without energetic barriers, leading to side-on adsorbed H$_2$NNO (structure 4), which returns Cu to oxidation state +1. Overall, the formation of H$_2$NNO and nitrous acid (HNO$_2$) from NO, NO$_2$ and NH$_3$ are relatively thermoneutral reactions with a free energy difference of -3 kJ/mol (from 1 to 1', see cycle II from Fig. 2b).

The decomposition of H$_2$NNO yields N$_2$ and H$_2$O and this is shown in cycle I of Fig. 2a. In agreement with previous work, we find that this reaction is most likely to occur on a Brønsted acid site rather than a Cu active site.[4, 14, 34, 69-71] Since ammonia binds strongly to the acid site at 200 °C, we start with the ammonium cation on a Brønsted acid site (structure A, cycle I). Hydrogen transfer of H$_2$NNO, catalyzed by the ammonium ion, leads to double-bond formation between the nitrogen atoms, creating the HN=NOH molecule. An additional hydrogen transfer leads to the simultaneous formation of H$_2$O and N$_2$, accompanied by a large gain in free energy of around 230 kJ/mol (structure D to E, depicted in cycle I from Fig. 2a). Both N$_2$ and H$_2$O are relatively weakly bound and readily desorb to close cycle I. This cycle is expected to be the fastest, having barriers lower than 100 kJ/mol.
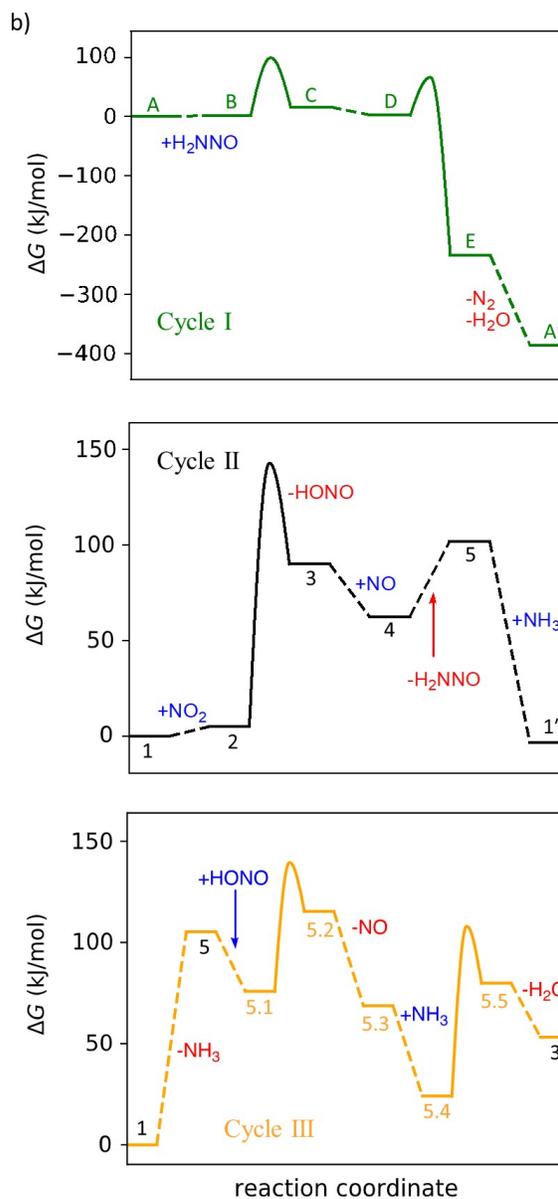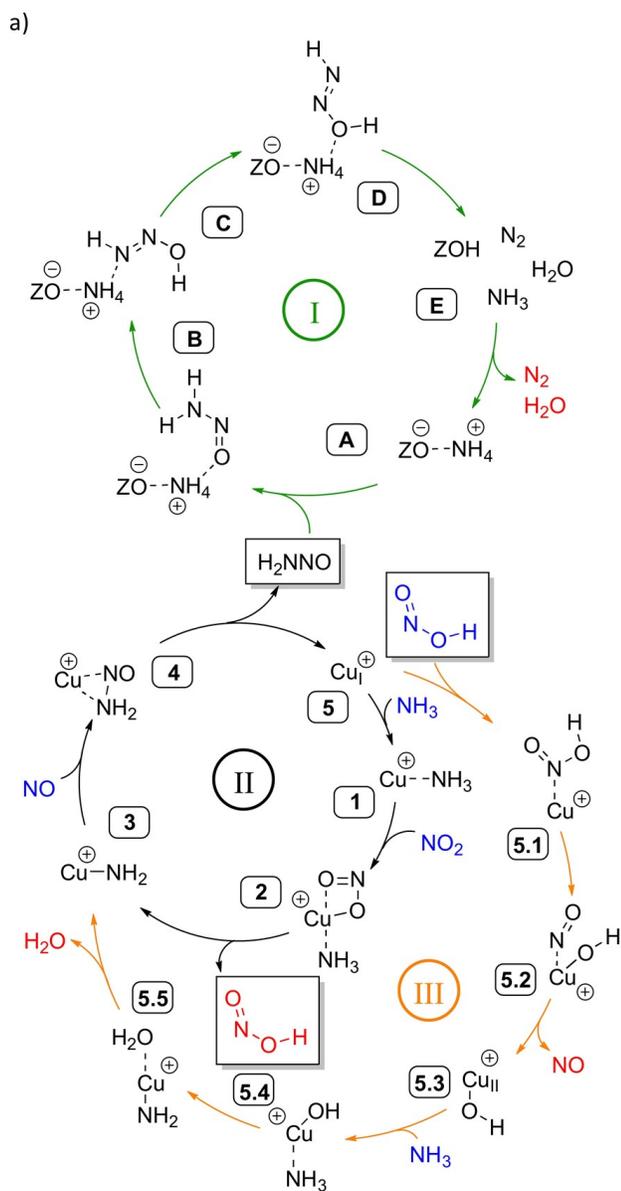
Figure 2. a) Overview of the mechanism investigated for the fast SCR cycle for catalytic conversion of NO_x into H_2O and N_2. The redox active site is abbreviated as "Cu+" (see Fig. 1a). The mechanism is split into three cycles, where the first (I) corresponds to the decomposition of H_2NNO released during cycle II, the second (II) additionally generates nitrous acid (HNO_2) that can further react on any free Cu^+ active site (cycle III). b) Gibbs free energy profiles at 473 K of cycles I, II and III are depicted in a). The resting state (ΔG = 0) is taken to be $ZOH-NH_3$ for cycles I and $Cu-NH_3$ for cycles II and III.

We now return to nitrous acid (HNO_2), which was a byproduct of cycle II. HNO_2 can further react as shown in cycle III of Fig. 2a. The reaction requires a free Cu active site that is not necessarily the same active site on which nitrous acid is formed and released in step 2-3. Since nitrous acid is a relatively small molecule and is expected to be able to diffuse through the pores of SSZ-13 it could also react at a different active site. After adsorption to form $Cu-NO_2H$ (structure 5.1), a barrier of 139 kJ/mol is required to cleave a N-O bond. This results in the formation of a separate OH and NO ligands bound to the same Cu-atom, which oxidizes Cu to oxidation state +2. NO is then readily released into the gas phase. The remaining Cu-OH (structure 5.3) can then react under co-adsorption of NH_3, with subsequent proton transfer forming free H_2O and an amide ($Cu-NH_2$). $Cu-NH_2$ (structure 3) can then react with NO, as described above in cycle II.

Examples of transition states for each cycle depicted in Figure 2a are illustrated in Figure 3. In Figure 3a, one of the two transition states from cycle I is shown, where a hydrogen transfer between the ammonium ion and NOHNH will simultaneously form N_2, H_2O and NH_3, while a proton is transferred to a different oxygen atom of the zeolite. Figure 3b and c show the rate-determining steps in cycles II and III, in which b) shows the hydrogen transfer between NH_3 and NO_2 and c) shows the N-O bond cleavage from HNO_2.

We have additionally studied standard SCR on single Cu active site and the investigated mechanism is shown in Fig 3a. Starting from a clean Cu-site (structure 5), adsorption of O_2 leads first to the formation of side-on bound oxygen. After rearrangement of the adsorbed O_2 and co-adsorption of NO (structure 5c), oxidation of NO leads to coadsorbed NO_2 and O (structure 5e). It is worth mentioning that 5e can rearrange with relatively low barriers to η^1- and η^2-bound nitrate (structures 5α and 5β), having free energies of 46 and -21 kJ/mol with respect to $Cu-NH_3$. Adsorption and oxidation of a second NO molecule leads to two coadsorbed NO_2 molecules, which are then desorbed to recover the active site. The involved barriers are a clearly too high for this cycle to be active (>250 kJ/mol) (see Fig. 4), at least for the mechanism investigated in this work. This agrees with previous investigations that propose that Cu-dimers are required for NO-activation.[8, 10, 15, 55, 61, 72-76]

a)   b)   c)

cycle I   cycle II   cycle III

Figure 3. Structure of important transition states for cycle I, II and III. a) Concerted decomposition of HNNOH into molecular N_2 and H_2O, TS(D-E). b) Proton transfer between NH_3 and NO_2 and subsequent nitrous acid desorption, TS(2-3). c) Dissociation of nitrous acid into copper-adsorbed nitric oxide and hydroxide, TS(5.1-5.2). Color scheme: Cu – Brown; Al – Blue; O – Red; Si – Yellow; H – Black; N – Purple.

Figure 2 b) shows the free energy profiles for cycles I, II and III depicted in Fig. 2a). We find that barriers are in a reasonable range, with the highest barrier for step 2-3, which is 143 kJ/mol (Fig 3b). The barrier for decomposition of nitric acid in step 5.1-5.2 is similar (139 kJ/mol, Fig 3c), while the decomposition of H_2NNO on the BAS, clearly required the lowest barriers (<100 kJ/mol). A quantitative analysis of the activity of the catalyst will of course require the use of microkinetic modelling using the actual partial pressures of NO_x and NH_3. Based on the free energy diagrams for cycle II and III shown in Fig.2c), it is clear that $Cu(NH_3)_n^+$ is computed to be the most stable state and likely the resting state of the catalytic cycle. For most other states, no significant coverage is expected.

Figure 4. a) Investigated NO activation cycle. b) Gibbs free energy profile at 473 K of the cycle depicted in a). Barriers with entropy corrections that result in slightly lower free energies (5c-5d) than their minima are raised to 5 kJ/mol. ^{3}5f and ^{1}5f are triplet and singlet states of structure "5f". The resting state is considered to be Cu-NH$_3$ ($\Delta G = 0$). Intrinsic reaction barriers between "5e", "5α" and "5β" are low and are hence omitted for clarity.

A Bader charge analysis was performed based on the electron density computed with PBE-D3 for periodic structures to analyze the oxidation state of copper during the reaction cycles II, III and NO oxidation (see Fig. 5a). Cu^I and Cu^{II} ranges are defined based on Bader charges of structures 5 (Cu^I) and 5.3 (Cu^{II}-OH), to which one can very clearly assign oxidation states.[8, 14, 77] Copper Bader charges closer to structure 5 (+0.72 e) are then considered to have an oxidation state of +1, while Bader charges closer to structure 5.3 (+1.0 e) are considered to have an oxidation state of +2, which is in line with ref.[55]

The assignment of the oxidation states of copper based on Bader charges within cycle II agrees with the formal oxidation states assigned based on Fig. 2a, although the Bader charge of the amide Cu-NH$_2$ is on the border between oxidation state +1 and +2. The oxidation state change in cycle III, where Cu is oxidized through the formation of an OH-ligand (structure 5.2) is also well reproduced by the Bader charge analysis. In the NO-oxidation cycle investigated in Fig. 3, Cu is in oxidation state +2, except in the initial state and this is again well-reproduced by the Bader charges in Fig 5b.
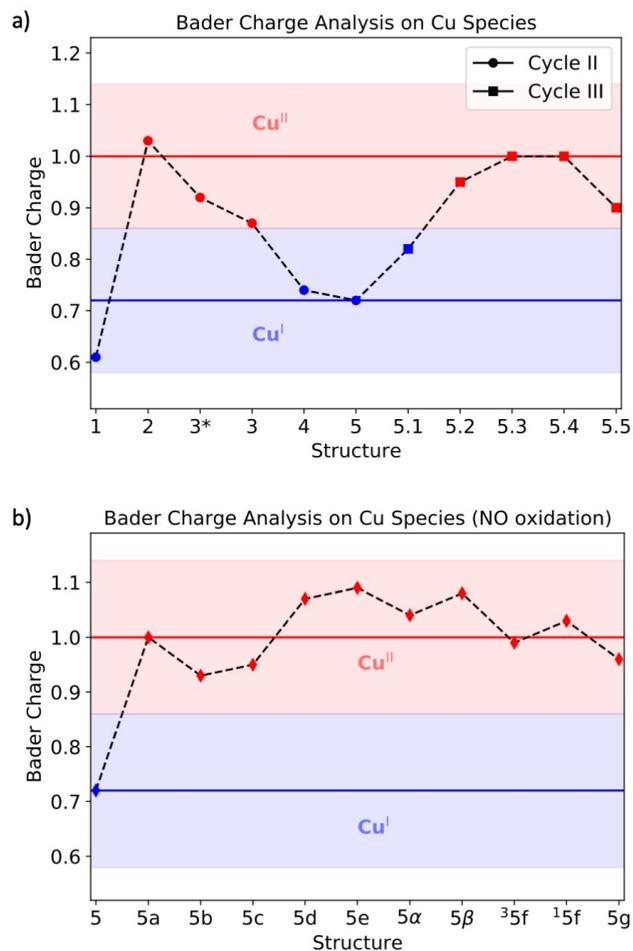
Figure 5. Bader charge analysis on copper species from a) cycle II/III and b) NO oxidation, referenced to structure 5 (Cu$^+$) and structure 5.3 (Cu^{2+}-OH), which have known oxidation states.[8, 14, 77] Structures are labeled according to Figure 2 a. 3* depicts structure 3 with nitrous acid desorbed but present within the cavity.

CONCLUSIONS

We have investigated the complete catalytic cycle for the Selective Catalytic Reduction (SCR) of NO$_x$ with NH$_3$ catalyzed by single Cu-sites in Cu-exchanged SSZ-13 and Brønsted acid sites. Periodic DFT calculations were supplemented with highly accurate DLPNO-CCSD(T) calculations on cluster models.

We find reasonably low free energy barriers (< 150 kJ/mol) for the fast SCR cycle in which NO and NO$_2$ are

available in equal amounts. The highest computed barrier (143 kJ/mol) occurs for nitrous acid (HNO_2) formation, which involves a hydrogen transfer from ammonia to nitrogen dioxide. The decomposition of nitrous acid, which requires N-O bond cleavage requires a similar barrier (139 kJ/mol). Reactions occurring on Brønsted acid sites mainly involve hydrogen transfer reaction and only require low barriers (< 100 kJ/mol). For standard SCR, we find insurmountable barriers of > 250 kJ/mol for the investigated mechanism for the NO oxidation with single copper sites, strongly suggesting that the reaction needs different active site motifs.

METHODS

Periodic DFT calculations were carried out using the VASP program package[78-82] with the PAW method[78, 82] and the PBE-D3 functional to find minima and transition states. TS scans were performed with constrained optimizations using ARPESS.[83] The dimer method[84] and Nudged Elastic Band[85-88] from the Atomic Simulation Environment[89] were also used.

To improve the reaction energies and barriers, a cluster is cut from the periodic structure, so that the entire cavity from the Cu-SSZ-13 is modelled and the H-terminations are at least five bonds away from the active site, containing 46 tetrahedral atoms. DLPNO-CCSD(T)/def2-TZVPP[50-51] single-point calculations were then performed with the Quasi-Restricted Orbital[90] treatment using the ORCA program package[90-91] as well as PBE-D3 with TURBOMOLE.[92-93] Energies were then computed according to Eq. 4. For calculations on the BAS, H-SSZ-13, we employ DLPNO-CCSD(T)/cc-VDZ calculations along with CBS-extrapolation using DLPNO-MP2/cc-pVXZ calculations. Here we extrapolate the correlation energy using the 2-point l^{-3} formula[94] with X=2,3 and the Hartree-Fock energy with the 3-point exponential formula[95] and X=2,3,4.

Harmonic frequencies were computed based on a partial Hessian computed with finite differences in which all adsorbate atoms and only the $(Si-O)_4$-Al fragment of the zeolite at the active site was considered.

We have evaluated D1 diagnostics on the canonical CCSD/def2-TZVPP[96-100] level of theory for T1 cluster models to check how reliable single-reference coupled-cluster results are. The T1 cluster models were optimized at the PBE-D3/dhf-SV(P)[96-97, 101-105] level of theory using the RI approximation[106]. All calculations on T1 clusters were performed with the TURBOMOLE program package.[92-93] Table S3 from the SI shows D1 diagnostics for the structures used in this work. Additionally, we compared DLPNO-CCSD(T) with DLPNO-CCSD to see the contribution of perturbative triples in reaction energies and transition states for the 46T cluster models (Table S4 from the SI). Structures and barriers that may indicate multi-reference character for the fast SCR (cycles II and III) are 4, 5.2 and TS_5.1-5.2 with D1 diagnostics of 0.19, 0.19 and 0.18 respectively which, according to ref.[100], already indicates multi-reference character (values above 0.15 for catalysts with transition metals). Also, adding perturbative triple excitations on total energies result in reaction energy changes below 30 kJ/mol except for structure 5.2, with a 55

kJ/mol difference with respect to the CCSD reaction energy ($\Delta E_{CCSD(T)}$ being lower). The NO oxidation cycle, on the other hand, contains several structures with a strong multi-reference character, with D1 diagnostics between 0.2 and 0.3 and perturbative triple excitations resulting in reaction energy changes between 32 and 92 kJ/mol, leading to less reliable results, see Tables S3 and S6. Likewise, spin contamination is much larger in UHF orbitals for the NO oxidation cycle, see Figures S5-S7. Nevertheless, it is clear that the overall barriers for NO oxidation are very high (above 200 kJ/mol) as the free energy barrier for the RDS is 271 kJ/mol with the M06 functional[107] (see SI) and 169 kJ/mol with PBE-D3, which is known for underestimating transition states.[41, 44]

The coordinates of all structures used in this work are available in the supporting information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Computed energies, further analysis and Cartesian coordinates (PDF).

AUTHOR INFORM9ATION

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Notes
The authors declare no competing financial interest.

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NO$_x$ SCR in Cu-SSZ-13

PBE-D3

DLPNO-CCSD(T)

ΔG

+NO$_x$

-N$_2$
-H$_2$O

TOC Graphic