Computational Study of the NH₃ de-NOₓ Selective Catalytic Reduction on the Mono-Cu Active Site of Cu-SSZ-13

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A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy at University College London.

March 2023
Declaration

I, Jasper Berry-Gair confirm that the work presented in my thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.
Abstract

The release of greenhouse gases such as NO\textsubscript{X} and the resulting climate change is a major global issue. Diesel engines are a prominent emitter and to mitigate against this, NO\textsubscript{X} is catalysed to H\textsubscript{2}O and N\textsubscript{2} in the exhaust gas flue by the zeolite Cu-SSZ-13 via the SCR reaction. The exact reaction mechanism this proceeds by is currently unknown despite significant progress in recent years. A precise understanding of the reaction will allow for rational design of new catalysts allowing for higher conversion of NO\textsubscript{X} into H\textsubscript{2}O and N\textsubscript{2}. This study provides new insights into the speciation of the active copper complex and further elucidates the reaction pathway and the elementary reaction steps, using a computational methodology.

It is found that the form of the active Cu complex is dynamic and shifting with multiple potential accessible minimum energy states under reaction conditions, and they can have significantly different geometries. The effect that different geometries have upon the activation barriers for steps in the reaction cycle is something overlooked by literature studies and is shown here to have an important effect; the lowest energy starting structure does not always give the lowest energy reaction pathway. Different reaction routes are proposed in literature, here we compare the routes on the same energy scale which has not previously been studied. It is found that for the reduction half cycle formation of NH\textsubscript{4}NO\textsubscript{2} via HONO is the lowest energy route, but others may become active at higher temperatures. The form of the active Cu complex during the oxidation half cycle is debated in the SCR literature with the general consensus being that it is dimeric at low temperatures when Cu is mobile. It is shown here that the oxidation half-cycle can proceed on a monomer via a peroxynitrite intermediate previously unknown to the SCR literature.
Impact Statement

The global issue of climate change is driven by the human release of greenhouse gases. We need to do everything in our power to mitigate against the raising temperatures and any dire consequence which may come with it. NOx are a group of greenhouse gasses including NO and N₂O that have a strong greenhouse gas effect; for example, N₂O is 300 times more potent as a greenhouse gas compared to CO₂.

Diesel car engines release significant amounts of NOx. A global scandal involving major car manufacturers has received widespread media attention, where the emissions controls systems were only activated under test conditions. This highlights how difficult it is to properly limit the NOx emissions from diesel engines. The selective catalyst reduction system which uses the zeolite catalyst Cu-SSZ-13 and ammonia decomposed from urea as the reducing agent converts NOx into H₂O and N₂ only.

This work aims to computationally study the reaction mechanism of NOx and NH₃ over the Cu-SSZ-13 catalyst to fully understand the exact elementary reaction steps involved in the reaction cycle. This will give a full understanding of the system and allow rational design of the next generation of catalysts to maximise conversion of NOx and selectivity towards N₂ and H₂O. In this thesis, it is shown that there is a varied and dynamic coordination environment around the active copper complex which will change with temperature, differentiated by the number and type of admolecules, and strength of association of Cu with the framework; this is further influenced by the Al distribution in the zeolite catalyst. This variation provides different starting points from which the SCR reaction could proceed, that have been shown here to provide significantly different activation energies. The lowest energy pathway overall is not necessarily the global energy minimum but could come from an activated state and show a different transition state geometry. This does not just have implications for the SCR literature but computational studies on heterogeneous catalysis in general, as a sample of initial geometries should be taken in order to find an accurate picture of the lowest energy transition state for a reaction path.

The reduction half cycle has been proposed to proceed via three distinct mechanisms in the SCR literature, but until now they have not been considered computationally on the same energy scale. We show that the route via HONO and NH₄NO₂ is the lowest energy one but at higher temperatures other pathways could become active, potentially explaining the seagull feature in the light-off curve. The finding that the reduction half-cycle proceeds via HONO and NH₄NO₂ moves the literature one step forward towards rational design of future SCR catalysts.

The oxidation half cycle is generally less understood than the reduction half-cycle. Here, it is shown that the oxidation half cycle can proceed via a peroxynitrite intermediate over a mono-Cu active site with a low barrier when in proximity to a 1AlCu active site. This not only shows that a dimer is not needed for the oxidation half-cycle, but also that Cu near 1Al rather than 2Al could promote lower activation energies.
Acknowledgements

Firstly, I would like to give my deepest thanks to my supervisor, Professor Furio Corà who provided me with the opportunity to complete my PhD as part of his group and under his mentorship. His passion for science and guidance over the years allowed me to complete my research and thesis while also providing the platform to explore my own ideas and various research areas. Furio’s knowledge, patience and experience have been key to my scientific and personal development. I also want to extend this gratitude to the entire UCL chemistry departmental staff for providing me the platform and support on which to be able to perform my research and to the entire Corà group. I also wish to thank and acknowledge the materials chemistry consortium funded by the EPSRC and the support staff for providing the necessary resource without my research would not be possible.

Furthermore, I wish to extend my gratitude to Johnson Matthey and the catalysis team especially Dr Misbah Sarwar and Dr Maria Pia Ruggeri for their constant support, trust in me and finally for the funds provided. Without your support, my work would not have been possible.

Finally, I would like to thank my friends and family for the support network they provided. Ivan and Arthur for the great times we have had and keeping me going when the going got tough. My parents for everything they have done and provided for me throughout my life. My incredible wife with whom I undertook this journey alongside and whose incredible strength, resilience and patience was an inspiration. And Zoe, you were always with me I know how proud you would have been.
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1. Introduction

1.1 Emissions Challenges
The global issue of climate change is an existential threat to humanity and is fast becoming a frontier that needs to be overcome to ensure the security of human civilization. The evident changes to observables which determine the level and impact of climate change are clear to see.\textsuperscript{1,2} Factors such as air temperature, sea temperature, sea level, glacial coverage and more, all unambiguously indicate human factors such as the burning of fossil fuels are the main contributing factor to climate change.\textsuperscript{3}

Climate change is driven by the release of greenhouse gases into the atmosphere. CO\textsubscript{2}, CH\textsubscript{4}, N\textsubscript{2}O and fluorinated compounds are the most abundant greenhouse gases emitted by human activity.\textsuperscript{4} CO\textsubscript{2} has largest greenhouse effect overall and accounted for 80 \% of all greenhouse gas emissions in 2019.\textsuperscript{5} The combustion of fossil fuels (coal, natural gas, and oil) is responsible for the vast majority of CO\textsubscript{2} emissions, with transportation accounting for the largest proportion of this at 35 \%. However, the warming effect induced by greenhouse gases is not the only consequence of burning fossil fuels. Nitrogen Oxides (NO\textsubscript{x}) which are a group of toxic air pollutants are also released unequivocally upon the combustion of fossil fuels in the atmosphere. NO\textsubscript{x} is comprised of NO, NO\textsubscript{2}, N\textsubscript{2}O, etc and road transport is also the largest emitter with a 40 \% contribution.

1.2 Environmental impact of NO\textsubscript{x}
NO\textsubscript{x} has detrimental effects upon both human health and the environment. Not only is NO\textsubscript{x} poisonous at mid to high concentration levels, but it is a precursor to other harmful pollutants such as aerosols and ozone. Furthermore, NO\textsubscript{x} reacts with volatile organic compounds (VOCs) forming photochemical smog. Therefore, NO\textsubscript{x} not only has a first-hand impact on human health and the environment, but a secondary effect too.

NO\textsubscript{x} is formed by the combustion reaction of atmospheric nitrogen and oxygen, particularly at high temperatures (equation 1.1).

\[ N_2 + O_2 \rightarrow 2NO \] 1.1
Further oxidation of NO by atmospheric oxygen can form NO₂ and other nitrogen oxides. There is mounting evidence that NOₓ and N-related air pollutants are detrimental for human health. Inhalation of NOₓ can cause suppression of the immune system, disruption of the autonomic nervous, and pulmonary inflammation.⁶ During summer, the complex reaction between NOₓ and VOCs which form ozone (O₃) is strongly promoted by sunlight.⁷ Ozone in the stratosphere forms a protective layer from harmful UVB rays, however ozone in the troposphere near ground level causes a risk to human health in high concentrations, or especially those with conditions like asthma. It is estimated that overall health complications due to NOₓ leads to 10,000 premature deaths per year.⁸

NOₓ has a negative environmental impact as well as causing health problems for humans. Acid rain is caused by high level of NOₓ in the atmosphere as it forms nitric acid upon interaction with water. Moreover, the acidification of surface water, if severe, can reduce biodiversity and kill aquatic life. Both ozone and NOₓ also damage forest ecosystems by soil acidification, depletion of soil nutrients and toxic algae. NOₓ is emitted mainly from on-road transport and emissions have in fact steadily declined since 1970 in the UK, mainly due to advancements in NOₓ abatement technology (Fig. 1.1). However, the current level of NOₓ emission from road transport is unsustainable and will negatively impact upon human health and the environment, therefore emissions need to be reduced further while, the number of automobiles on the road concurrently grow.
1.3 NO\textsubscript{X} Emissions and Emission Standards
The euro 6 emission standards are currently in action, with the euro 7 emission standards coming into play in 2025. They regulate the emissions of NO\textsubscript{X}, total hydrocarbon, non-methane hydrocarbons, CO, and particulate matter for new automobiles. Euro 6 focuses heavily on reducing NO\textsubscript{X} emissions in diesel engines while the euro 7 legislation is expected
to focus on further reducing NO\textsubscript{X} from diesel engines and on reducing N\textsubscript{2}O as well. For an exhaust after treatment technology to be viable it must meet the stringent criteria for NO\textsubscript{X} and particulate matter outlined in emission standard legislation. Over the last decade the permissible NO\textsubscript{X} emissions have decreased drastically in both the UK and the US (Fig. 1.2).

![Figure 1.2](image)

**Figure 1.2** | The permissible heavy-duty diesel emissions for NO\textsubscript{X} for US (solid line) and Europe (dashed line) along with particulate matter.  

In 2015, it was discovered that car manufacturers were optimising emission performance for catalytic tests, rather than actual on road performance. It was found that Volkswagen fitted engine management firmware which could detect test conditions and lowered the emissions, but at a cost to the automobile’s performance. Whereas, under normal road conditions certain diesel engines produced over 40 times more NO\textsubscript{X} than allowed by the emission regulations but retained optimum on road performance. The emission scandal gave diesel engines a bad reputation, especially in European media, which lead to far fewer sales of diesel engines and even a ban of certain diesel engines in some countries such as Germany.

The recent negative publicity and attitude towards diesel engines does not accurately represent the emissions and science behind the comparison of diesel and petrol engines. The
lean-burn nature of diesel engines means they use significantly less fuel than petrol, as more oxygen from the atmosphere is used during combustion, allowing them to be more efficient, while maintaining a similar performance level. In fact, on average diesel engines have a better fuel consumption or miles per gallon than petrol engines, with petrol and diesel having 41.9 and 46.8 mpg respectively.\textsuperscript{12} Furthermore, diesel engines emit on average 120 g/km of CO\textsubscript{2} compared to 200 g/km for petrol engines.\textsuperscript{13} However, the lean-burn conditions mean that approximately 30\% more NO\textsubscript{x} is produced from diesel engines than petrol engines. Also, the after treatment of the exhaust gas to abate the harmful and polluting gases is a more difficult task in diesel engines than petrol engines, due to the excess O\textsubscript{2} during combustion.

1.4 Current Abatement Technologies and Strategies
Due to the intrinsic difference in the way petrol and diesel engines operate, a different composition of exhaust gas is generated. This, therefore, requires different technologies to abate the pollutants from diesel and petrol exhaust gas flues.

The effective and efficient ‘three-way’ catalytic converter is the exhaust gas post-processing technology of choice for petrol engines. It directly oxidises both CO and hydrocarbons into CO\textsubscript{2} and water, while also reducing NO in to N\textsubscript{2} using CO, to form N\textsubscript{2} and CO\textsubscript{2}:\textsuperscript{14}

\begin{align*}
2NO + 2CO & \rightarrow N\textsubscript{2} + 2CO\textsubscript{2} \quad 1.2 \\
2CO + O\textsubscript{2} & \rightarrow 2CO\textsubscript{2} \quad 1.3 \\
2C\textsubscript{2}H\textsubscript{6} + 7O\textsubscript{2} & \rightarrow 4CO\textsubscript{2} + 6H\textsubscript{2}O \quad 1.4
\end{align*}

However, very specific exhaust gas conditions are required for high conversion of all the reactants (Fig. 1.3). Under fuel-rich conditions there is not enough oxygen present for total combustion leading to high levels of CO and hydrocarbons, whereas under lean-burn or excess O\textsubscript{2} conditions low levels of hydrocarbons and CO are emitted but significantly more NO\textsubscript{x}. Therefore, an exact ratio of air to fuel of 14.7:1 is required for optimum catalytic performance.
The composition of commercial three-way catalysts is complex. A ceramic honeycomb shaped monolith substrate is coated in a washcoat and then the active platinum group material and promoter materials. The monolith is usually cordierite, while the washcoat is comprised of doped alumina ($\text{Al}_2\text{O}_3$) to increase the surface area.\textsuperscript{16,17} The active material coated upon the washcoat is usually a Pt and Pd blend with some Rh included to help the reduction of NO\textsubscript{X} to N\textsubscript{2}, finally a ceria ($\text{CeO}_2$) based material is added to provide an oxygen storage capability, which increases the window of the air to fuel ratio.\textsuperscript{16,17}

The three-way catalytic converter processes hydrocarbons, NO and CO all at once, however diesel engines only run under lean-burn excess oxygen condition so the use of the three-way catalyst is not possible. Therefore, a succession of different catalyst and abatement technologies are used to process the exhaust gases. The main components of diesel exhaust technologies are the diesel oxidation catalyst (DOC) which converts CO and hydrocarbons into CO\textsubscript{2} and water, the selective catalytic reduction (SCR) catalyst which converts NO\textsubscript{X} into N\textsubscript{2} and H\textsubscript{2}O using NH\textsubscript{3} as the reducing agent, a diesel particulate filter to remove the particulate matter and more recently a NO\textsubscript{X} adsorber has also been included (Fig. 1.4).
The diesel oxidation catalyst (DOC) is comprised of a honeycomb monolith coated with a platinum group metal, it oxidises hydrocarbons and CO into less harmful CO$_2$ and H$_2$O and a proportion of NO into NO$_2$.\textsuperscript{19} The formation of NO$_2$ in the DOC can assist with the SCR catalyst. The SCR catalyst is the focus of this work and converts oxides of nitrogen into N$_2$ and H$_2$O only, using a metal-exchanged zeolite. The diesel particulate (DPF) removes particulate matter from exhaust gases by physical filtration. There are many different types available but the most common uses a honeycomb shaped ceramic material with some method of regeneration of the filter.\textsuperscript{20} Recently, an additional section to the diesel exhaust gas system has been added to aid in the low temperature conversion of NO$_x$ commonly referred to as the cold start (not shown in the diagram). Low temperature NO$_x$ adsorbers can be passive or active. Passive NO$_x$ adsorbers or traps, store NO$_x$ at low temperature, which is then re-released back into the gas stream to participate in the SCR reaction at higher temperatures regimes, which exhibits better overall NO$_x$ conversion.\textsuperscript{21} Active NO$_x$ adsorbers, which are an older version of the technology stores NO$_x$ and releases it periodically during short bursts of rich air-to-fuel ratio environments where NO$_x$ is reduced in a process similar to that of the three-way catalyst, but is not highly efficient and predates current SCR technologies.\textsuperscript{22}

1.5 Research Aims
The issues caused by NO$_x$ emissions have been discussed in section 1, and here the goals of this thesis are outlined. In this thesis the main aim is to further understand the atomic-level reaction mechanism for the de-NO$_x$ SCR reaction using NH$_3$ as the reductant. A full understanding of how the reaction proceeds, including various distinct pathways promoted
by different temperatures, gas mixtures, and catalyst compositions will greatly assist in rational design of new catalysts to improve the conversion and selectivity. Currently the conversion of NO\textsubscript{x} and the selectivity toward N\textsubscript{2} and H\textsubscript{2}O in the SCR reaction is good enough to meet the EURO6 emission standards, however with the advent of the new EURO7 legislation due in 2025, it is essential for a deeper understanding of how and why NO\textsubscript{x} is catalysed to N\textsubscript{2} and H\textsubscript{2}O over the industrial catalyst Cu-SSZ-13 in order to keep pace with ever tightening emission standards. There are multiple different proposals for the reaction mechanism in the thriving SCR literature, however it is difficult to compare them to each other and to completely ascertain if one pathway is dominant and then if so, which. This thesis aims to further understand the microscopic details of the reaction mechanism and rationalise contentious points within the literature. To understand the reaction mechanism, it is first essential to fully comprehend the nature and exact speciation of the active Cu site, as this will have a vital impact on how the reaction proceeds. Furthermore, the SCR literature highlights multiple active sites which are thought to change as a function of temperature, and even during the reaction cycle itself. The atomic level reaction steps involved during the formation of key SCR intermediates are essential to understand, along with their characteristic spectroscopic signals, in order to be able to detect and confirm their presence. This study will be undertaken computationally using density functional theory (DFT). DFT simulations allow for the optimisation and calculation of energies of exact structures which can in tern provide microscopic details which are unattainable using experimental techniques. DFT can compute the stable geometries of complexes which correspond to a minimum point on the potential energy surface and can be used to find the likely structures involved during the reaction cycle. Furthermore, with the use of computational techniques, metastable and transition states can be found which provide valuable insight on how the reaction proceeds and it is possible to simulate their spectroscopic signals for comparison to experimental findings. With these tools it is possible to expand our knowledge of the SCR reaction mechanism with the overall aim to improve the abatement of NO\textsubscript{x} from diesel exhaust gas flues.
2. Computational Theory and Details

Thanks to rapid development of software and the ever-growing computational resource available, it is now possible to tackle computationally the study of chemical systems of substantial size and complexity, including chemical reaction mechanisms involved in heterogeneous catalysis.

Computational techniques give a different level of insight compared to experiment, essential for the study of the de-NO\textsubscript{x} SCR reaction with Cu-SSZ-13 as the catalyst. Atomic level control given by computational techniques allows one to probe microscopic details such as the energies of different configurations, the local environment of the active site, coordination numbers and geometries, and the spin states which can elucidate the mechanism of redox reactions. Experimental techniques do not permit the level of control that computational techniques can as variables can be controlled very precisely, whereas most experimental techniques give a larger scale and average ensemble view, especially during the evolution of a reaction, complicating analysis.

There are two main branches of computational techniques: classical, and quantum mechanical. Classical techniques use parameterised force fields and allow computation of very large systems at a small computational cost; however, the accuracy of the results is compromised as all electronic effects are lost. Quantum mechanical techniques are significantly more expensive but allow for the inclusion of electronic effects which are essential in studies involving redox reactions, such as this one. Both methods allow one to calculate the energy of a system dependent upon its geometry. Once the energy has been calculated it is then necessary to optimise the structure to find the minimum energy by following the curvature of the potential energy surface (PES) to a minimum point. Introducing and varying constrained internal coordinates into the optimisation is one way to explore more of the PES than the minima, for example saddle points, which represent transition states and are used to obtain activation barriers for atomic level reaction steps.

This study only uses quantum mechanical calculations, as electronic contributions are an integral aspect of the de-NO\textsubscript{x} SCR reaction. All quantum mechanical approaches used here attempt to solve the time-independent Schrödinger equation. However, the Schrödinger equation is analytically impossible to solve for a multi-electron system, as the electron-
electron interactions cannot be computed exactly. Therefore, we need to use a range of approximations and mathematical formulations in order to obtain an estimate of the wavefunction, from which useful chemical properties can be obtained. For multiple-electron systems the Hamiltonian can be expanded into its constituent parts; the kinetic energy operator for nuclear motion, the kinetic energy operator for the electronic motion, the potential energy operator for the inter-nuclear interactions, the potential energy operator for the inter-electron interaction, and the external potential experienced by the electrons from the nuclear-electronic interactions. This Hamiltonian and specifically the operator for the potential energy operator for the inter-nuclear interactions presents a many-body problem, meaning the motion of the electrons are correlated with each other and therefore their degrees of freedom cannot be separated and hence an exact solution cannot be found. Consequently, approximations must be made in order to find a solution to the Hamiltonian.

Any quantum mechanical system can be described by the Schrödinger equation, where the time independent version takes the form:

\[ \hat{H} \psi = E \psi \]  \hspace{2cm} (2.1)

The Hamiltonian operator \( \hat{H} \) is comprised of the kinetic and potential energy operators for both the electronic and nuclear coordinates where \( E \) represent the energy and \( \psi \) the wavefunction. Despite the simple appearance the Schrödinger equation is very challenging to solve and can only be solved analytically for systems containing one electron. In cases where there are two or more electrons the Hamiltonian becomes:

\[ \hat{H} = T_n + T_e + V_{nn} + V_{ee} + V_{ext} \]  \hspace{2cm} (2.2)

Where \( V_{ext} \) represents the external potential acting upon the electrons caused by the electron-nuclear interaction and \( V_{ee} \) and \( V_{nn} \) are the potential energy operators for electron-electron and nuclear-nuclear interactions respectively and \( T_e \) and \( T_n \) are the kinetic energy operators for the electronic and nuclear motion respectively. The kinetic energy is defined by:

\[ T_i = -\frac{\hbar^2}{2m} \Delta_i^2 \]  \hspace{2cm} (2.3)

\( \Delta_i \) represents the Laplace operator for a particle \( i \) and the Coulomb term is given by:

\[ V_{ij} = \frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_i-\mathbf{r}_j|} \]  \hspace{2cm} (2.4)
Where \( r_i \) and \( r_j \) give the positions of the particle i and j. The Hamiltonian is frequently written in terms of atomic units (\( \hbar, e, m_e \) and \( 4\pi\varepsilon_0 = 1 \)) for ease of notation.

Solving this many-body Hamiltonian is impossible due to the presence of the electron-electron interaction \( V_{ee} \) term. This fundamental problem arises due to the fact the electronic motions are correlated and therefore the electronic degrees of freedom within the system cannot be separated. Subsequently, if the electrons don’t interact a solution is from the product of N non-interacting single-electron systems as this leaves out essential inter-electron correlation interactions. Furthermore, as systems can contain a larger number of particles, they become very difficult to compute, but the use of symmetry and periodic boundary conditions can assist in this greatly. In order to provide any solution to this many-body Hamiltonian approximations must therefore be made.

The first and most general approximation to make is the Born-Oppenheimer approximation, which allows the separation of the nuclear and electronic wavefunctions.\(^{23}\) It assumes the electrons move in an electric field generated by a fixed nuclear configuration, as the mass of the nucleus is much greater than the mass of the electrons meaning the electrons move at such a speed the movement of the nucleus is negligible. Relativistic effects are also usually ignored, as in most systems their contribution is negligible. This allows the re-formulation of the time independent electronic Schrödinger equation where we can ignore the kinetic energy operator \( T_n \) for the nuclear motion. The Born-Oppenheimer Approximation then becomes:

\[
\hat{H} = T_e + V_{nn} + V_{ee} + V_{ext}
\]

This work uses a combination of two quantum mechanical approaches: density functional theory (DFT) and the Hartree-Fock method (HF). Both these methods use mathematical approximations and constructs to model reality, so it is essential to consider their limitations. Although pure HF calculations are not directly used in this work the derivation of DFT uses aspects of HF, and DFT hybrid exchange-correlation functionals which are extensively used incorporate HF, therefore HF methods will be discussed.

2.1 Hartree-Fock Methods
Hartree attempted to give an approximation to the Schrödinger equation by using self-consistency, which is referred to as the Hartree method.\(^{24,25}\) The N-body wavefunction which
makes the Schrodinger equation analytically unsolvable can be approximated to a product of independent orbitals:

\[ \psi(r_1, r_2, ..., r_N) = \psi_1(r_1)\psi_2(r_2) ... \psi_N(r_N) \]  \hspace{1cm} (2.6)

As the electron orbitals are independent from one another, it means that their motion cannot be correlated. Therefore, the electrons can only interact via a potential of mean field which gives a series of solvable one electron Schrödinger equations dubbed the Hartree equations:

\[ -\frac{\Delta^2 \psi_i(r)}{2m_i} + V(r)\psi_i(r) = \varepsilon_i\psi_i(r) \]  \hspace{1cm} (2.7)

where \( V(r) \) is the potential acting upon the electron and contains two parts: \( V_{\text{nuc}}(r) \) which is the nuclear-electron interaction and \( V_{\text{elc}}(r) \) which is the mean-field resulting from the remaining N-1 electrons within the system. This means that instead of considering the electron individually, they are smeared to give an average charge density \( \rho(r') \). Therefore, the Hartree potential is given by:

\[ V(r) = V_{\text{nuc}}(r) + V_{\text{elc}}(r) = -Z \sum_i \frac{1}{|r-R_i|} - e \int \frac{\rho(r')}{|r-r'|} \, dr' \]  \hspace{1cm} (2.8)

with

\[ \rho(r) = \sum_i |\psi(r)|^2 \]  \hspace{1cm} (2.9)

Now the Hartree equations can be solved in a self-consistent manner, however they do not describe the fundamental physics of the system very well. This is because the Pauli exclusion principle states that the wavefunction must be antisymmetric regarding the exchange of any two electrons:

\[ \psi(r_1, r_2, ..., r_N) = -\psi(r_2, r_1, ..., r_N) \]  \hspace{1cm} (2.10)

This requirement is not met by equation 2.6, but the exchange condition can be remedied by the inclusion of Slater determinant, which satisfies the anti-symmetric requirements and therefore the Pauli exclusion principle.

The inclusion of the Slater determinant to satisfy the anti-symmetric requirements was Fock’s addition to Hartree’s theories giving the Hartree-Fock equations which take the form:

\[ -\frac{\Delta^2 \psi_i(r)}{2m_i} + V(r)\psi_i(r) - \sum_{i,j} \frac{\psi_j(r')\psi_j^*(r')\psi_i(r)\psi_i^*(r)}{|r-r'|} \, dr \, dr' = \varepsilon_i\psi_i(r) \]  \hspace{1cm} (2.11)
The Hartree-Fock equations now differ from the Hartree equations because of the inclusion of the exchange term. In the Hartree equations $V_{elec}$ contains a repulsive interaction between an electron and itself. This is because an electron moves in a field with an average potential from the wavefunction which includes itself. This is a completely unphysical situation and leads to an error dubbed ‘the self-interaction error’. Therefore, the inclusion of the exchange term in the Hartree-Fock equations treats the exchange exactly, completely negating the self-interaction error. However, this comes at an increased computational cost compared to the Hartree method due to the more complex equations. Furthermore, electron correlation is not described at all by the Hartree-Fock method. This is because a mean-field approach cannot describe a correlated system and these contributions are important for many systems, especially in the solid state.

To summarize, the HF method factorises the solution of the N electron system into the product of one electron states, it assumes that the electrons move in the field generated by the nucleus and a mean field generated by the other electrons in the system. Essentially, it is assumed that the electrons are independent of each other, and a condition to fulfil the antisymmetric principle as determined by the Pauli exclusion principle is then added. The antisymmetric principle states that any wavefunction describing fermions must be antisymmetric to both spatial and spin coordinates. This anti-symmetric exchange condition is satisfied by using Slater determinants to represent the wavefunction. The variational principle allows us to calculate an estimate for the energy of the system; it states that the lowest energy calculated cannot be lower than the true ground state. Therefore, we can solve for the energy by making an initial guess at the orbitals, which give the electron-electron interactions which are then used to produce a new set of orbitals. The procedure is repeated until the energy does not change; this is called the self-consistent field (SCF) method.

The HF method does, however, completely ignore the phenomenon of electron correlation, which describes the tendency for electrons to avoid each other as they move, while describing the electron exchange exactly. This causes the overall energy of the system to be too high as electron correlation reduces the energy and means HF leads to under binding. There are methods of improving the theory behind HF, such as configurational interaction (CI) or Møller–Plesset perturbation theory. CI takes a linear combination of Slater determinants (the expression that describes the anti-symmetric nature of the wavefunction) each with a
different electronic configuration of the system, this improves the description of the wavefunction by building up to a full solution of the Schrödinger equation. However, full CI (including all possible excited configurations) is incredibly expensive, for example a calculation on water, one would need to solve $\approx 5 \times 10^8$ Slater determinants, whereas HF would only need one.\textsuperscript{26}

2.2 Density Functional Theory
DFT is a more widely used technique within computational chemistry, solid state physics and material science compared with Hartree-Fock methods. DFT uses the ground state total electron density $\rho(r)$ rather than the wavefunction $\psi(r)$ in order to calculate the total energy, which allows for a significant simplification of the many-body problem. This is since the electron density is a single value at each point in space. So in three dimensions it depends on only three variables, whereas an N-body wavefunction is dependent upon $3N$ variables, where $N$ represents the number of interacting particles. One of the earliest DFT proposals defined the kinetic energy as a function of the total electron density and treated the electron correlation as a mean-field.\textsuperscript{27} The exchange energy was subsequently formulated in terms of the electron density, but neither of these models were particularly representative of physical systems.

DFT used today stems from the Hohenberg-Kohn theorems which state\textsuperscript{28}:

1) The external potential and therefore the total energy is a unique functional of the electron density.

2) The ground state energy can be obtained using the variational principle, hence the density that minimises the total energy is the exact ground state energy.

Varying the total energy of the system allows one to obtain the ground state electron density and therefore the wavefunction of the system. The theorems defined by Hohenberg and Kohn allow the formulation of a functional which gives an expression for the energy of the system only dependent upon the density, which is given by:

$$ E[\rho(r)] = F[\rho(r)] + \int V_{ext}(r)\rho(r)dr $$  \hspace{1cm} 2.12

$V_{ext}$ represents the interaction between the electrons and the external potential and the $F[\rho(r)]$ is the sum of the electron-electron interaction $U(\rho)$ and the kinetic energy of the
electrons $T(\rho)$. The $F[\rho(r)]$ term cannot be found exactly as it contains effects caused by electron correlation which present the many-body problem. Kohn and Sham derived equations to be able to solve for the functional which is the main foundation of DFT. They allow for a set of interacting electrons with density $\rho(r)$ to behave as an equivalent but fictitious non-interacting system. This allows for a computationally tractable problem as the electron coordinates are subsequently de-coupled from one another. The Kohn-Sham potential is defined as $V_{ks}(r)$ and the Kohn-Sham functional $F[\rho(r)]$ is represented by:

$$ F[\rho(r)] = T[\rho(r)] + U[\rho(r)] = T_s[\rho(r)] + U_H[\rho(r)] + E_{XC}[\rho(r)] $$  \hspace{1cm} (2.13)

It is possible to express the kinetic energy term as the kinetic energy of the non-interacting system $T_s$ and the interacting or correlated system $T_c$:

$$ T[\rho(r)] = T_s[\rho(r)] + T_c[\rho(r)] $$ \hspace{1cm} (2.14)

Therefore, the unknown terms such as $T_c$ can be contained within $E_{XC}$ meaning that this term is a correction due to electron exchange and correlation, which is defined as:

$$ E_{XC} = (T - T_s) + (U - U_H) = T_c + (U - U_H) $$ \hspace{1cm} (2.15)

The kinetic energy term of the non-interacting system can then be denoted in terms of the single particle orbitals:

$$ T_s[\rho(r)] = \frac{1}{2} \int \psi_i^*(r) \Delta r^2 \psi_i(r) dr $$ \hspace{1cm} (2.16)

where the Hartree energy term is:

$$ U_H[\rho(r)] = \frac{1}{2} \iint \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 $$ \hspace{1cm} (2.17)

The Hartree energy term now includes the electron-nuclei interaction as well as the mean-field contribution.

If the number of particles in the system are held constant it is now possible to use the Hohenberg-Kohn theorem which states that the variational principle can be used to find the ground state energy as the electron density which minimises the total energy is the ground states energy. The total energy now becomes:

$$ \delta \frac{\delta}{\delta \rho(r)} [F(\rho(r)) + \int V_{ext}(r)\rho(r)dr - \mu(\int \rho(r) dr)] = 0 $$ \hspace{1cm} (2.18)

where $\mu$ is a Lagrange multiplier which takes the form:
\[ \mu = \frac{\delta F[\rho(r)]}{\delta \rho(r)} + V_{\text{ext}}(r) \]

and \( V_{\text{ks}}(r) \) is the Kohn-Sham potential:

\[ V_{\text{ks}}(r) = V_{\text{ext}}(r) + V_{H}(r) + V_{XC}(r) \]

which contains the Hartree potential:

\[ V_{H}(r) = \frac{\delta U[\rho(r)]}{\delta \rho(r)} = \int \frac{\rho(r)}{|r_1 - r_2|} \, dr \]

and the exchange correlation potential:

\[ V_{XC}(r) = \frac{\delta E_{XC}[\rho(r)]}{\delta \rho(r)} \]

Therefore, it is now possible to express the Kohn-Sham equations in the same form as the Hartree equation, but importantly it is now dependent upon the electron density rather than the wavefunction.

\[ \rho(r) = \sum_{i}^N |\psi_i(r)|^2 \]

As the variational principle can be applied the Kohn-Sham equation can be solved self-consistently. Starting from an arbitrary guess of the initial density it is possible to calculate \( V_{\text{ks}} \) and find the wavefunction. From this wavefunction a new guess of the density can be found and the cycle repeats until the density is converged to a desired tolerance.

It is essential to note that the Kohn-Sham DFT equations include a self-interaction error as they contain a Hartree potential. In particular, the local form of the expression for \( V_{XC} \) in eq 2.20 Kohn-Sham DFT differs from conventional wavefunction theory because it contains interactions between particles and themselves as the interaction of each electron with all other electrons and importantly its own density are contained within one single sum. Whereas coulomb interactions in conventional wavefunction theory are only included for two or more particle interactions, but not for interaction of particles and themselves. As with other unknown terms it is possible to remove this self-interaction term by enveloping it within \( V_{XC} \). If the exact form of \( V_{XC} \) is known, then the self-interaction error can be cancelled, however it is currently not. Therefore, approximations must be made for \( V_{XC} \) which include the self-interaction and the functional form of \( V_{XC} \) determines the level of error.
2.3 The Functional Zoo
Despite DFT being in theory an exact method, approximations are unavoidable for practical use, as the true functional form is not known; and therefore, several approximated versions have been proposed. The only unknown functional form is the exchange-correlation energy $E_{XC}$, which is defined as the difference between the exact energy and the contributions to the energy that may be evaluated exactly. Hence, it contains all the errors from approximation and the non-classical contributions to the energy. The $E_{XC}$ energy may only account for a small proportion of the total energy of the system, however it is essential for describing the chemistry of the system; therefore, the accuracy of DFT is highly dependent on the choice of functional used and it is vital to understand pick the best cost/accuracy trade-off for the appropriate system.\(^{30}\)

Several formulations of $E_{XC}$ have been proposed, such as the local density approximation (LDA), generalised gradient approximation (GGA), meta-GGA, and hybrid exchange-correlation functionals. This functional ‘zoo’ is often classified using the ‘Jacobs Ladder’ of DFT in order to organise it dependent upon each functionals constituent ingredients (fig 2.1) The simplest form of the $E_{XC}$ and the lowest rung on the ladder (above Hartree methods) is the LDA. It assumes that $E_{XC}$ is only dependent upon the electron density at any point and assumes a uniform local electron density. It obtains the electron exchange term from the uniform electron gas model and the electron correlation term is fitted to high level quantum Monte-Carlo calculations. The LDA exchange-correlation therefore takes the form of:

$$E_{XC}^{LDA} = \int \rho(r) \epsilon_{XC}^{LDA}[\rho(r)]dr$$  \hspace{1cm} 2.24

Considering the simplicity of the model, LDA is surprisingly good at modelling the properties of certain systems. For example, in some metals where the electron density of the real system does indeed vary reasonably smoothly it models them acceptably. However, there are issues with LDA as it overestimates the correlation energy and underestimates the exchange. Therefore, it overestimates binding energies and poorly reproduces dispersion forces and overestimates bond energies on the order of 100 kJ mol\(^{-1}\).\(^{31}\)
The GGA can be considered ‘one step’ higher in the level of its complexity than LDA. It considers both the density and its gradient at a certain point. It takes the form of:

\[ E_{XC}^{GGA} = \int \rho(r) \varepsilon_r^{GGA} [\rho(r), \Delta \rho(r)] dr \]  

2.25

Therefore, it reproduces physical systems better than the LDA as electron density in most systems is inhomogeneous and does not vary smoothly rather than the assumption in LDA that the gradient is homogeneous. The parametrisation for the functional form of \( E_{XC}^{GGA} \) almost always stems from the uniform electron gas and can give a wide variation of different functional forms. GGA functionals reproduce lattice parameters of crystal systems to a very high degree of accuracy and show improved binding energies and band gaps compared to LDA. However, they still contain the electron self-interaction error which gives very inaccurate descriptions of systems with highly correlated electrons such as localised states. This error is very prominent in the transition metals and considering this study focuses on a Cu\(^{2+}\) active site within a zeolite catalyst a method is needed which adjusts for this error well.

Whereas GGA functionals only considers the first derivative of the electron density meta-GGA goes one step further and includes the second derivatives. However, in practice calculating the second derivatives is not always numerically stable, therefore often the kinetic energy density term is used instead. These functionals take the form:
In principle one could include higher and higher derivatives of the electron density in the form of a Taylor expansion to improve the description of the local electron density, but this would become far too computationally demanding and subsequently unfeasible.

In DFT, a well-known source of inaccuracy referred to as the self-interaction error (SIE) is present. Its origin in Kohn-Sham DFT stems from the fact that energy is a functional of the single particle (spin) density, so there is no possible way to distinguish two body Coulomb interactions from self-interaction. This is because in wavefunction theory Coulomb interactions can only be included for two particle reactions, so an electron cannot interfere with itself.

There are two common approaches to combat the SIE error prominent in strongly localised systems: DFT+U and hybrid exchange correlation functionals. DFT+U uses a Hubbard like additional term U, which acts as a corrective term on the strongly localised electrons. It is added to the relevant orbitals within the system which can improve the electron localisation description as compared to standard DFT and allows for better formulation of properties such as the band gap. However, as the U term is system and in fact species dependent the U term must be chosen for the appropriate orbitals for each individual system and species. Therefore DFT+U is less appropriate for complex systems with different species with strongly localised electrons as the Hubbard terms can become more of a trial-and-error method in which the parameters are change until the results match with experimental values.

Hybrid exchange-correlation functionals are a more rigorous method for correcting for the SIE as there is no need to tailor the Hubbard U term to each individual system. Hybrid exchange-correlation functionals improve upon standard DFT by adding a proportion of exact Hartree-Fock exchange as a linear combination of HF exchange and DFT exchange-correlation to the functional form. The two-electron term in LDA and GGA DFT functionals have correlation and exchange terms that do not cancel out, which gives the infamous SIE whereas HF methods are self-interaction free. Therefore, using the Kohn-Sham equations that have some form of HF included allows for a mixture of their formulations and reduction of the self-interaction error. The non-local Hartree-Fock exchange term is:

\[
E_X^{HF} = -\Sigma_{i,j} \int \frac{\psi_j(r)\psi_j^*(r')\psi_i(r)\psi_i^*(r')}{|r-r'|} dr dr'
\]
Therefore, $E_{xc}$ is formulated from a specified fraction of the Hartree-Fock exchange, the retaining fraction of local DFT exchange and the DFT correlation energy:

$$E_{xc} = \alpha E_{x}^{HF} + (1 - \alpha)E_{x}^{DFT} + E_{c}^{DFT}$$

This significantly improves the description of non-localised orbitals and combats against the SIE. It is generally accepted that hybrid exchange correlation DFT significantly improve descriptions of systems with highly localised states as compared to LDA and GGA without the need for empirical fitting, as in DFT+U methods. For systems with highly localised electrons such as Cu$^{2+}$ with its d$^9$ electron configuration hybrid functionals are essential, otherwise the open-shell nature of the ion means the electrons will delocalise unphysically using GGA-DFT causing calculations to be unreliable as the theoretical system will not be representative of nature. The most commonly used hybrid functionals are B3LYP (20 % HF) and PBE0 (25 % HF).33–36

DFT completely ignores contributions to the energy from any Van der Waals (VdW) forces such as the London dispersion force. In this study the adsorption of molecules is essential to the system, therefore VdW forces contribute significantly to the overall state and energy of the system. The D3 dispersion correction is a widely used technique which employs a damped London type pairwise term in order to correct for the energy of the dispersion forces as an additional parameter alongside the DFT energy.

The leading methods to account for dispersion force in DFT have been developed by Grimme and are very widely used.37,38 The first method developed was denoted DFT-D and used a semiclassical atom pair-wise scheme where an additional term is added to the DFT (or HF) mean-field energy calculated. More recently DFT-D3 has been developed and is used throughout this work.39 In this formulation the dispersion correction scheme is again an atom-pairwise sum but using a two-body term. DFT-D3 takes the form:

$$E_{disp}^{D3} = \sum_{AB} \sum_{n=6,8} c_{n}^{AB} f_{damp}(R)$$

A and B are atom labels and $c_{n}^{AB}$ are dispersion coefficients raised to the nth order for the atom pairs A and B, which is dependent upon the arrangement of the atoms and is calculated by fitting data to higher level time dependent DFT calculations and post HF methods such as
MP2. The $s_{6,8}$ connection terms and parameters depend on the functional used. R represents the distance between atoms A and B and $f_{damp}$ is damping function which is also fitted to the specific functional used. DFT-D3 is a highly popular dispersion correction scheme and has been extensively shown to accurately reproduce a wide range of structural properties of a large range of materials and better account for adsorption energies.$^{40}$
3. Literature Overview

3.1 Zeolite Science
The word zeolite originates from the Greek words ‘zeo’ and ‘lithos’ meaning boil and stone respectively. The Swedish chemist Axel Fredrik Cronstedt devised the term after observing large amounts of steam from a zeolite material upon rapid heating which resembled a ‘boiling stone’ exhibiting the materials strong adsorbing properties.\(^{41}\)

Zeolites are aluminosilicates built into a three-dimensional framework via corner sharing tetrahedra. This creates a crystalline solid consisting of (SiO\(_4\)) and (AlO\(_4\)) tetrahedral units in a microporous network with various unique topologies.\(^{42}\) The framework creates a series of rings, pores and channels of certain discernible sizes, which can allow chemical species of a certain size into the microporous network, or block and exclude larger ones from entering, a vital aspect to the chemistry of zeolites.\(^{43}\) This is analogous to a sieve, but on a molecular scale, therefore they have been termed ‘molecular sieves’. Zeolites occur both naturally and synthetically with 253 unique frameworks found to date, with over 40 occurring naturally and each possessing different physical properties allowing for a large variation in their chemistry.\(^{44,45}\) When aluminium is included in the silica framework a charge imbalance is created, which must be balanced for the material to be stable. The charge compensating species are usually protons, creating Brønsted acid sites, or cations creating Lewis acid sites, allowing for a rich variety of chemistry depending on the balancing species. When a transition metal ion is exchanged into the zeolite, the chemistry can become like that of homogeneous inorganic catalysis by organometallic compounds. The variable oxidation states of transition metal ions allow for facile electron transfer to and from the ion, allowing for complex redox chemistry, essential for the SCR reaction. Homogeneous catalysts are renowned for their high conversion rates, but the separation of the final products is difficult as they are of the same phase, however this is not an issue for transition metal exchanged zeolites. The combination of high conversion, selectivity, molecular sieve-like behaviour, and ease of separation is what gives metal exchanged zeolites excellent catalytic properties.

Metal exchanged zeolites have drawn attention as catalysts for multiple chemical processes, in particular the partial oxidation of methane and more recently the methanol to olefin
reaction. However, the application that has attracted the most attention over the last 40 years is the abatement of NO\textsubscript{x} from lean-burn combustion engines.

3.2 Uses and Synthesis of Zeolites
The main industrial processes in which zeolites are used for catalysis; separation or adsorption of gases; and ion exchange. Each process utilises the interconnected pores, cages and channels created by the topology of the zeolite, which allow for the molecular sieve type behaviour. Furthermore, chemical species such as molecules, Brønsted acid sites and transition metals can occupy sites or rings within the zeolite and make it active for adsorption or catalytic reactions. Zeolites’ catalytic properties are often employed in the petrochemical industry in cracking and hydrocracking and can act as solid-state acids when protons are used as the charge balancing species – referred to as Brønsted acid sites. This allows for multiple acid catalysed reactions such as isomerisation and alkylation. If Transition metals are exchanged into the zeolite it can act as a host framework for organometallic redox chemistry, but without the difficult separation of products. This is the basis of the SCR reaction. Zeolites also exhibit shape selectivity, due to the size of the zeolite pores and cages. This means that certain molecules cannot enter the zeolite and participate in reactions, or that certain transition states or products also cannot be formed as the size of the cage in which the reaction is happening is too small to allow them to form.

Apart from heterogeneous catalysis, zeolites have wider applications. One of the most notable is their use within commercial water purification by utilizing their potential for ion exchange. The aperture size, defined by the number of tetrahedral units in a ring, can be controlled by using different zeolite framework types, and can allow for precise separation of molecules like O\textsubscript{2}, N\textsubscript{2}, noble gases and formaldehyde from low grade natural streams and more. Furthermore biochemical uses of zeolite are in development, using the molecular sieve properties to produce purified oxygen from the atmosphere and in agriculture to regulate the release of nutrients such as potassium and nitrogen. Furthermore the biomedical properties of zeolites are also of interest. They can exhibit antibacterial properties, be used in the detection of cancer markers and also show strong potential in drug delivery applications.
As mentioned, zeolites are porous crystalline aluminosilicates consisting of corner sharing SiO$_4$ units arranged in such a way as to create distinctly different molecular sieve frameworks of varying interconnectivity and topology. Modern zeolite science began in the early 1940s with Richard Barrer who conceived the first zeolite classification system based upon molecular size considerations and also performed the first zeolite synthesis by conversion of mineral phases, using strong salt solutions at high temperatures. With these methods the first two synthetic zeolites were created in 1948, where one was the synthetic analogue of the naturally occurring zeolite mordenite, and a then unknown zeolite, later determined to follow the KFI framework. It was then Milton in the 1950s who progressed the synthesis of zeolites further by using more reactive aluminosilicate gels as starting materials which required lower temperatures. It was under these conditions that the chabazite framework was first synthesised, despite existing already in nature. Building on the foundations laid in the 1940s and 1950s quaternary ammonium cations were introduced into the synthesis of zeolites forming new zeolites A and X. These methods also allowed for high silica zeolites to be made with the use of tetaethylammonium.

In general, zeolites are crystallised using a silica-alumina gel in the presence of a structure directing agent (SDA), usually an organic template and OH$^-$ or F$^-$. The hydroxide or fluoride act as mineralising agents which assist in the assembly of the silica/alumina tetrahedral units during crystallisation and the SDAs control the topology of the framework by guiding the building blocks into certain crystal structures. SDAs can also govern the amount of Al (Si/Al ratio) incorporated into the zeolite as the number of cationic SDAs used direct the position of the anionic AlO$_4$ tetrahedra within the lattice and therefore the content. For example, during ZSM-5 synthesis tetrapropylammonium is used as a SDA to incorporate Al at 10 member ring (10MR) channel intersections, whereas a mixture of Na$^+$ and tetrapropylammonium, positions Al ions more uniformly between the 10MR channels and the intersections. Therefore, precise conditions during synthesis can influence both the material composition and distribution of Al ions throughout the framework. This idea is used to precisely control the synthesis and composition of Cu-SSZ-13, the leading SCR catalyst.

3.3 Cu-SSZ-13 Catalyst

NH$_3$-SCR was first developed as a method for abatement of NO formed during nitric acid production, where these catalysts were made from precious metals. Then, in the 1970s
metal oxides supported on titania, such as vanadia (V₂O₅) became the research focus.⁷³ It was in 1977 that Seiyama et al first reported the use of transition metal-exchanged zeolite Y for NH₃ SCR.⁷⁴ They reported a favourable low temperature activity of Cu²⁺ exchanged zeolite Y and proposed a reaction mechanism where NO and NH₃ are coadsorbed on Cu²⁺ to initiate the cycle.⁷⁴ However, the poor hydrothermal stability of the large pore zeolite halted progress, as the zeolite would degrade under reaction conditions and become inactive. Iwamoto first reported that metal exchanged zeolites allowed for the decomposition of NO into O₂ and N₂.⁷⁵,⁷⁶ Soon after, the technology was further devolved by understanding the same material could selectively catalyse NO into N₂ by using a hydrocarbon reductant.⁷⁶ Cu exchanged ZSM-5 and other zeolites were heavily researched for the abatement of NO by direct decomposition and using hydrocarbons as reductants, however their performance was not good enough to meet industrial requirements.⁷⁷,⁷⁸ The NH₃ de-NOₓ SCR processes using the Cu and Fe exchanged zeolites such as ZSM-5 and BEA developed in the 1980s and 1990s, showed a marked improvement upon prior vanadia based catalysts thanks to improved hydrothermal stability. However, they degrade at temperatures of about 500 °C and therefore catalytic activity is reduced (Fig. 3.1).⁷⁹ They also store significantly more NH₃ than vanadia catalysts which contributes to the formation of the undesirable product N₂O and the release of NH₃ into the atmosphere referred to as NH₃ slip. This led to lean NOₓ traps also called active NOₓ adsorbers being the preferred method of NO after treatment rather than SCR during this period.⁸⁰
Figure 3.1 | Conversion of NO\textsubscript{x} under steady state SCR conditions with 200 ppm NO and 200 ppm NH\textsubscript{3} for vanadia based catalyst and Cu and Fe exchanged ZSM-5. 79

At a similar time to the novel development of NH\textsubscript{3} de-NO\textsubscript{x} SCR using ZSM-5 and BEA, progress was being made in relation to the synthesis of small pore zeolites. 81 Zones et al. documented the first synthesis of SSZ-13, the high silica zeolite following the chabazite topology. It was Bull et al. in 2008 who initially reported that Cu-SSZ-13 had similar NO\textsubscript{x} conversion to the first iterations of de-NO\textsubscript{x} SCR technology using medium-pore zeolites, however Cu-SSZ-13 exhibited better resistance to hydrocarbon poisoning and increased hydrothermal stability. 82 Despite the acid form of SSZ-13 initially being investigated as a methanol to olefin catalyst, the Cu-exchanged form soon became the leading technology for de-NO\textsubscript{x} SCR using NH\textsubscript{3} as the reductant. 83 Kwak et al. compared the SCR performance of different zeolites after hydrothermal aging in 10 % H\textsubscript{2}O at 800 °C for 10 hours. It was found that Cu-SSZ-13 showed superior NO\textsubscript{x} conversion than medium and large pore zeolites such as Cu-ZSM-5, Cu-Y and Cu-Beta over a wide temperature range. (Fig. 3.2) These features quickly led to the first iterations of NH\textsubscript{3} de-NO\textsubscript{x} SCR being used in on-road automobiles in 2010.
Zeolites are well suited to be used as catalysts in general. They are cheap, non-toxic, hydrothermally stable up to high temperatures, and act as a molecular sieve leading to shape and size selectivity of molecules accessing the active sites.

Metal exchanged small pore zeolites, in particular Cu-SSZ-13 are currently the industry leading catalysts for NOx abatement, after their commercialisation in 2010.\textsuperscript{84,85} They show superior activity across all temperature ranges and a greater hydrothermal stability than large pore zeolites such as ZSM-5 and other older catalysts such as vanadia.\textsuperscript{75,86} Cu-SSZ-13 is the most studied zeolite for the selective catalytic reduction of NOx, and exhibits the best activity.\textsuperscript{87} It is based on the chabazite structure which has double 6 member rings (6MR) and 8 member rings (8MR) stacked in an AABBCCAA fashion with interlocking sloped 4 member rings (4MR) giving a pore opening of 3.8 Å (Fig. 3.3). The view in figure 3.3b is how most geometries of the zeolite, Cu active site and ligands are represented in the results section for the clearest view.

\textbf{Figure 3.2} | Conversion of NOx under steady state SCR conditions with 350 ppm NO, 350 ppm NH\textsubscript{3}, 14 \% O\textsubscript{2}, and 2 \% H\textsubscript{2}O with a balance of N\textsubscript{2} for different zeolite catalysts under a range of different temperatures.\textsuperscript{83}
Figure 3.3 | a) Unit cell of SSZ-13. The structure and stacking arrangement with the double six member rings, eight-member ring and the chabazite cage shown. b) The 8MR and connected 6MR are shown explicitly for better visualisation of the Cu active complex in subsequent results figures. Colour scheme for elements: dark grey=Si; red=O.

The pore size, which is governed by the number of O atoms in the ring, is a significant reason why the small pore zeolite Cu-SSZ-13 shows greater SCR performance than medium and large pore zeolites. Firstly, Cu-exchanged small pore zeolites exhibit a higher hydrothermal stability than Cu-exchanged large or medium pore zeolites. This can be attributed to destructive Cu/Al₂O₃ interactions at high temperatures which is suppressed more in small pore zeolites than large pore ones. Secondly, the aperture size of the pores control access to the active sites in the inner cages of the molecular sieve. Larger hydrocarbons, which can poison the catalyst, are excluded from small pore 8-MR zeolites whereas they can enter the cages of 10 and 12 ring large and medium pore zeolites reducing the SCR activity.

3.4 Synthesis and Ion-Exchange of Cu-SSZ-13
Zeolites are comprised of corner sharing SiO₄ and AlO₄ tetrahedral units which link together under different topologies to create the 253 unique frameworks known to date. The inclusion of Al into the framework creates a charge deficiency, which must be balanced by a cationic species for the zeolite framework to be stable. The location and the distribution of the Al within the zeolite framework influences the position of extra framework transition metals which provide the catalytic activity. Importantly, it is possible to have some level of
control of the Al distribution depending upon the synthesis techniques used. Lowenstein’s rule states that an Al arrangement corresponding to Al-O-Al or Al pairs is forbidden. Taking this into account, the local arrangement of the Al ions can be defined: when two Al ions are separated by 1 or 2 Si ions it is referred to as paired Al or 2Al sites and can exchange divalent complexes or ions, whereas when two Al ions are separated by 3 or more Si ions, it is referred to as isolated Al or 1Al sites, and only monovalent complexes or ion can be exchanged in its proximity. The chabazite unit cell has 36 distinct T-atoms (tetrahedral centres), but they are crystallographically identical, which means there is only one unique T-site in the unit cell. Therefore, in purely aluminosilicate SSZ-13 the arrangement of paired or isolated Al is the only parameter that governs the exchange of monovalent or divalent complexes as each T-site is part of a 4-6- and 8-member ring.

Depending on the synthesis technique and method, the Al distribution and therefore the valency of the exchanged active species can be subtly controlled. The favoured synthesis method for low silica zeolites where the silica to alumina ratio (SAR) < 8 is the recrystallisation of low silica FAU zeolite into CHA using N,N,N-trimethyl-1-adamantylammonium (TMAda⁺). The interconversion is driven by the fact both FAU and CHA share the double-6MR unit, and that TMAda⁺ occupies the whole of the CHA cavity allowing the tetrahedral units to crystallise in the chabazite topology. Synthesis from a FAU starting point for low silica zeolites allows for a high proportion of paired Al sites which will be occupied by divalent complexes, as expected from the high Al content. Other routes to produce low silica SSZ-13 in the absence of SDAs tend to give extra-framework Al. As NMR shows fewer protons compared to Al, and the number of protons can vary widely even under identical synthesis.

Direct hydrothermal techniques are typically used for the synthesis of high-silica zeolites. Molecular precursors of Al such as Al₂O₃, Al(OH)₃ or NaAlO₂ are used, whereas Si precursors are colloidal silica, fumed silica or tetraethyl orthosilicate in the presence of either TMAda⁺ and Na⁺ in hydroxide media; TMAda⁺ in hydroxide media; or TMAda⁺ in fluoride media, giving different SARs of 10-65, 15-30 or 10 to ∞ respectively. Furthermore, high silica SSZ-13 can also be synthesised from dealuminated FAU zeolites in the presence of benzyltrimethylammonium cations (BTMA⁺).
It is possible to gain some level of synthetic control over SSZ-13 by using different types of media, which can control the location and type of Al.\textsuperscript{96,99} For example, when TMA\textsuperscript{+} and Na\textsuperscript{+} are used together in hydroxide media at SAR=10-65, the resultant SSZ-13 catalyst exhibits a high percentage of framework Al with Al/H\textsuperscript{+} near unity. Whereas, if only TMA\textsuperscript{+} in hydroxide media there is also high Al framework incorporation, but amorphous phases are obtained at high Al content (SAR<10).\textsuperscript{94} Di Iorio et al. show that it is possible to control the arrangement of Al ions between paired and isolated in SSZ-13 distributions within the framework even at a fixed elemental condition.\textsuperscript{94} SSZ-13 (SAR=15-30) where predominately isolated Al samples can be crystallised in hydroxide media with only TMA\textsuperscript{+}, showed by their inability to exchange divalent species such as Cu\textsuperscript{2+} and Co\textsuperscript{2+}. However, the simple addition of Na\textsuperscript{+} to the zeolite crystallisation medium with every other parameter consistent, gives SSZ-13 zeolites with paired Al content, which increases linearly with the amount of Na\textsuperscript{+} used in the crystallisation, and these samples can now exchange divalent species.

Cu\textsuperscript{2+} can be exchanged into SSZ-13 and will reside in the zeolite pore cavities, cages and channels rather than in the actual framework and is referred to as extraframework. Due to the negligible de-NO\textsubscript{x} SCR activity of H-SSZ-13, it is evident that Cu in some form is the catalytically active centre in Cu-SSZ-13.\textsuperscript{100} The divalent Cu\textsuperscript{2+} exchanges at paired Al sites, which balances the double negative charge and is commonly referred to as Z\textsubscript{2}Cu. However, at the single Al site Cu\textsuperscript{2+} cannot exchange as an isolated species due to the charge imbalance, therefore an additional negatively charged species must be present in the proximity of Al and Cu\textsuperscript{2+}. This nomenclature will be used throughout the thesis. Furthermore, a Cu\textsuperscript{+} ion exchanged in proximity to an isolated Al ion is referred to as ZCu\textsuperscript{+}, and Cu\textsuperscript{+} exchanged in proximity to paired Al and a charge balancing NH\textsubscript{4}\textsuperscript{+} ion the active site is referred to as ZCu-Z/NH\textsubscript{4}\textsuperscript{+}. When referring to a Cu ion which undergoes a redox cycle in proximity to either isolated or paired Al the active site is referred to as 1Al and 2Al sites respectively. It is now accepted that the additional charge compensating species is a hydroxide ion forming (CuOH)\textsuperscript{+} complex commonly referred to as ZCuOH.\textsuperscript{93,94,101} Over a range of Cu loadings Cu-SSZ-13 can contain both Z\textsubscript{2}Cu and ZCuOH, which can make precise characterisation of the active site and deducing the mechanistic details difficult as both species can contribute to the catalytic activity and participate in the reaction.\textsuperscript{92,93,101–103}
Aqueous ion-exchange of Cu into SSZ-13 was used to prepare the first copper exchanged de-NO\textsubscript{x} SCR catalyst.\textsuperscript{75,104,105} The exchange properties of SSZ-13 were first used as far back as the 1940s for the separation and exchange of aqueous ions and is now extensively used in filtration and purification.\textsuperscript{106–109} Upon ion-exchange, in order to control the amount of copper incorporated into the zeolite the molarity of the copper solution is changed, and is independent of the Cu salt used such as: Cu(CH\textsubscript{3}CO\textsubscript{2})\textsubscript{2}, Cu(NO\textsubscript{3})\textsubscript{2}, CuCl\textsubscript{2}, CuSO\textsubscript{4}, whereas both temperature and pH of the ion-exchange solution can affect the speciation of the Cu ion. For example, at high temperatures the formation of unwanted Cu oxide clusters is promoted. Furthermore, at low Cu loadings (Cu wt % < 3 %) only isolated Cu species (Z\textsubscript{2}Cu or ZCuOH rather than clusters) are obtained.\textsuperscript{76,100,104,107} However at higher Cu loading (Cu wt % > 4 %) and high silica zeolites (SAR = 4.5), or in the presence of amines at high pH values (>5) Cu oxide clusters have been observed after intercalation.\textsuperscript{100,110}

Aqueous ion-exchange is an effective and simple method to exchange a controlled amount of Cu into zeolites, however one needs to take caution as intercalation into SSZ-13 with different parameters and conditions can give different Cu species. Solid state ion exchange (SSIE) and one-pot synthesis methods are alternative ways to obtain Cu-SSZ-13. SSIE works by physically mixing a protonated zeolite with a bulk Cu salt such as CuF\textsubscript{2}, CuCl\textsubscript{2}, CuO or Cu\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} and then heating to high temperature above 900 K.\textsuperscript{111,112} It is proposed that the Cu precursor is oxidised into CuO that is then able to migrate through the zeolite and then undergoes acid-catalysed dehydration at a Brønsted acid site to give an isolated Cu\textsuperscript{2+} site.\textsuperscript{113} However, recently techniques have been developed which require lower temperatures for SSIE. NH\textsubscript{3} assisted SSIE allows Cu exchange from CuO precursors into SSZ-13 zeolites at temperatures under 523K.\textsuperscript{114} Ammonia solvates Cu\textsuperscript{+} as [Cu\textsuperscript{+}(NH\textsubscript{3})\textsubscript{2}]\textsuperscript{+} after it has been reduced from CuO, and is more mobile through the zeolite compared to aqueous conditions therefore allowing for easier ion exchange. In general, aqueous ion exchange is more commonly used and is the method of choice for industrially produced Cu-SSZ-13 samples as SSIE even NH\textsubscript{3} assisted requires high temperatures which is more expensive than the lower temperature aqueous route.\textsuperscript{115}

One-pot synthesis methods allow for Cu-SSZ-13 to be synthesised in one step by using a SDA agent that contains copper. Cu-tetraethylenepentamine (Cu-TEPA) can be used as a SDA in hydroxide media for one-pot synthesis, however this method only gives high Al Cu-SSZ-13
(SAR=4-8), but if TMAda⁺ is also included the Al content can be reduced (SAR>10). In order to obtain isolated Cu species the organic TEPA complex must be burnt off under high temperatures. In addition, Cu-SSZ-13 synthesised by one-pot methods contains a high amount of Cu (up to 10 wt % Cu), therefore, to avoid the formation of CuO the zeolite must be washed in HNO₃ or NH₄NO₃ to remove excess Cu.

To summarise, the Al distribution is controlled by the exact synthesis method and conditions used. The SAR, Cu content, percentage of extra-framework Al and the proportion of paired to isolated Al are all parameters affected by the choice of synthesis method, SDA and media used. The one-pot synthesis method with Cu-TEPA only allows a small range of SAR and Cu content compared to the use of TMAda⁺, however Cu-TEPA is cheaper than TMAda⁺. Also, post-synthesis treatment is still required to produce an operational catalyst making the one pot synthesis method not as efficient. Therefore, no discernible advantage is gained from using the one pot method over hydrothermal crystallisation in the presence TMAda⁺, where the SAR and Al distribution has a greater amount of control. To obtain high Al SSZ-13 (SAR < 8) conversion from FAU zeolite in the presence of TMDad⁺ is used. This gives a random distribution of Al but as the content is high a mainly paired Al is expected, however, a significant amount of extra-framework Al will also be present. Using a hydroxide media containing a mixture of TMAda⁺ and Na⁺, high silica zeolites (SAR > 10) can be formed. Changing the ratio of TMAda⁺ and Na⁺ allows for the subtle control of paired Al and isolated Al between 0 % and apparent random Al distribution which corresponds to 18 % paired Al. Increasing Na⁺ gives more paired Al. To achieve a high silica content (SAR up to infinity) fluoride media with TMAda⁺ can be used, where exclusively isolated Al will form. To incorporate Cu into the framework either aqueous or solid-state ion exchange can be used with similar end results, but with aqueous being the more widely used of methods and the speciation of Cu will depend on the Al exchange site. Therefore, it is essential to understand the Al arrangement determined by the synthesis method to give a clear understanding of the Cu²⁺ speciation which will have a bearing upon the SCR reaction.
3.5 Characterisation of Cu-SSZ-13

Given the industrial importance of Cu-SSZ-13 as the de-NOₓ SCR catalyst, it has been probed using a variety of techniques. Interpretation of results is difficult given the variability of an environment as function of synthesis and operating conditions. In this section the most important and relevant data from experiments from the literature will be summarised.

Solid state catalysts can be investigated by ex-situ or in-situ techniques, i.e. under non-catalytic or catalytic conditions respectively. The aim is to understand the nature of the active sites, the coordination chemistry and reaction mechanism, which will assist in the building of a structure-activity relationship to understand how the structure and the controllable parameters of the catalyst affect the reaction. We can subsequently tweak the controllable parameters of the catalyst with rational design in mind, to improve the conversion of NO and selectivity toward N₂ and H₂O.

Since the advent of the commercial Cu-SSZ-13 de-NOₓ SCR catalysts there has been an extensive literature focus upon the characterisation of the catalyst under a range of different conditions. Investigations have been carried out under different conditions and environments such as ambient temperatures and standard atmosphere; high temperature oxidative, or inert conditions; SCR conditions; or the use of probe molecules such as NO and NH₃. These different conditions are used to gain information about the catalyst from multiple perspectives and to fully understand how and why the catalyst changes in different environments and how this affects the reaction parameters under different conditions relative to reaction conditions.

Furthermore, computational, experimental and spectroscopic techniques are used in conjunction to deduce the nature and location of the Cu active site within the chabazite framework and to investigate the reaction mechanism. Computational techniques give a different level of insight compared to experiment, essential for the study of the de-NOₓ SCR reaction with Cu-SSZ-13 as the catalyst. Atomic level control given by computational techniques allows one to probe microscopic details such as the energies of different configurations, the local environment of the active site, coordination numbers and geometries, and the spin states, which can help elucidate the mechanism of redox reactions. Experimental and spectroscopic techniques do not permit the level of control that computational techniques can, as variables can be controlled very precisely, whereas most
experimental and spectroscopic techniques give a larger scale overall view, especially during the evolution of a reaction therefore complicating analysis.

The timescales at which key reaction intermediates are present makes their detection a rather difficult task. Therefore, high level and complex experimental techniques must be employed in order to detect their presence. Computational techniques are also extensively used in order to investigate intermediate species further and corroborate experimental and spectroscopic findings.

3.5.1 X-Ray Diffraction

X-Ray diffraction (XRD) techniques can provide structural information about a material such as the chemical composition, crystallographic structure, and physical properties. However, it operates in such a way that the average of all ionic locations and properties are taken, meaning, for example XRD is not well suited for distinguishing $Z_2$Cu from ZCuOH sites and results may be difficult to rationalise alongside other techniques as Si and Al are indistinguishable from one another. This also means understanding the order and disorder of a material is challenging. For example, the location of Cu$^{2+}$ synthesized using the hydroxide route (SAR=18, Cu/Al = 0.5) and after treatment in 10 % O$_2$ at 500 °C is revealed to be in the 6MR using Rietveld refinement of the XRD whereas EXAFS analysis shows ZCuOH species in the 8MR. It is likely that distribution of both sites is present with the sample. Cu-SSZ-13 (SAR = 6, Cu/Al = 0.35) prepared by FAU conversion and treated in air at 435 °C XRD shows three-fold Cu coordination situated in the 6MR, this could be analogous to the $Z_2$Cu site, agreeing with other techniques. Furthermore the same study shows that the hydrothermal stability of SSZ-13 is significantly increased after intercalation of Cu$^{2+}$ compared to that of the H-form of SSZ-13.

In-situ XRD can in fact be used with Rietveld refinement to follow and understand the degradation of Cu-SSZ-13 under hydrothermal ageing by plotting the average electron density over a range of temperatures to see how the average structure changes over time. It is found that the c lattice parameter contracts significantly during aging in 10 % H$_2$O over a range of high temperatures. It is also observed that the Cu$^{2+}$ ion moves from the face of the 6MR to the centre of the 6MR. The authors propose that the contraction in c lattice parameter drives the movement of Cu$^{2+}$ into the centre of the hexagonal prism formed by two 6MR which
induces the collapse of the chabazite framework. After 6 h and 14.4 h of aging only 50 % and 30 % crystallinity remain respectively and the migration of Cu from the face to the centre of the 6MR can be seen in the electron density plot (Fig. 3.4).

![Time resolved XRD patterns at different time across the zeolite aging and the subsequent electron density distribution maps. Colour scheme for elements: blue=Si; red=O; light yellow=Cu](image)

3.5.2 Electron Paramagnetic Resonance

Electron paramagnetic resonance (EPR) is a method for exclusively studying species containing unpaired electrons. Therefore, it is sensitive to Cu$^{2+}$ and NO but not Cu$^{+}$ or other species involved in the SCR reaction. EPR can probe the local coordination environment and magnetic coupling to other species. EPR spectra collected under ambient conditions for low Cu loaded Cu-SSZ-13 sample are consistent with other experimental techniques and show a single feature consistent with aqueous \([\text{Cu}^{2+}(\text{H}_2\text{O})_6]^{2+}\).\textsuperscript{122–124} Interestingly, as the Cu content is increased additional features are evident in the EPR spectrum.\textsuperscript{125} These features are assigned to dipolar interactions between solvated Cu$^{2+}$ complexes implying they are interacting and are therefore mobile throughout the zeolite. The EPR spectra also change as a function of temperature at a fixed Cu loading of 0.378 wt %, where features are assigned to dipolar interactions between Cu$^{2+}$ ions (Fig. 3.5). These results could also imply the interaction between two distinct Cu complexes signifying the possible existence of dimeric or multinucleic Cu complexes at high loadings and/or low temperatures.\textsuperscript{124} In addition, the EPR spectra of different Cu containing zeolites (BEA, ZSM-5) under ambient conditions show differences to that of Cu-SSZ-13 which have been interpreted as further evidence of mobile
The difference between ZCuOH and Z\textsubscript{2}Cu sites can be observed indirectly in samples synthesized to contain a majority of one site. Upon dehydration the sample containing mainly ZCuOH loses some of the Cu\textsuperscript{2+} signal whereas the Z\textsubscript{2}Cu does not. This is evidence of more than one Cu\textsuperscript{2+} species with different reducibility in ZCuOH and Z\textsubscript{2}Cu where ZCuOH could be subject to autoreduction (reduction of Cu\textsuperscript{2+} without the use of a reducing agent).\textsuperscript{126}

![Figure 3.5](image-url) | The EPR spectra of Cu-SSZ-13 during dehydration over different temperatures. \textsuperscript{124}

### 3.5.3 UV-Vis Spectroscopy

UV-visible spectroscopy targets the electronic transitions between occupied and unoccupied valence states. This gives detailed spectra which probe the d states of transition metal ions and can reveal features of the specific chemical environments.

Spectra produced for a range of different Cu/Al ratios (0.02-0.2) for a consistent SAR=5 at ambient conditions, all show a broad Cu\textsuperscript{2+} d-d transition consistent with the signal of aqueous \([\text{Cu}\textsuperscript{2+}(\text{H}_2\text{O})_6]\)\textsuperscript{2+} and a main and shoulder feature from ligand to metal transfers assigned to a transition from oxygen framework species (O\textsubscript{fw}) to Cu d states at 35000 and 45000 cm\textsuperscript{-1} (Fig. 3.6).\textsuperscript{125,127} The occurrence of both \([\text{Cu}\textsuperscript{2+}(\text{H}_2\text{O})_6]\)\textsuperscript{2+} and O\textsubscript{fw} signatures and the width (6000-17000 cm\textsuperscript{-1}) of the Cu\textsuperscript{2+} d-d transition features implies a dynamic coordination environment of the Cu complex under ambient conditions, where Cu is mobile and coordinates to multiple
different species. Furthermore, at a Cu/Al ratio of 0.35, shoulder features appear at 20000 and 32000 cm$^{-1}$ that have been assigned to Cu oxide formation.\textsuperscript{127} 

After dehydration in air at 500 °C Cu-SSZ-13 with SAR=5 and Cu/Al > 0.31 UV-vis spectra give high energy transitions around 20000 and 32000 cm$^{-1}$, which are assigned to Cu oxides that do not appear under ambient conditions. This suggests that Cu oxides can be produced after dehydration.\textsuperscript{125}

UV-vis spectroscopy struggles to resolve Z$_2$Cu and ZCuOH. There are no features in the spectrum from samples containing mainly ZCuOH which distinguish ZCuOH from Z$_2$Cu.\textsuperscript{126} It is suggested that ZCuOH is UV-visible silent due to degeneracies caused by the ZCuOH trigonal environment.

![UV-Vis spectra for a range of Cu-SSZ-13 samples with varying Cu/Al ratios collected under ambient conditions. The H-SSZ-13 spectrum is subtracted from the Cu-SSZ-13 spectra.\textsuperscript{126}](image)

**Figure 3.6** | The UV-Vis spectra for a range of Cu-SSZ-13 samples with varying Cu/Al ratios collected under ambient conditions. The H-SSZ-13 spectrum is subtracted from the Cu-SSZ-13 spectra.\textsuperscript{126}

3.5.4 X-Ray Spectroscopy

X-ray absorption (XAS) spectroscopy probes the oxidation state and coordination environment of the active Cu complex. Core electrons are excited by tuneable x-rays, which
produces an adsorption spectrum dependent upon the local environment of the absorbing complex.

Under ambient conditions X-ray near edge spectra (XANES) show characteristic pre-edge features near 8978 eV and 8980 eV of aqueous Cu$^{2+}$ ions which are the only feature present in XANES spectra for Cu exchanged SSZ-13 under these conditions. This holds true irrespective of synthesis route. At higher Cu loadings (SAR = 5 and Cu/Al ratio = 0.31 and 1.6) however, an additional shoulder near 8985 eV appears, which is assigned to unwanted Cu oxides in regards to the SCR reaction. Extended X-ray absorption fine structure (EXAFS) can give an additional level of information compared to XANES, including the first and sometimes second neighbours distances, coordination numbers and the spatial location of the Cu complex. Under ambient conditions Cu-SSZ-13 samples at Cu loadings where Cu oxides do not form, exhibit spectra nearly identical to aqueous [Cu$^{2+}$(H$_2$O)$_6$]$^{2+}$ complexes and to that of Cu-ZSM-5 and Cu-BEA zeolites in the same conditions. Furthermore, Cu-SSZ-13 samples show Cu 4-fold coordination in the first solvation shell and second shell solvation which does not show any obvious order, no matter the synthesis route, which is indicative of a [Cu$^{2+}$(H$_2$O)$_6$]$^{2+}$ Jahn-Teller distorted complex in aqueous environment.

Under high temperature oxidising conditions (20-50 % $O_2$) XANES spectra show an additional shoulder near 8.985 keV compared to ambient conditions, irrespective of whether the samples contain majority $Z_2$Cu or ZCuOH species. Interestingly, the shoulder is observed at marginally different positions and is thought to be caused by Cu in square planar or distorted planar geometries and shows features and intensities consistent with Cu-O bonds. The characteristic Cu$^+$ 8.983 keV edge is not present in any of these samples meaning the majority of Cu is present as Cu$^{2+}$ in high temperature oxidising conditions. Paolucci et al. show that EXAFS performed under high temperature oxidising conditions are markedly different for samples prepared to contain mainly ZCuOH or $Z_2$Cu (Fig. 3.7). The authors reason the spectra differ because the samples which contain mainly ZCuOH are best fit to three-fold coordination DFT models, whereas samples containing predominantly $Z_2$Cu are better fit to four-fold DFT models as they predict these coordination environments as the most likely Cu speciations.
Figure 3.7 | XANES and EXAFS spectra collected over 1Al and 2Al containing Cu-SSZ-13 samples after treatment in 20% O₂ at 673 K and Cu-Si/O/Al ab initio molecular dynamics (AIMD) RDFs. 

Under high temperature inert or vacuum environments there is a clear difference between the susceptibility to autoreduction between samples containing mainly Z₂Cu or ZCuOH. Cu-SSZ-13 (SAR = 13.1 Cu/Al = 0.44; SAR = 12 Cu/Al = 0.44) prepared with fluoride media is expected to contain mainly ZCuOH and shows the characteristic 8.983 keV XANES edge which is assigned to the Cu⁺ 1s → 4p transition upon vacuum treatment at 400 °C. In addition, as the Cu⁺ feature increases, the Cu²⁺ feature decreases and the coordination number of the first shell is inferred to decrease from three to two. This implies that during autoreduction ZCuOH loses OH and is reduced to ZCu. This is in contrast to Cu-SSZ-13 samples, (SAR=5 Cu/Al=0.08) which contain mainly Z₂Cu, as they exhibit no change compared to that under high temperature oxidising conditions and the characteristic Cu⁺ 8.893 keV feature cannot be detected.

More information can be gained about the SCR reaction when the catalyst is exposed to probe molecules and conditions analogous to the SCR environment and X-ray absorption, or emission (XES) spectroscopy is performed. XES measures the emitted photons from the sample after the recombination of electrons with sufficient spectral resolution to analyse the effect of the chemical environment on the X-ray energy.
After exposure to NH₃ and O₂ at 200 °C, XANES spectra show a 20 % reduction of Cu²⁺ to Cu⁺ for materials synthesised via the fluoride route, (TMA-da⁺ or FAU conversion) whereas 50 % of Cu is reduced on samples synthesised via the hydroxide route.⁹³,¹⁰²,¹³⁵,¹³⁶ The reason for XANES and XES showing mixed oxidised and reduced Cu at different amounts from the different samples is currently unresolved but is likely related to the presence of different Cu sites. EXAFS spectra can be fitted to four-fold coordinated Cu²⁺ without a defined second shell structure.⁹³,¹³⁵,¹³⁷

In ammonia and helium atmosphere, NH₃ alone acts as a stronger reducing agent than NH₃ + O₂ for samples containing predominantly ZCuOH as evidenced by XES.¹³⁴ XES indicates linear \([\text{Cu}^+(\text{NH}_3)_2]^+\) as the most prominent Cu⁺ containing species after reduction.¹³⁴ The mechanism for reduction of Cu²⁺ by only NH₃ is not well understood, but it could be a result of autoreduction, especially on samples containing mainly ZCuOH.

XANES spectra have been collected for a range of samples containing Z₂Cu, ZCuOH and a mixture of both under dosing of NO and NH₃. All samples exhibit complete reduction of Cu²⁺ to Cu⁺ shown by the emergence of the 8.983 keV feature and is very similar to that of aqueous linear \([\text{Cu}^+(\text{NH}_3)_2]^+\).¹³⁵ The reduction occurs much faster than Cu²⁺ reduction by either NH₃ alone or NH₃ and O₂, over any Cu-SSZ-13 catalyst sample, therefore signifying that NO and NH₃ together is the best reducing environment. DFT theory can elucidate the mechanism by which NO and NH₃ reduce Cu²⁺ to Cu which will be discussed later.⁹³

Under standard SCR conditions analysis of data becomes more difficult as the data is more convoluted. SCR conditions are represented as 10 % O₂ and a stoichiometric amount of NO and NH₃ of the order 300-1000 ppm, to model exhaust gas conditions as closely as possible. XES spectra collected under standard SCR conditions at 200 °C are very similar for catalysts prepared in different ways in order to obtain either ZCuOH, Z₂Cu and a mix of sites catalyst samples. XANES and EXAFS reveal a 50/50 mix of Cu²⁺ and Cu⁺ where an average coordination number of three is found at 200 °C, which would be consistent with a mixture of 4-fold coordinated Cu²⁺ species and 2-fold coordinated Cu⁺ species.¹⁰²,¹³⁶,¹³⁸,¹³⁹ The results suggest that neither the oxidation or reduction half cycle is rate limiting, which implies the highest activation barrier for each half cycle are similar. Under fast SCR conditions with NO₂ as oxidant, XAS analysis shows 100 % Cu²⁺ during steady-state catalysis, suggesting that NO₂ is able to more effectively re-oxidise Cu⁺ than is O₂ alone at these conditions.¹⁴⁰ XES spectra also
find two oxidation states for Cu, and a Cu-O feature which evolves into a Cu-N feature under SCR conditions, which could be related to SCR mechanistic considerations such as the conversion of OH to H₂NNO or equilibrium considerations such as O\textsubscript{fw} (O\textsubscript{fw} refers to an oxygen atom in the framework) or H₂O species competing with NH₃ for adsorption on to Cu sites.

At higher temperatures of 400 °C, XAS spectra collected under SCR conditions show only Cu²⁺ spectral features as the Cu signal disappears, while the average coordination number increases to 4 from 3, regardless of the catalyst sample or synthesis route. At higher temperatures (> 300 °C) under SCR conditions only Cu²⁺ is detectable whereas at lower temperatures (< 200 °C) under SCR conditions both Cu²⁺ and Cu⁺ are detectable in equal proportions. This could indicate that at higher temperatures there is a change in reaction route or active site, which makes the oxidation half cycle rate limiting. Analysis shows that at elevated temperatures Cu²⁺ is likely bound to the framework in the 6MR as the XANES and EXAFS are similar to that of calcined Cu-SSZ-13. At temperatures of 300-400 °C XANES and EXAFS results suggest that NH₃ solvation is lost and coordination of Cu to O\textsubscript{fw} species increases corresponding to an increase in SCR activity, therefore showing the coordination environment and oxidation state depend heavily upon the temperature and have a bearing on the SCR reaction.

3.5.5 Vibrational Spectroscopy
Vibrational spectroscopy techniques include infrared (IR) and Raman spectroscopy. The spectra produced are due to changes in the vibrational modes of the molecules or bonds in the sampled due to adsorption, emission or reflection caused by interaction with radiation, which can be measured with a spectrometer. IR and Raman techniques are similar; however, they are sensitive to different vibrational modes. IR active vibrational modes result from a changing dipole moment and adsorption of IR radiation whereas Raman active modes result from a change of polarizability and by scattering of light, (which can be IR, UV or visible frequencies) by vibrating molecules. Chemical functional groups give certain fingerprints or signatures upon interaction with certain frequencies of light which are used to probe and deduce the nature of the sample. For example, the T-O-T vibrations have characteristic signatures at approximately 800 and 1030 cm⁻¹ and can be used to identify Cu²⁺ exchanged into zeolites as these spectral features are intensified upon interaction with Cu²⁺. This
increase in strength of these bands upon increasing temperature is evident signifying dehydration of Cu-SSZ-13 and the subsequent coordination of Cu$^{2+}$ to the framework.$^{128}$

Under ambient conditions, features in the IR spectrum are present at 1630 cm$^{-1}$, then upon heating to 400 °C these features disappear and have been assigned to the H-O-H bending modes of Cu bound water, which shows the dehydration of the catalyst. In addition, characteristic broad bands of various O-H stretching at ~2200 to 3800 cm$^{-1}$ are observable and assigned to Brønsted acid sites,$^{141}$ silanol$^{142}$ and H$_2$O bound to the zeolite framework$^{128}$

H-X stretching modes at 3550-3750 cm$^{-1}$ can be used to probe the nature of a dehydrated Cu-SSZ-13 catalyst as no water exhibiting O-H stretching is present to mask any signals from other species. After dehydration, characteristic signatures of Brønsted acid sites (Si-OH-Al) at 3585 and 3605 cm$^{-1}$ and ZCuOH at 3655 cm$^{-1}$ become visible.$^{93,101,125,134,141,143}$ In fact, the signature of ZCuOH can be tracked in correlation with the proportion of exchanged Cu. Interestingly, for a Cu-SSZ-13 sample where SAR=15 the ZCuOH signature at 3655 cm$^{-1}$ is absent until Cu/Al=0.1 then increases linearly, which could indicate that Z$_2$Cu is populated before ZCuOH upon ion-exchange. There is further evidence of a second Cu environment of different speciation of that to Z$_2$Cu when IR spectra are collected on Cu-SSZ-13 samples with SAR=6 and Cu/Al ratio of 0.1-0.5. Z$_2$Cu sites are responsible for the perturbation of T-O-T band at 890 cm$^{-1}$ and are fully occupied at Cu/Al=0.2. Beyond this Cu loading level, a new band at 940 cm$^{-1}$ is appears and its intensity increases with increasing Cu loading (Fig. 3.8). This distinct feature is proposed to be due to T-O-T perturbations caused by ZCuOH rather than Z$_2$Cu.$^{86}$ Importantly, both the 940 cm$^{-1}$ and 890 cm$^{-1}$ bands are present in commercial samples of Cu-SSZ-13 showing both ZCuOH and Z$_2$Cu are present in detectable proportions.
Figure 3.8 | DRIFT spectra collected over Cu-SSZ-13. a) oxidation at 400°C b) reduction in H₂ at 200 °C. Showing the presence of ZCuOH as well as Z₂Cu for samples with Cu loading >0.2 Cu/Al (black and pink in a). 86

Raman spectroscopy is sensitive to low frequency vibrational modes, which are not possible to observe in IR spectroscopy due to the different selection rules. Raman spectroscopy is a technique less utilised for the study of Cu-SSZ-13 and the SCR reaction compared to IR, however the few studies performed reveal the existence of multiple Cu species. For Cu-SSZ-13 samples prepared by one-pot synthesis methods at SAR=4.3 and Cu/Al ratios of 0.04 and 0.09 Raman spectroscopy finds only one band at 475 cm⁻¹, whereas for samples with higher Cu loading (up to Cu/Al ratio of 0.37) another band appears near 610 cm⁻¹. This feature is assigned to oxo-bridged Cu⁺ dimers. 132 Furthermore, this feature matches DFT simulated spectra of (CuO₂Cu)²⁺ and other spectroscopic observations, showing that at high Cu loadings Cu dimers are present in Cu-SSZ-13.¹¹⁷,¹⁴⁴

3.5.6 Temperature Programmed Reduction and desorption
Temperature programmed reduction (TPR) or temperature programmed desorption (TPD) can be used as a probe study to understand the number and types of active or adsorption sites in zeolites. For TPR, the catalyst is pre-prepared in order to remove as much water as possible before a mixture of H₂ and other inert gases are fed over the catalyst while monitoring how much H₂ is consumed as Cu is reduced from Cu²⁺ to Cu⁺ to Cu as a function of temperature. TPD is a method for observing the desorption of molecules from the pre-treated
catalyst which has adsorbed the probe molecule, as a function of temperature to understand the type of adsorption sites and their relative strengths.\textsuperscript{145}

H\textsubscript{2}-TPR reported by Kwak \textit{et al.} on Cu-SSZ-13 (SAR = 6, Cu/Al = 0.1–0.5) synthesized by FAU conversion shows that at 0.1 Cu/Al=0.1 there is only one peak at 340 °C in the TPR profile which corresponds to H\textsubscript{2} consumption (Fig. 3.9).\textsuperscript{86} This is consistent with the assumption that at these conditions only Z\textsubscript{2}Cu should be present. Samples at higher Cu/Al ratios do indeed show a second shoulder peak at 250 °C which increases as the Cu content does, also signifying the growing proportion of ZCuOH. This adds more evidence supporting that Z\textsubscript{2}Cu sites are occupied before ZCuOH upon Cu exchange.\textsuperscript{87} In addition, a sample synthesised to contain a majority of ZCuOH sites shows only one peak centred at 250 °C, also showing that ZCuOH is more easily reduced than Z\textsubscript{2}Cu.\textsuperscript{93} Evidence of Cu oxides forming at very high levels of Cu exchange is also evident as a peak at 230 °C is observed, as they are thought to more reducible than isolated Cu species.\textsuperscript{87,132} The dual site consumption of H\textsubscript{2} is also present on commercial catalysts during TPD showing that both Z\textsubscript{2}Cu and ZCuOH are present.\textsuperscript{146}

\textbf{Figure 3.9} | \textit{H\textsubscript{2}-TPR on calcined Cu-SSZ-13 showing the H\textsubscript{2} consumption profiles during heating with rate = 10 /1 C min\textsuperscript{-1}; total flow rate = 60 ml in 2 % H\textsubscript{2}/Ar. The different colours show the different Cu ion exchange level: 20 % (red), 40 % (green), 60 % (blue), 80 % (purple), and 100 % (black).} \textsuperscript{86}
TPD using ammonia as the adsorbate, can act as a titration to quantify the amount of both Brønsted and Lewis acid sites in zeolites and is a widely used technique, especially for quantification of Brønsted acid sites.\textsuperscript{147,148} \textsuperscript{1}NH\textsubscript{3} is the best probe molecule of choice for small pore zeolites such as SSZ-13 as larger molecular bases such as pyridine are unable to reach the chabazite cavity as the 8MR aperture is not large enough to allow them through.\textsuperscript{149–151} There are various different sites that NH\textsubscript{3} can adsorb onto making the deconvolution of TPD data for Cu-SSZ-13 difficult. NH\textsubscript{3} adsorbs to both Lewis and Brønsted acid sites, to any extraframework Al present and forms hydrogen bonds in a second solvation shell to more strongly bound NH\textsubscript{3} molecules, or NH\textsubscript{4}\. To understand the NH\textsubscript{3}-TPD on Cu-SSZ-13, it is helpful to first analyse the NH\textsubscript{3}-TPD on H-SSZ-13. The NH\textsubscript{3}-TPD profile for H-SSZ-13 exhibits two slightly overlapping peaks corresponding to the desorption of physisorbed NH\textsubscript{3} located in the large chabazite cavity, and the desorption of NH\textsubscript{3} from NH\textsubscript{4}\(^+\) leaving H\(^+\) Brønsted acid behind, at 450 K and 633 K respectively.\textsuperscript{152,153} Therefore, the convolution of the two peaks due to physisorbed NH\textsubscript{3} can mean it is difficult to quantify H\(^+\) sites. It is, however, possible to remove the physisorbed NH\textsubscript{3}, and NH\textsubscript{3} bound to Lewis acid sites by treatment in H\textsubscript{2} with 3 % water at 433K. Then, the remaining NH\textsubscript{3} is only present as Brønsted adsorbed NH\textsubscript{4}+ and the TPD profile only gives one peak clearly corresponding to desorption of Brønsted acid NH\textsubscript{3}.\textsuperscript{100,152}

Upon Cu exchange, additional features are visible in the subsequent NH\textsubscript{3}-TPD profile. Without a purge step or pre-treatment, a new intermediate temperature desorption feature is present in the NH\textsubscript{3}-TPD profile of Cu-SSZ-13, which overlaps with the both the high and low temperature features visible in the NH\textsubscript{3}-TPD profile of H-SSZ-1 (Fig. 3.10).\textsuperscript{153} These high, intermediate and low desorption features in the NH\textsubscript{3}-TPD profile of Cu-SSZ-13 (FAU conversion and high Al content) have been indexed to a three-site model using adsorption energies of -18.6, -137.8, and -149.0 kJ mol\textsuperscript{-1}.\textsuperscript{154} This was evidenced by the fact calorimetric measurements show that the adsorption energy for non-specifically adsorbed NH\textsubscript{3} is -19 kJmol\textsuperscript{-1}. The three-site DFT computed adsorption energy for NH\textsubscript{3} to Z\textsubscript{2}Cu, ZCuOH and the reduced ZCu site span the range of -120 to -140 kJ mol\textsuperscript{-1}, and the adsorption energy of NH\textsubscript{3} to a Brønsted acid site is calculated to be -151 kJ mol\textsuperscript{-1}, matching the energies of the three-site model. Therefore, the DFT model supports the assignment of the different features to each type of site.
Density Functional Theory Analysis

Density functional theory and other simulation techniques have been used to study metal exchanged zeolites and heterogeneous catalysis for well over 20 years. In principle, DFT can be used to predict the favoured locations, coordination environment and even spectroscopic signatures of exchanged species while also being able to simulate and calculate activation barriers for atomic level reaction steps.

The structure of the CHA framework is such that every T site is identical and is connected to a 4-6- and 8-member ring. Variation is introduced when Al is inserted into the framework. A Cu$^+$ ion charge compensates a single Al and is commonly referred to as ZCu. The favoured position of Cu$^+$ is in the 6MR with the 8MR being 50 kJ mol$^{-1}$ less stable and coordinates to two O$_{fw}$ atoms, consistent with Cu$^+$ coordination in other environments. When two Al species are present in a unit cell there is an increased amount of structural diversity and complexity available despite Lowenstein’s rule. Lowenstein’s rules states that Al pairs must be separated by at least one T site or at the second nearest neighbour position. The favoured configuration of exchanged Cu$^{2+}$ balanced by two Al species and with no additional ligands is
generally accepted to be such that Cu$^{2+}$ is located in the plane of the 6MR and is 100 kJ mol$^{-1}$ lower in energy that Cu$^{2+}$ occupying either the 4MR or 8MR, irrespective of Al distribution.$^{127}$ When Al distribution is considered, and Cu$^{2+}$ is situated in the 6MR it is found that an Al distribution of either 2NN or 3NN is 50 kJ/mol more stable than any other configurations, with a coordination number of 4 in a distorted square planar configuration (Fig. 3.11).$^{162,163}$ This configuration of Cu$^{2+}$ exchanged at the 6MR with either a 3NN or 2NN Al distribution is commonly referred to as $Z_2$Cu. If only 1Al is exchanged in proximity to Cu$^{2+}$ the excess charge on Cu$^{2+}$ is balanced by OH$^-$ and is commonly referred to as ZCuOH. This terminology will be used throughout this work.

![Figure 3.11](image)

**Figure 3.11** | different positions for Cu$^{2+}$ in SSZ-13. For (a–e), both Al atoms are found in the same unit cell, while sites (f–h) correspond separated Al. The energy is given in kJ/mol in the bottom right of each image. Colour scheme for elements: yellow=Si; light blue=Al; red=O; blue=Cu.$^94$
A previous study investigated the structure and energetics of adsorption and reaction at Cu active sites. The general trend of adsorption is that for every adsorbed molecule onto Cu one framework bond is displaced and the Cu complex is lifted out of the 6MR and into the CHA cavity, maintaining the four-fold coordination of Cu.\textsuperscript{128,164} In general, adsorption energies are reported as the difference in computed total DFT energies of the adsorbed model and the separate energies of the adsorbate and the adsorbent (equation 3.1)

$$E_a = (E_{\text{adsorbent}} + E_{\text{adsorbate}}) - E_{\text{system}}$$  \hspace{1cm} 3.1

Where $E_a$ is the adsorption energy, $E_{\text{system}}$ is the energy of the adsorption model after adsorption has taken place, $E_{\text{adsorbent}}$ is the energy of the adsorbate in a vacuum and $E_{\text{adsorbate}}$ is the energy of the system which is adsorbing.

For example, a single water molecule adsorbed onto Cu\textsuperscript{+} or Cu\textsuperscript{2+} sites gives an adsorption energy of between -70 and -90 kJ/mol using widely used functionals.\textsuperscript{93,136,140,165} Successive adsorption energies of H\textsubscript{2}O to either Z\textsubscript{2}Cu or ZCuOH are also within the range of -70 and -90 kJ/mol and results show that four-fold coordination is generally preferred, and that fully hydrated species are liberated from the framework as H\textsubscript{2}O successively displaces framework oxygen bonds.\textsuperscript{93} Since hydrated Cu complexes are free from the framework, it follows that Cu complexes could be mobile throughout the zeolite. The dynamics of Cu hydration in SSZ-13 were sampled using the semi empirical forcefield ReaxFF using 30 water molecules and both Z\textsubscript{2}Cu and ZCuOH sites, at a range of temperatures from 100 to 1000 °C for a 500 ps simulation.\textsuperscript{166} It was found that Cu ions detach from the zeolite framework and subsequently form hydrated Cu complexes at high temperatures and/or at long simulation times. Interestingly, it was observed that OH bridged transient dimers are formed from partially hydrated Cu complexes at higher temperatures and are more easily formed from ZCuOH species. Any conclusions drawn from the semi-empirical forcefield methods must be taken with caution as the method does not contain any electronic effects such as from d-orbital splitting or VDW forces and is parametrised from higher-level data sets. At very high temperatures of 900-1100 K it is also observed that Cu ions cross the 8MR and migrate into another CHA cavity over the 500 ps simulation, signifying this could be a common event over macroscopic timescale. Paolucci et al performed ab initio molecular dynamics simulations on both Z\textsubscript{2}Cu and ZCuOH sites for both dehydrated and hydrated complexes. By plotting the volume of space visited by the Cu ion over the MD run it was estimated that hydration
increases the mobility of Cu ions at either 1Al or 2Al sites by approximately 10 times (Fig. 3.12). These results from both ab initio and semi-empirical methods indicate that H₂O solvates and mobilises Cu²⁺ ions throughout the zeolite cages.

![AIMD simulation in Cu-SSZ-13](image)

**Figure 3.12** | AIMD simulation in Cu-SSZ-13. The grey points show the Cu positions visited over the 90 ps simulation at 298K. The zeolite framework is shown for ease of visualization but was unconstrained during dynamics. Colour scheme for elements: yellow=Si; green=Al; red=O; grey dots=Cu

The solvation shell around Cu in SSZ-13 is seen to be a dynamic and shifting environment in the presence of water only. Therefore, it can be implied that the level of complexity and interplay between molecules is likely to increase when the more strongly adsorbing ammonia is involved, or standard SCR conditions are considered. To understand the likely combination of ligands in the coordination sphere of the Cu exchange site under certain conditions Paolucci et al. investigated the most favourable species present under specified conditions, which can be represented on phase diagrams. For example, under wet oxidising conditions Cu can exist as Cu²⁺ or Cu⁺ and can be coordinated to any number of H₂O, OH⁻ or even O₂ in any configuration. Using a free energy, first principle’s analysis and entropy calculations it is possible to plot a phase diagram of the most favourable combination of ligands under certain temperatures and partial pressures of gases. Geometries were generated by first performing a short AIMD run then a geometry optimization using the HSE06 functional. This
method is not guaranteed to find the lowest energy configuration of ligands and bonding conformations around the Cu complex, but it can provide a good guess and a configuration which is likely to be lower than most. The analysis was performed on both 1Al and 2Al sites and the results show that at 25 °C and conditions representing 20 % O₂ and 2 % H₂O the lowest energy species are fully hydrated Z₂Cu and ZCuOH, fully liberated from the framework, where the ZCuOH has one fewer water molecule coordinated to it than Z₂Cu. (Fig. 3.13) This confirms the theory that 1Al sites exist as ZCuOH. At higher temperatures the ground state configuration is calculated to be completely dehydrated, free of all water molecules and bound to 4 framework oxygen species in the 6MR for both Z₂Cu and ZCuOH. Therefore, this thermodynamic model predicts Cu to be in its 2⁺ oxidation state across all wet oxidising conditions and that the amount of hydration changes as a function of temperature, while keeping four-fold coordination to oxygen containing species. In addition, the model predicts that ZCuOH is subject to auto reduction via loss of OH, but Z₂Cu is not.
Figure 3.13 | The free energy of formation for CuHxOy species at 298 K, 2 % H₂O, 20 % O₂ (left), and at 673 K, 2 % H₂O, 20 % O₂ (right) on both the 2Al (Z₂Cu) and 1Al (ZCu) sites.

It is established that commercial Cu-SSZ-13 exhibits Cu exchanged in proximity to both single and paired Al sites referred to as ZCuOH and Z₂Cu respectively. Therefore, it is interesting to consider the energetic preference for Cu²⁺ to exchange at either of these sites. Using supercell DFT calculations it is possible to calculate the hypothetical exchange energy of the two sites modulated by a water molecule:

\[ Z_2Cu + Z/H + H_2O \rightarrow ZCuOH + 2Z/H \]

Using the HSE06-TSvdW functional this energy is calculated to be 66 kJ/mol and corresponds to the offset in free energy between 1Al and 2Al sites at 673 K. This result strongly implies that 2Al sites as Z₂Cu will be populated before 1Al sites as ZCuOH upon Cu²⁺ exchange into SSZ-13 as also shown by various other spectroscopic and experimental techniques. If it is assumed that Al randomly populates T sites subject to Löwenstein's rule, it is subsequently...
possible to deduce the variation in concentration of \( Z_2Cu \) to \( ZCuOH \) as a function of Si/Al and Cu/Al ratios (Fig. 3.14). The white line denotes the Cu/Al ratio where all 2Al or paired sites are fully occupied by \( Cu^{2+} \) and the colour corresponds to the ratio of Cu present as \( ZCuOH \), while the white dots are synthesised samples of Cu-SSZ-13 and match the theoretical result. It is important to consider the synthesis route as established in section 2.4 because different methods promote different Al distributions. This result implies that over a wide range of both Si/Al and Cu/Al ratios both sites should be present within Cu-SSZ-13, but under specific Al and Cu content and synthesis conditions it is possible to control the type of site which is in the majority.

![Figure 3.14](image)

**Figure 3.14** | Compositional phase diagram which predicts type of Cu sites in Cu-SSZ-13 depending upon Si:Al and Cu:Al ratios. The colour scale shows the predicted fraction of \( ZCuOH \). White line gives transition from \( Z_2Cu \) only region to mixed \( Z_2Cu/ZCuOH \) region and the white points show compositions of synthesized Cu-SSZ-13 samples.\(^{93}\)

\( NH_3 \) plays an essential role in the de-NOx SCR as the reducing agent, therefore it is necessary to understand how it interacts with the zeolite sites. \( NH_3 \) can bind to either Lewis acid \( Z_2Cu \), \( ZCuOH \) or \( ZCu \) sites or Brønsted acid sites. DFT can provide a level of detail about adsorption inaccessible from experiment alone, however it is important to consider the functional used in the calculation as adsorption energies can vary. For example, \( NH_3 \) adsorption energy onto a Brønsted acid site in H-SSZ-13 forming \( Z/NH_4 \) is calculated by the GGA functional BEEFvdW to be -118 kJ/mol and by the hybrid functional HSE06-TS-vdW to be -151 kJ/mol.\(^{93,167}\) \( NH_3 \) adsorption energy determined using microcalorimetry gives -155 kJ/mol, meaning hybrid
functionals including a correction for VDW forces match experimental results better than GGA functionals. The proton on the Brønsted acid detaches from the zeolite and coordinates to NH₃ forming a tetrahedral ammonium cation located in the face of the 8MR hydrogen bonded to a single framework oxygen. DFT calculations of the adsorption energy of NH₃ onto multiple Cu sites in Cu-SSZ-13 have been reported by different groups. Adsorption of NH₃ onto Cu sites (Z₂Cu, ZCuOH and ZCu) behaves in a similar way to water, but it is reported that adsorption of NH₃ is only favourable up to 4 ligands rather than 6, depending upon the temperature. However this exact behaviour is not found by all groups. Like water, each adsorbed ammonia ligand displaces a framework oxygen bond and lifts the Cu²⁺ ion out of the plane of the 6MR meaning there is mixed NH₃ and Ofw coordination under certain conditions. Paolucci et al calculate the sequential adsorption energies of NH₃ to Cu²⁺ to be in the range of -120 to -135 kJ mol⁻¹ on Z₂Cu whereas for ZCuOH NH₃ adsorption is approximately 10 kJ mol⁻¹ less and the adsorption sequence terminates with a [Cu²⁺(OH⁻)(NH₃)₃]⁺ ion whereas for Z₂Cu it terminates as a [Cu²⁺(NH₃)₄]²⁺ ion. Adsorption of NH₃ onto Brønsted acid is calculated to be ~20 kJ/mol stronger than onto Lewis acid sites. For ZCu which contains Cu⁺, only two NH₃ ions are needed to completely free Cu⁺ from the framework and they coordinate in a linear fashion mobilising the Cu⁺ complex throughout the zeolite. Adsorption of NH₃ onto Cu⁺ is computed to be 10 kJ/mol stronger than on Cu²⁺. Overall, NH₃ adsorbs to the Lewis acidic sites, ZCuOH, Z₂Cu and ZCu at comparable energies, but saturating at different coordination numbers and always displacing a framework oxygen coordination upon adsorption to Cu. The work by Paolucci et al provides a comprehensive overview of NH₃ adsorption onto Cu sites in SSZ-13, and further considers the adsorption energy of physisorbed NH₃, NH₄⁺ in the 8MR, calculated to be in the range of -40 to -70 kJ mol⁻¹. However, it does not take into account any energy differences induced by changes to the configuration of the ligands around the Cu centre, or by molecules occupying the second solvation shell in a hydrogen bonded network. This will be discussed in section 6 and 7 along with a comparison of adsorption energies.

It is established that NH₃ and NO work together to reduce Cu²⁺ to Cu⁺ in the reduction half cycle, and NO is the targeted molecule for abatement. Therefore, it is essential to understand how NO interacts with the Cu active sites. There is a rich literature history focusing on NO interaction with Cu-exchanged zeolites. NO has a varied and interesting behaviour as
a ligand because it is a neutral radical. This means it can act as a reducing (NO\(^+\)), oxidising, (NO\(^-\)) or neutral ligand, upon adsorption to a transition metal active site. The early DFT calculations applied to NO adsorption on Cu-exchanged zeolites (ZSM-5) found that NO binds to Cu\(^+\) in a bent configuration as a neutral radical not affecting the change on Cu\(^+\).\(^{172}\) Later studies find the adsorption energy of NO to Cu\(^+\) in SSZ-13 to be -90 kJ/mol using HSE06 functional.\(^{173}\) The interaction between Cu\(^{2+}\) and NO is complex and is very sensitive to the functional used. This is because DFT calculations are subject to delocalisation errors which stem from electron self-interaction errors meaning electrons in the calculation can delocalise unphysically.\(^{174}\) For example, GGA calculated adsorption energy of NO onto Cu\(^{2+}\) is -100 kJ/mol but decreases to a negligible energy when HSE06 is used.\(^{93,173}\) Using GGA functionals, the Cu-NO bond is shortened when adsorbed on Cu\(^{2+}\) compared to Cu\(^+\), implying that a charge transfer has taken place between Cu\(^{2+}\) and NO, however Bader charge analysis shows Cu stays as Cu\(^{2+}\).\(^{93,165}\) Therefore, caution must be taken with the functional when performing DFT calculation including NO and Cu\(^{2+}\) and it is imperative to understand the affect the choice of functional could have upon the results.

More recently Kerkeni et al. used DFT to analyse the first solvation shell of Cu\(^{2+}\) as a function of temperature and partial pressures of H\(_2\)O and NH\(_3\) (Fig. 3.15).\(^{175}\) The results are consistent with Paolucci et al. as at high temperatures Cu loses its solvation of both H\(_2\)O and NH\(_3\). Unsurprisingly, the more basic species NH\(_3\) out-binds H\(_2\)O to Cu\(^{2+}\) over most temperature and partial pressure ranges, but at high partial pressures of H\(_2\)O, water is shown to be present in the first coordination sphere. Interestingly, the phase diagrams show a difference in solvation environment depending on whether unsolvated Cu occupies the 6MR or 8MR initially, highlighting the complexity of the potential energy surface (PES) for Cu\(^{2+}\) in the chabazite cavity. The diagrams were produced by calculating the Gibbs free energy for each complex over the range of temperatures and pressures shown in figure 3.15 by considering the vibrational, translational, and rotational degrees of freedom of the system. A detailed description of this approach is outlined in references.\(^{176,177}\)
Figure 3.15 | Phase diagrams for H₂O and NH₃ co-adsorption from DFT calculations as a function of temperature and pressure. (a) and (b) have Cu starting in the 6MR and (b) and (d) Cu starts in the 8MR. The most stable coordination environment in each condition is represented by \( (n,m) \), where \( n \) is the number of water molecules, and \( m \) is the number of ammonia molecules coordinated to \( \text{Cu}^{2+} \).

Fig. 3.16 shows a detailed phase diagram for 1 AL and 2 AL sites with varying T and P of O₂ at 300 ppm of NH₃ and 2 % H₂O.⁹³ The free energies are calculated using DFT in conjunction with first-principles thermodynamics models. A range of different adsorbate combinations are calculated on both \( Z_2\text{Cu} \) and \( \text{ZCuOH} \) taking into account reduced and oxidised Cu. The relative free energies are written as a function of calculated entropies and enthalpies of adsorption and also related to the gas phase chemical potentials of the adsorbed molecules. The results show that there is little difference in free energy between complexes of reduced (\( \text{Cu}^+ \)) and oxidized (\( \text{Cu}^{2+} \)) in oxidising conditions. Both sites are predicted to be fully solvated by NH₃ which is consistent with operando X-ray techniques in section 2.5.4 at 200 °C and 10 % O₂. Furthermore, the lowest free energy redox couples are calculated to be \( Z[\text{Cu}^{2+} (\text{OH}) (\text{NH}_3)_3] \leftrightarrow Z[\text{Cu}^+ (\text{NH}_3)_2] \) and \( Z_2[\text{Cu}^{2+} (\text{NH}_3)_4] \leftrightarrow Z\text{NH}_4/Z[\text{Cu}^+ (\text{NH}_3)_2] \) on \( \text{ZCuOH} \) and \( Z_2\text{Cu} \).
respectively. The free energy difference for the 2Al site is ~15 kJ mol\(^{-1}\) and very similar to the 10 kJ mol\(^{-1}\) measured for \([\text{Cu}^{2+}(\text{NH}_3)_4]^{2+}/[\text{Cu}^+(\text{NH}_3)_2]^+\) aqueous redox couple at 25 °C.\(^{78}\) It should be noted that this analysis is not guaranteed to give the redox couples involved in the SCR reaction but it can certainly aid in our understanding by ruling out high energy species, not involved in the reaction.

![Figure 3.16](image)

**Figure 3.16** | Compositional phase diagrams for 1Al and 2Al sites, left and right respectively. Temperature and \(O_2\) pressure are varied and 300 ppm of \(NH_3\) and 2 % \(H_2O\) is held constant. The bottom structures are the most stable at these conditions.\(^{93}\)

3.6 The SCR Reaction on Cu-SSZ-13

3.6.1 SCR Chemistry

It is established that a reductant must be used for the abatement of \(NO_X\), as the reverse of the direct oxidation of nitrogen is kinetically unfeasible and thermodynamically unstable. Ammonia is the reductant of choice as it can react with \(NO_X\) and is less likely to react with the excess oxygen present within diesel exhaust gases. Hydrocarbons are also able to reduce \(NO_X\), and in theory diesel fuel could be used as the source, meaning an easier engineering task for automobile manufacture.\(^{87}\) However, the conversion of \(NO_X\) using hydrocarbons is not good enough for commercial use and the necessary catalysts such as silver are expensive, so \(NH_3\) de-\(NO_X\) SCR is the leading method.

There are altogether three comparable overall pathways by which the SCR can proceed. They are determined by the ratio of NO and \(NO_2\) in the exhaust gas feed.\(^{179–181}\) The ‘standard SCR’
proceeds under typical diesel exhaust conditions when there is a negligible amount of NO\textsubscript{2} compared to NO, as shown in equation 3.2

\[4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}\]  \hspace{1cm} (3.2)

When there are equal amounts of NO and NO\textsubscript{2} the SCR proceeds at an accelerated rate compared to the standard SCR, so it has been dubbed the ‘fast SCR’, as shown in equation 3.3

\[4\text{NH}_3 + 2\text{NO} + 2\text{NO}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}\]  \hspace{1cm} (3.3)

At conditions where there is a negligible amount of NO compared to NO\textsubscript{2} the SCR proceeds at a slower rate, and it has been called the ‘slow SCR’ as shown in equation 3.4

\[8\text{NH}_3 + 6\text{NO}_2 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O}\]  \hspace{1cm} (3.4)

The slow SCR is unlikely to occur as it proceeds without the presence of O\textsubscript{2}. The direct oxidation of NH\textsubscript{3} is an unwanted side reaction that competes with the standard SCR equations 3.5, 3.6

\[4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}\]  \hspace{1cm} (3.5)

\[4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}\]  \hspace{1cm} (3.6)

The complexity of the SCR reaction becomes evident when the necessary redox balance is inspected, and the potential side reactions are taken into account. As NO is a two-electron oxidant and NH\textsubscript{3} a three-electron reductant, an additional oxidant is required for full chemical balance. In the standard and fast SCR, it is provided by four electron oxidants O\textsubscript{2} and NO\textsubscript{2} respectively. Therefore, the selectivity of the reaction must be more heavily weighted toward NH\textsubscript{3} with NO rather than the reaction of O\textsubscript{2} and NH\textsubscript{3}, which is made difficult by the fact there is a much greater amount of O\textsubscript{2} within the gas feed than NO. This, therefore, implies a highly complex reaction network with multiple intermediate species with many different potential routes due to the variation in chemistry of the transition metal active site.

The literature describing the atomic level catalytic mechanism has yet to come to a complete agreement regarding how the reaction proceeds. Despite full catalytic mechanisms being proposed the highly complex chemistry involved means identification of the global pathways requires a detailed and comprehensive reaction network for a satisfactory description. In addition, there is still contention regarding the precise elementary reaction steps, which intermediate species form, in what order, and the rate limiting steps. The chemistry of the
standard SCR is evidently complex because there are three different species to activate (NO, NH₃, and O₂) to allow the reaction to proceed. Furthermore, the complex stoichiometry required to fully oxidise and reduce the reactants implies multiple different steps are needed to complete the reaction cycle. To be able to unequivocally prove a certain reaction mechanism is responsible for the conversion of NOₓ into N₂ and H₂O is rather difficult. This is because one can easily suggest that a reaction mechanism exists and be able to record evidence that supports the hypothesis, but to prove that it is the only one occurring at certain conditions requires a very robust and detailed analysis piecing together data from thermodynamic, kinetic, and spectroscopic studies. The complexity of the problem increases when one considers the possibility of different reaction mechanisms, speciation of active sites and side reactions coexisting at the same conditions. This, coupled with the fact there likely exist two or more temperature regimes over the potential exhaust conditions, therefore makes experimental results difficult to interpret and deconvolute.

3.6.2 Reaction Kinetics
The most common way of reporting catalytic activity within the de-NOx SCR literature is with a ‘light-off’ curve. It shows the conversion of NOₓ as a function of the temperature for experiments undertaken at fixed space velocities. Interpreting the data can be difficult, especially as it contains information about both the transport rates and the reaction rates over a catalyst bed, which could either be a monolith or a powder. Therefore, data obtained from light-off curves can be used to gauge the performance of a catalyst for emissions standards, however it can only give indirect information on the kinetic behaviour and its subsequent relationship to the catalyst structure and composition. This can be seen in the infamous ‘seagull’ feature of the de-NOx SCR light-off curve, which occurs at ~350°C (Fig. 3.17).¹²⁴,¹⁸² This phenomenon has been proposed to be caused by changes to the dominant active site or its structure, changes to the reaction mechanism, the increasing activity of side reactions, or any combination of these factors or more.¹²⁴,¹⁸²
In order to provide direct information about the kinetics of a catalytic system and gain an understanding of how the kinetics changes with catalyst composition and structure, rate measurements must be obtained without any heat or mass transfer from the system. Therefore, a differential reactor in which the catalyst is situated must maintain constant contact with a gas stream of uniform composition and temperature. This allows any changes in the reaction parameters to be linked to changes to the reaction conditions. For example, the temperature at which certain gases are detected can give information about the activation energy, and the amount and composition of the gas feed can give information about the reaction rate orders which in turn can be then related to microscopic mechanistic details. It is possible to fully compare and understand the kinetic behaviour of Cu-SSZ-13 catalysts with different composition and therefore structure as the discrete nature of Cu active sites allows for normalization of rate data to produce a microscopically detailed reaction mechanism for the de-NO\textsubscript{x} SCR.

Figure 3.17 | NO\textsubscript{x} conversion in steady-state condition as a function of temperature for commercial Cu-SSZ-13 catalyst.\textsuperscript{124}
There is a strong literature focus upon the reaction mechanism in the low temperature range of 100-200 °C, as during the ‘cold start’ of the diesel engine is when a significant proportion of NO\textsubscript{x} is emitted. The rates for the standard SCR (NO\textsubscript{2} is not present and O\textsubscript{2} is the oxidant) are typically measured in the laboratory using gas streams with the composition of 10-15 % O\textsubscript{2}, 2-5 % H\textsubscript{2}O, 2-5 % CO\textsubscript{2}, a stoichiometric amount of 300-500 ppm of NO and NH\textsubscript{3} and the rest N\textsubscript{2}. Different compositions of Cu-SSZ-13 with varying Si/Al and Cu/Al ratios, which contain majority of either ZCuOH or Z\textsubscript{2}Cu sites as outlined in section 3.4 can be used to infer how the different sites affect the rate and mechanism.

Fig. 3.18 shows how the standard SCR rates change as a function of Cu loading from 0 to 6.39 wt % (Cu/Al 0.02-0.35), for a sample synthesised by FAU conversion (SAR = 5).\textsuperscript{127} It was established that catalysts only exhibit Z\textsubscript{2}Cu sites in the range of Cu/Al 0.01-0.20 by XAS and UV-Visible spectroscopy and by NH\textsubscript{3} titration of the residual H\textsuperscript{+} sites after reduction.\textsuperscript{100} The results collected at 200 °C show that the pure H form of SSZ-13 is inactive for the SCR reaction, then the reaction rate increases linearly with Cu loading until a Cu/Al ratio of 0.2. This suggests that these Cu sites are identical in terms of SCR activity. After 0.2 Cu/Al ratio (4 wt % Cu) the SCR turnover rate decreases, presumably because the sample now forms Cu oxide clusters which do not contribute to the SCR activity, and potentially hinder it.\textsuperscript{132} For a Cu-SSZ-13 sample with SAR = 6, a similar trend holds at 140, 155, 170, 185 and 200 °C, where SCR rate increase linearly with Cu content up to ~3 wt %, then only depends weakly in increasing Cu (Fig. 3.19).\textsuperscript{124}
Figure 3.18 | Standard SCR rates of Cu-SSZ-13 catalysts at 473K. Cu/Al ratios range from 0 to 0.35. The conditions are 320 ppm NO, 320 ppm NH$_3$, 10 % O$_2$, 8 % CO$_2$, 6 % H$_2$O, and balance Helium at 473 K, which correspond to standard SCR conditions.

Figure 3.19 | Reaction rates for the standard SCR as a function of temperature for Cu/SSZ-13 samples with different Cu-loadings. The gas feed contains 350 ppm NO, 350 ppm NH$_3$, 14 % O$_2$, 2.5 % H$_2$O balanced with N$_2$. The dashed line represents NO and NH$_3$ conversions of 20 %.
The differential turnover rates for the standard SCR at 200 °C do not change significantly depending upon the synthesis route. For FAU conversion, hydroxide mediated routes and fluoride mediated routes the SCR rate is approximately $8 \times 10^{-3}$ mol NO mol Cu$^{-1}$ s$^{-1}$. Furthermore, it has been calculated by multiple groups that the apparent activation energy for all Cu-SSZ-13 materials with Cu content 0.31 to 6.39 wt % is $\sim 70$ kJ/mol. It is interesting to note that reported apparent activation energies are similar for samples containing mainly Z$_2$Cu, ZCuOH or a mixture of sites, indicating that the zeolite topology or the Cu speciation does not have a strong influence upon the standard SCR rates. However, at low Cu loading of less than 0.5 wt % the SCR rate behaviour changes upon closer inspection. In this region the standard SCR rate is shown to have a quadratic dependence upon the Cu loading rather than linear in the low temperature regime. Furthermore, the same publication reports a lower activation energy of 40 kJ/mol at this low Cu loading and hold true for samples expected to contain a majority of either Z$_2$Cu or ZCuOH sites. The existence of a quadratic rate dependence at certain Cu content is an important result for the speciation of the active Cu complex.

In the high temperature regime (> 250 °C) it becomes more difficult to measure the standard SCR rate as the intrinsic reaction rate is higher. Despite limited results, there are two evident differences from the low temperature regime. Firstly, the apparent activation energy is higher at 140 kJ mol$^{-1}$ at 0.065 to 0.516 wt % Cu rather than 40-70 kJ mol$^{-1}$ as in the low temperature regimes. This implies a significant change in mechanism or change in the speciation of the active site. Also, the dependence of the standard SCR rate on Cu loading is linear for the full range of Cu loading rather than quadratic dependence as low temperature low loading regimes exhibit.

3.6.2.1 The Existence of Dimeric Cu Species
Kinetic measurements clearly show that for Cu-SSZ-13 samples with SAR=15 and a Cu density below $1.13 \times 10^{-4}$ Å$^{-3}$ that there is a quadratic dependence upon the SCR reaction rate as a function of Cu content, whereas, at Cu density above $1.9 \times 10^{-4}$ Å$^{-3}$ the SCR reaction rate has a linear dependence. To understand the mechanistic causes of this kinetic behaviour XANES spectroscopy has been used to follow the Cu oxidation state during steady state SCR for a range of Cu-SSZ-13 samples with different compositions. As expected, Cu$^{2+}$ species evolve into a combination of both Cu$^+$ and Cu$^{2+}$ signifying redox cycling. XANES is used to understand the
relationship between Cu\(^{+}\) proportion and Cu volumetric density at steady state SCR operation. It shows that at the highest Cu density and the smallest Cu-Cu average separation (< \(\sim 15\) Å) Cu\(^{+}\) is the minority oxidation state, whereas at the lowest Cu density and the highest Cu average separation (\(\sim 30\) Å) it becomes the predominant oxidation state. At the largest separation and most dilute Cu content the EXAFS spectra become identical to linear Cu\(^{+}\)(NH\(_3\))\(_2\) or fully reduced Cu-SSZ-13. Therefore, these observations show an inverse relationship between Cu\(^{+}\) proportion under steady state catalysis and Cu density, and that Cu reoxidation rates increase with Cu density. This implies that the oxidation half cycle is more difficult on a Cu single site, which is more prominent at lower Cu density.\(^{185}\) Furthermore, it is found that an expression which is second order in relation to Cu\(^{+}\) density is the best fit for the data. This is however only true for samples containing Cu at a high density. The authors postulate this second order dependence arises from the formation and participation of Cu\(^{2+}\) dimers formed from [Cu\(^{+}\)(NH\(_3\))\(_2\)]\(^{+}\) ions and O\(_2\) in a pseudo-bimolecular reaction, as oxygen bridged Cu dimers are well known in zeolite chemistry.\(^{186-188}\) DFT calculations confirm that the diffusion barrier for [Cu\(^{+}\)(NH\(_3\))\(_2\)]\(^{+}\) through the 8MR is low (35 kJ mol\(^{-1}\)) and the pairing cost of the two ions in the same cage is 23 kJ mol\(^{-1}\), therefore transport between cage is expected to happen under standard SCR conditions.\(^{185}\) In addition, it is calculated that two [Cu\(^{+}\)(NH\(_3\))\(_2\)]\(^{+}\) ions in the same cage bind O\(_2\) easier than 1 [Cu\(^{+}\)(NH\(_3\))\(_2\)]\(^{+}\) ion (60 kJ/mol vs -25 kJ/mol respectively) The dissociation of O-O bond to form the bridges dimer is estimated to be 24 kJ mol\(^{-1}\) meaning the rate limiting process is the diffusion of the Cu ion into the same cage.

Gao et al investigate the reaction kinetic of the SCR reaction either side of the seagull feature (200 °C and 380 °C) for catalyst samples at low, medium and high loadings.\(^{189}\) They find that at low Cu loadings there is a transition from quadratic to linear rate at 200 to 380 °C, which is not present for the medium and high loaded catalysts. The rationalization is that at low Cu loadings the rate limiting step is the migration of single Cu species to form the Cu dimers which is induced by NH\(_3\) solvation effects, whereas at 380 °C, the Cu complexes loses the NH\(_3\) solvation and anchors to the framework becoming a single site reaction. The low temperature pathway at medium and high Cu loadings has been suggested to still occur over dimeric species despite not exhibiting quadratic dependence on Cu loading as there is a large entropy penalty to form Cu dimers at low loadings, which no longer contributes, as the average distance between Cu ions is smaller, and the formation of the active dimer is no longer rate
limiting. Gao et al also use DFT at the PBE level of theory to further understand the low-temperature reaction mechanism and that the rate limiting step is Cu-loading dependent.\textsuperscript{189} They only consider 1Al sites and not the 2Al site and calculate activation barriers for both [NH2-Cu-NO]\textsuperscript{+} and [NH3-Cu-HONO]\textsuperscript{+} pathways on the dimeric species and find that the pathway via HONO and NH2NO2 is significantly more energetically favourable compared to the monomer. In addition, they show that two [Cu'\textsuperscript{+}(NH3)\textsubscript{2}]\textsuperscript{+} species can combine to form [Cu'\textsuperscript{+}(NH3)\textsubscript{2}-O\textsubscript{2}-Cu'\textsuperscript{+}(NH3)\textsubscript{2}] after migration into the same CHA cavity. Subsequently, Cu is oxidised by electron transfer from Cu to O. However, as this process forms two O\textsuperscript{2-} ions, it is a four-electron transfer and only two Cu centres are involved, therefore an additional oxidant is required, which is provided by NO, which is oxidized to NO\textsubscript{2}. Ultimately the resultant [Cu\textsuperscript{2+}(NH3)\textsubscript{2}-O-Cu\textsuperscript{2+}(NH3)\textsubscript{2}] species is hydrolysed to two [Cu\textsuperscript{2+}(NH3)\textsubscript{2}-OH]\textsuperscript{+} species by H\textsubscript{2}O, therefore closing the oxidation half cycle.

The kinetic measurements by Gao et al imply there is a change in rate limiting step dependent on the Cu loading.\textsuperscript{189} They propose that at low loadings the migration of [Cu'\textsuperscript{+}(NH3)\textsubscript{2}]\textsuperscript{+} is rate limiting, whereas at medium and high loadings the formation of NO\textsubscript{2} and the reoxidation of Cu\textsuperscript{+} to form Cu\textsuperscript{2+}(NH3)\textsubscript{2}-O-Cu\textsuperscript{2+}(NH3)\textsubscript{2} is rate limiting. The authors suggest this is due to transport kinetics of [Cu'\textsuperscript{+}(NH3)\textsubscript{2}]\textsuperscript{+} not being as important at higher Cu loadings as at low loadings the migration [Cu'\textsuperscript{+}(NH3)\textsubscript{2}]\textsuperscript{+} through the 8MR is less likely. Furthermore, Gao et al calculate a high activation barrier of 175 kJ mol\textsuperscript{-1} for the reaction of O\textsubscript{2} and NO on a single Cu\textsuperscript{+} site to form Cu\textsuperscript{2+} via a nitrate intermediate which strengthens the proposal that the oxidation half cycle proceeds via a dimer intermediate. It must be noted that no direct evidence of the dimeric Cu species has been found, only inferred and indirect evidence of fitted SCR rate data, and theoretical calculations. The arguments for active dimeric species are convincing, but the second order SCR rate in relation of Cu\textsuperscript{+} and the inverse relationship between Cu\textsuperscript{+} proportion and Cu density, could be due to unconsidered artifacts. Also, the SCR reaction still proceeds at dilute Cu content where the reaction rate is linear with respect to Cu\textsuperscript{+} content, where only mono-Cu is expected. The study by Lomachenko shows clearly that FT-EXAFS do not show any Cu-Cu scattering paths, which should be visible if dimers were present (Si/Al = 15, Cu/Al = 0.48).\textsuperscript{138} A possible explanation is that the transient nature of the dimer makes it very difficult to detect spectroscopically as they are short lived, a common phenomenon within catalysis.
3.6.3 The Reaction Mechanism

Cu in Cu-SSZ-13 has been shown to exist in two oxidation states Cu$^{2+}$ and Cu$^+$ in equal proportions at 200 °C in standard SCR conditions.$^{86,93,140,165,190,191}$ Taken with the fact that at ambient temperature only Cu$^{2+}$ is present and that under fast SCR conditions only Cu$^+$ is present, it can be assumed a Cu$^{2+}$/Cu$^+$ redox cycle is pivotal to the reaction cycle. The seagull feature in the light-off curve discussed in section 3.2 suggests there is an intrinsic change in how the reaction proceeds as a function of temperature, potentially caused by a change in the structure of the active site, an increase in the prominence of a side reaction, a change in the reaction mechanism or a transformation of the active site. It could also be related to the fact that at about 300 °C the Cu ion is likely to lose solvation, which could induce the one of the other potential reasons mentioned and cause the dip in activity at this temperature.$^{138,192}$

At 200 °C the lowest free energy redox couples predicted by the phase diagram discussed in figure 3.15 are solvated by 4 and 3 NH$_3$ ligands for Z$_2$Cu and ZCuOH sites respectively, and 2 NH$_3$ ligands for the Cu$^+$ species, where an NH$_4^+$ ion is generated on the Z$_2$Cu site which balances that charge.$^{93}$ The thermodynamic analysis used to obtain these results is not guaranteed to give the exact redox couple which participate in the standard SCR reaction. The analysis, however, can exclude high energy complexes and intermediate species and leave a sensible guess at the ground state structures. However, it is possible there is a distribution of different configurations of NH$_3$ and framework coordinated Cu complexes as redox couples, which change as a function of temperature. As the temperature increases it is established that Cu complexes lose their solvation and coordinate to the O$_{fw}$ species and therefore lose their mobility.$^{93,175}$

The early consensus in the literature was that NO alone can reduce Cu$^{2+}$ to Cu$^+$. This was based on the detection of a Cu$^+$-NO vibrational feature in certain vacuum activated Cu-SSZ-13 samples.$^{193,194}$ However, subsequent samples synthesized to contain either only ZCuOH or a mixture of both ZCuOH and Z$_2$Cu do not exhibit the characteristic Cu$^+$ 8.983 eV edge in the XANES spectra when exposed to NO and either He or N$_2$ at 200 °C.$^{102,135,137}$ A potential explanation for the observation of Cu$^+$-NO in certain samples is that NO could adsorb on to autoreduced ZCu sites created during high temperature treatment in the vacuum. Furthermore, DFT does not predict the adsorption of NO onto Cu$^{2+}$ with the subsequent reduction of Cu to Cu$^+$ using either GGA or hybrid exchange functionals.$^{135,137,165,173}$ NH$_3$ alone has also been proposed to reduce Cu$^{2+}$ to Cu$^+$ in the SCR, however this reaction proceeds at a
significantly slower rate the standard SCR does, meaning this process is unlikely to occur and be detected under SCR conditions.\textsuperscript{102,134,136,168}

A common tactic employed to understand the nature of the redox steps is to investigate them under varying conditions relevant to the reaction. Also, to avoid any unintended changes in oxidation state of Cu that can arise from pre-treatment of the catalyst, it is common to first analyse the samples using XAS to quantify the proportion of Cu\textsuperscript{2+} and Cu\textsuperscript{+}. Regardless of SAR and Cu/Al ratio or synthesis method, Cu-SSZ-13 exhibits a Cu\textsuperscript{2+}/Cu\textsuperscript{+} ratio close to one, under standard SCR conditions between 150 and 200 °C.\textsuperscript{93,102,103,138} Ribeiro et al have measured the changes in oxidation states of Cu with operando XES as NH\textsubscript{3}, NO, or O\textsubscript{2} are removed from the gas feed.\textsuperscript{136} When NH\textsubscript{3} is removed from the gas stream, on a catalyst sample only containing Z\textsubscript{2}Cu sites the SCR rate drops to a negligible level and the Cu\textsuperscript{+} fraction also falls to near undetectable levels.\textsuperscript{136} Furthermore, on samples prepared to only contain ZCuOH sites when NO and O\textsubscript{2} only are flowed over the catalyst only Cu\textsuperscript{+} sites are observed again just like the Z\textsubscript{2}Cu sample. Upon the removal of NO from the SCR gas mixture the SCR rate also becomes negligible whereas the proportion of Cu\textsuperscript{+} becomes 0.1-0.2, which is similar to when catalysts are exposed to only O\textsubscript{2} and NH\textsubscript{3} at 200 °C.\textsuperscript{102,135} When O\textsubscript{2} is removed from the SCR gas stream Cu converts to Cu\textsuperscript{+} very quickly on samples containing only ZCuOH or Z\textsubscript{2}Cu or a mixture of both.\textsuperscript{93,135,136} This, therefore, strongly implies that only NH\textsubscript{3} and NO together are able to reduce Cu\textsuperscript{2+} to Cu\textsuperscript{+}, an important finding for SCR chemistry.

At increasing temperatures, it is generally accepted that NH\textsubscript{3} solvation of the active Cu sites is reduced. Understanding the difference in SCR activity at 200 °C and 350 °C is crucial as this is where there is a clear change in the SCR activity. At 250 °C the predicted redox couples on 1 Al and 2Al sites become [ZCuOH(NH\textsubscript{3})] and [ZCuNH\textsubscript{3}], and [Z\textsubscript{2}CuNH\textsubscript{3}] and Z[Cu(NH\textsubscript{3})\textsubscript{2}]/ZNH\textsubscript{4} respectively. Furthermore, multiple experimental and spectroscopic techniques such as XAS/XES, EPR and NH\textsubscript{3} TPD confirm that NH\textsubscript{3} solvation is lost at 250-400 °C.\textsuperscript{134,138} It is therefore reasonable to postulate that the decreased conversion near 350 °C could be related to the loss of NH\textsubscript{3} solvation either directly by increasing activation barriers or indirectly by inducing a different reaction pathway.\textsuperscript{124,182} The reported increase of apparent activation energy at elevated temperatures from \textasciitilde 70 kJ mol\textsuperscript{-1} to \textasciitilde 140 kJ mol\textsuperscript{-1} and the change from quadratic to linear dependence of the SCR rate on the Cu loading both suggest a change of reaction
mechanism, change of speciation of active site, or perhaps both as being responsible for the dip in activity.

Within the literature there are contrasting schools of thought regarding the reaction mechanism, how it proceeds and how temperature changes the pathways. The first full SCR reaction cycle was reported by Janssens et al. and was developed using an “Occam’s razor” type approach (Fig. 3.20). The most convenient and simple way the reaction could proceed from the initial mixture of SCR gases was postulated while applying certain constraints to increase the validity of the proposal:

1) All side reactions are disregarded

2) The total charge and mass are conserved in each step while keeping the overall stoichiometry of the SCR reaction constant

3) There is a redox cycle between Cu$^{2+}$ and Cu$^{+}$

4) Only stable molecular species can adsorb and desorb from the zeolite.

They propose the reduction half cycle is initiated by the formation of the HONO intermediate via attack of NO to OH$^{-}$ and simultaneous reduction of Cu$^{2+}$ to Cu$^{+}$. H$_2$NNO and H$_2$O are then formed, and H$_2$O desorbs from the Cu complex. This step is not discussed further in the paper, but it potentially proceeds via a proton transfer from NH$_3$ to HONO forming NH$_2^{-}$, H$_2$O and NO$, then NH$_2$ and NO$^+$ react to form H$_2$NNO which dissociates into H$_2$O and N$_2$ closing the reduction half cycle.

The oxidation half cycle is proposed to proceed by either O$_2$ and NO reacting to form a nitrate adsorbed upon Cu$^+$, or attack by NO$_2$ directly to Cu$^+$, which both ultimately form NO$_2^-$ which will then react with NH$_3$ to form N$_2$ and H$_2$O and leave ZCuOH. There is a particular elegance to this mechanism; the chemistry is rather simple and intuitive as it is essentially analogous to the fast SCR. There is one main point of contention, which is the activation of NO to adsorb in conjunction with O$_2$ to reoxidise the Cu ion as elementary reaction steps are not proposed, and the 4 electron transfers needed for charge balance is very unlikely to happen at once. It also does not address the dual site nature of the Cu active site, which is likely at high Cu loadings and low temperatures. DFT modelling also supports the feasibility of the reaction.
scheme, the intermediate species have all been modelled and are energetically feasible, but activation barriers have only been computed for the formation of the nitrate ion from O\textsubscript{2} and NO and the subsequent nitrate formation from NO\textsubscript{2} and NO. This process has an activation energy of 104 kJ mol\textsuperscript{-1} calculated with supercell GGA, however details of elementary reaction steps and intermediate structures are not reported. It is likely that this reaction mechanism is more relatable to the high temperature regime as any NH\textsubscript{3} solvation is neglected during simulations, and this mechanism would be consistent with SCR rate independent of the Cu loading, exhibited at high temperatures.

**Figure 3.20** | Reaction cycle proposed by Janssens et al. The fast SCR cycle is shown in black and the standard SCR in blue.\textsuperscript{135}

Paolucci et al. developed a reaction mechanism that accounts for both 1Al and 2Al sites (Fig. 3.21 left).\textsuperscript{93} They propose that the reduction half cycle proceeds via the direct formation of the nitrosamine (H\textsubscript{2}NNO) intermediate, which is a familiar species in nitrogen chemistry such as oxide-catalysed SCR and thermal de-NOx chemistry.\textsuperscript{195,196} H\textsubscript{2}NNO also has the correct stoichiometry and is known to easily decompose into N\textsubscript{2} and H\textsubscript{2}O only at low temperatures.\textsuperscript{197} Furthermore, H\textsubscript{2}NNO has also been proposed as an intermediate species after Cu-exchanged
zeolites Cu-Y and Cu-FAU have been exposed to NO and NH$_3$ gasses. In this reaction scheme it is proposed that the reduction half cycle is initiated by the adsorption of NH$_3$ to Cu$^{2+}$, then NO attacks NH$_3$ to form the intermediate H$_2$NNO via a proton transfer from NH$_3$ to a basic species, while reducing Cu$^{2+}$ to Cu$^+$, H$_2$NNO then dissociates into H$_2$O and N$_2$ completing the reduction half cycle. The oxidation half cycle is less well quantified; it is suggested that O$_2$ and NO react with NH$_3$ to form an ammonium nitrite species, which then decomposes into H$_2$O and N$_2$ to close the half cycle.

Figure 3.21 | Proposed standard SCR reaction cycle for Cu ions at 1Al (black) or 2Al (green) sites (left panel). Reaction energies corresponding to each step of the cycles (right panel)

Activation barriers for the formation of the H$_2$NNO intermediate in the reduction half cycle have been calculated using DFT and CI-NEB pathways (Fig. 3.21 right) at the HSE06 level of theory. The pathways differ slightly on 1Al and 2Al sites as the proton acceptor is different. On the 1Al site a proton is transferred from NH$_3$ to OH$^-$, whereas on 2Al the authors calculate that the proton is transferred to an O$_{fw}$ species to form a new Brønsted acid site. The barriers for these processes on 1Al and 2Al sites are calculated to be 74 and 71 kJ mol$^{-1}$ respectively, whereas the formation of H$_2$NNO on 1Al sites is a much more exothermic process (-267 kJ mol$^{-1}$) due to the strong driving force of the formation of water compared to the 2Al site (-68 kJ mol$^{-1}$) where water doesn’t form (Fig 3.22). The two pathways over the different sites are similar in nature where the transition state is dominated by desorption of NH$_3$ to allow the attack of NO and the N-N separation at the transition state is over 2 Å whereas the N-H bond is only slightly elongated.
Figure 3.22 | Calculated activation energies for reduction of Cu$^{2+}$ 1Al (black) and 2Al (green) sites using the HSE06 functional forming H$_2$NNO.

An interesting feature arises due to a key difference in the proposed pathways at 1Al or 2Al sites. In theory, the reduction of Z$_2$Cu will leave a Brønsted acid site per Cu$^{2+}$ reduced but there will be no Brønsted acids sites left after a ZCuOH site is reduced. NH$_3$ temperature programmed desorption can then be implemented to test the ratio of H$^+$ Brønsted acid sites. Paolucci et al then predicted theoretically the ratio of H$^+$ sites that should be present after reduction and compared them to experimental values. The experimental results do seem to correlate to the theory, however only a limited number of experiments were undertaken so more data is needed to show this conclusively, as it is possible some of the H$^+$ left by the Z$_2$Cu site could be taken up by another ligand to form an ionic molecule. It should be noted that this test can only add strength to the reduction half cycle proposal not the oxidation half cycle.

Gao et al propose a reaction mechanism which proceeds on a Cu monomer for the reduction half cycle and over a Cu dimer for the oxidation half cycle. (Fig. 3.23) The reduction half-cycle proceeds via the formation of the HONO intermediate then an ammonium nitrite intermediate (which is not shown in the diagram, but discussed in the publication), which decomposes into N$_2$ and H$_2$O. NH$_4$NO$_2$ is possibly formed via a proton transfer from HONO to
NH$_3$ forming NH$_4^+$ and NO$_2^-$. These processes happen upon a monomeric Cu species. The reduction half cycle is thought to leave [Cu$^+$/(NH$_3$)$_2$]$^+$ species which are thought to be very mobile through the zeolite.$^{199,200}$ The authors hypothesise that two of these species migrate through 8MR windows into the same cavity and form [(NH$_3$)$_2$Cu$^+$-O$_2^-$-Cu$^+$/(NH$_3$)$_2$] which is then oxidized by NO, forming NO$_2$ and [(NH$_3$)$_2$Cu-O-Cu/(NH$_3$)$_2$], subsequently decomposing to close the oxidation half cycle. There are no elementary reaction steps proposed for the decomposition step and reformation of the Cu monomers and is an area further computational studies can help understand.

![Figure 3.23](image.png) | A proposed reaction mechanism of low-temperature NH$_3$-SCR that involves a Cu monomer in the reduction half cycle and a Cu dimer in the oxidation half cycle.

Cu$^{2+}$ dinuclear or dimeric active sites have also been proposed as an active centre for the low-temperature reduction half cycle. DFT calculations have been used to propose a mechanism which invokes a [(NH$_3$)$_2$Cu$^{2+}$(OH)$_2$Cu$^{2+}$(NH$_3$)$_2$] intermediate where the OH$^-$ species bridge the Cu$^{2+}$ ions. The reaction proceeds via HONO and H$_2$NNO intermediates which desorb from the Cu dimer and dissociate over Brønsted acid sites where the largest activation energy is 94 kJ mol$^{-1}$ and corresponds to the activation of O$_2$.\(^{201}\) Hu et al used a NO$_x$ storage material BaO/Al$_2$O$_3$ as a chemical trapping method to stabilise nitrate or nitrate precursors as Ba(NO$_3$)$_2$.\(^{202,203}\) The authors found that Cu$^{2+}$-OH$^-$ species invoke NO oxidation into nitrite like
intermediates. Furthermore, their DFT calculations suggest that the activation of NO is induced by Cu$^{2+}$-OH, which subsequently forms HONO intermediate species. CO oxidation can be used as a probe to confirm the presence of Cu-oxo species. Da Costa et al. have shown that CO can reduce multinuclear Cu species in the zeolite ZSM-5 to isolated Cu$^+$ ions, therefore it follows if Cu dimers are present in Cu-SSZ-13 then after O$_2$ treatment and subsequent reduction by CO only isolated ZCuOH or Z$_2$Cu sites will be left.\textsuperscript{204,205} Li et al find that catalyst samples synthesised to contain only isolated Al, therefore only ZCuOH sites, exhibit the disappearance and shifting of d-d transitions in UV-vis spectroscopy after they were held in a stream of CO at 523 K which does not happen for Z$_2$Cu samples, inferring the existence of dimeric Cu species as only dimers can be reduced by CO.\textsuperscript{204} This is because dry CO oxidation to form the product CO$_2$ involves the transfer of two electrons which cannot happen at monomeric Cu sites.\textsuperscript{206} Hu et al fit both first and second order rate kinetics to the Cu loading for the low temperature reduction half-cycle (RHC) and find that the quadratic relationship between Cu$^{2+}$ content is reported to be significantly better than the linear fit.\textsuperscript{203} To understand if and how the multi-nucleic Cu centre participates in the RHC the authors turned to DFT calculations. First, the energy of two-isolated, dimeric and two-proximate Cu species were compared. It was found that dimeric Cu$^{2+}$ species [(NH$_3$)$_3$Cu$^{2+}$-OH-$\cdot$Cu$^{2+}$2(NH$_3$)$_3$(H$_2$O)] is 32kJ/mol more favourable than two [Cu$^{2+}$2(OH$^-$)(NH$_3$)$_3$]$^+$ species in separate CHA cages and that the two-proximate Cu species where two [Cu$^{2+}$2(NH$_3$)$_3$]$^{2+}$ complexes are in close proximity within the same CHA cage is 79 kJ mol$^{-1}$ more favourable than the two isolated Cu complexes. The reaction is calculated to proceed via HONO and NH$_4$NO$_2$ which forms twice over each Cu centre within the same CHA cage.\textsuperscript{203} The highest activation barrier is calculated to be 60 kJ mol$^{-1}$, which corresponds to the formation of HONO. NH$_4$NO$_2$ is known to rapidly dissociate into N$_2$ and H$_2$O only.\textsuperscript{93} Interestingly, the same chemical trapping technique used on a sample containing only Z$_2$Cu sites shows no NO activation, implying that Z$_2$Cu cannot activate NO alone even in the presence of a HONO scavenger, corroborated by DFT calculations. However, rate measurements are also better fitted to second order kinetics in relation to Cu loading than first order on Z$_2$Cu sites as well under SCR conditions, implying the low-temperature SCR RHC also proceeds via a dimer on paired Al sites. A possible explanation is that Z$_2$Cu first converts to ZCuOH before migrating through the 8MR.
3.7 Literature Review Summary
To summarise the state of the current literature and outstanding problems regarding the de-NOx SCR reaction it is essential to consider how the speciation and coordination environment of the active Cu complexes changes under different conditions.

It is clear that the Cu coordination environment is both complex and dynamic. Under standard conditions Cu is fully solvated by water in a hexaaqua configuration shown by multiple spectroscopic techniques and upon heating the complex loses solvation and coordinates to the framework oxygen species. Under typical SCR conditions the complexity of the coordination environment increases. Theoretical phase diagrams and adsorption studies produced using DFT calculations by multiple groups confirm that NH$_3$ is the most strongly adsorbing species. However, at high partial pressures of water, water is found to be directly coordinated to Cu implying there is interplay between the different ligands. Furthermore, as the temperature increases, the Cu loses its solvation and coordinates to the framework oxygen species. It is possible to use thermodynamic analysis to infer the most likely coordination environment as a function of temperature and partial pressures of gases. However, to be completely accurate the ground state configuration of the adsorbing molecules around the Cu complex and its relative position in the chabazite cavity would need to be found. Upon optimisation, only the nearest minimum to the starting position on the PES is found. To provide a better guess at the global minimum a common tactic is to use molecular dynamics to first sample the PES then pick and optimise the lowest energy configuration found. This method might not provide the global minimum but will provide a reasonable guess and give a single low energy configuration. If there are multiple different configurations possible, with molecules in the first and second solvation shells, but with similar energies these results might be misleading. Therefore, it is sensible to sample multiple coordination configurations. The complexity of the PES is highlighted by the fact the upon sequential adsorption of water or ammonia to Cu$^{2+}$ different low energy adsorption configurations with different number of water and ammonia are found dependent upon the starting position of the Cu complex. In addition, MD simulations highlight that the coordination environment is dynamic and changes at timescales relevant to the SCR reaction. The solvated Cu complexes at low temperature conditions are generally accepted to be mobile throughout the zeolite,
and upon loss of solvation they anchor to the framework oxygen species and are no longer mobile.

The intrinsic properties of Cu-SSZ-13 such as the SAR and Cu/Al ratio and external factors like the temperature all have a substantial effect upon the speciation of the active Cu complex. The SAR determines the Al content in the zeolite and can be controlled during the synthesis by using different concentrations of precursors. At low Si/Al ratios there is high Al content and high Si/Al ratio there is mainly Si. Depending on whether Cu$^{2+}$ is exchanged into the zeolite in proximity to 1 or 2 Al ions an additional negative charge is required to balance the charge at the 1Al site, which is provided by OH$^{-}$ and is not present at the 2Al site. The presence of the intrinsic and strongly basic hydroxide ion at the 1Al site and not the 2Al site could possibly affect the chemistry of the reaction and is an area which is not well studied.

Monomers, dimers and Cu oxide clusters have all been considered as the active site for the SCR reaction, however Cu oxide clusters have been shown to be detrimental for SCR activity. The Cu loading or the Cu/Al ratio determines how much Cu there is in the zeolite. It is also established that under low temperatures conditions (< 250 °C) Cu is mobile throughout the zeolite. At low loadings the Cu density and therefore the concentration is low, meaning that at low temperatures upon migration the probability that another Cu species will be met is low, implying Cu species are likely always present as monomers. At medium to high loadings the Cu density is higher and upon migration in low temperature conditions isolated Cu is likely to meet in a chabazite cavity and form a Cu dimer, a process calculated to be energetically favourable and with low barrier. However, at very high Cu loadings it has been shown that Cu oxides start to form. The existence of dimers has been inferred as reaction rates as a function of Cu loading are fitted better to second order rates than first order rates under temperatures below 250°C and at medium to high Cu loadings. No spectroscopic evidence has been provided to date for the existence of dimers, however this could be due to these being transient and short-lived in nature. At temperatures between 250-350 °C the Cu complex loses solvation and attaches to the framework meaning it is no longer mobile and therefore is present as a monomeric species above these temperatures regardless of Cu loading. This temperature also corresponds to the ‘seagull’ features in the SCR light-off curve, which shows a dip in activity and is likely related to the changing Cu speciation either directly or indirectly. Therefore, the diverse range of Cu coordination environments and speciations complicates
analysis and makes it difficult to determine the reaction mechanism. As the active site is condition dependant it is possible that the microscopic details are different and that the different active sites could provide different activation barriers.

Each mechanistic proposal discussed has experimental evidence, and theoretical calculations utilising DFT to support the claims in their representative publications. However, none exhibit a complete atomic level reaction mechanism that fully describes the elementary reaction steps. Furthermore, each DFT simulated mechanism has been calculated using different parameters such as basis sets, functionals and the code used. This therefore means that the energies are on a different scale and cannot be directly compared to one another. There has yet to be a study in the literature which compares the different proposed reaction mechanisms to one another upon the same energy scale. Outstanding mechanistic considerations are still yet to be rationalised in the literature considering the elementary reaction steps and the precise electron movement in both the reduction and oxidation half-cycles. The reduction half-cycle is proposed to proceed via a combination of or all of the potential intermediates species HONO, H$_2$NNO and NH$_4$NO$_2$. It is currently undetermined which, and in what order the SCR reaction intermediates are formed. The oxidation half cycle is less well quantified. On the monomeric active site, it is proposed to proceed via nitrates and nitrites which dissociate into N$_2$ and H$_2$O, but the exact atomic level reaction steps are undetermined, and currently proposed steps have multiple electron transfers and likely contain multiple steps. On the dimeric active site the dissociation of the dimer or reforming of Cu monomers and evolution of N$_2$ is unknown. It is likely that each mechanism discussed is feasible and probably contributes to the overall activity in some minor way or that different mechanisms dominate under different conditions. The proposal by Paolucci et al proceeds over a single site and includes mechanistic details over 1Al and 2Al sites. Therefore, it could proceed over a range of SARs, but the monomeric site means it would be best suited to either low Cu loading or high temperatures. The proposals by Janssens et al is analogous to the fast SCR and requires a step oxidising NO to NO$_2$ and proceeds over the monomeric Cu site. This therefore could imply that this mechanism may dominate in the high temperature regimes irrespective of the zeolite parameters. The proposals by Gao et al and Hu et al proceed over dimeric species, and Hu et al hypothesize that two Cu monomers in close proximity is the
active site for the reduction half-cycle. These proposals could proceed at low temperatures and at medium to high Cu loadings. In reality there is likely a combination of each of these mechanisms proceeding all at once, which complicates analysis. Therefore, it would be beneficial to understand what conditions and zeolitic parameters promote certain favourable reaction steps and if anything can lower activation barriers.
4. Computational Details of This Work

With the advent of larger and faster computers, the techniques used for first principle calculations have on average moved on from cluster models to periodic boundary conditions (PBC) calculations, which can more accurately and explicitly represent the zeolite. Discrete cluster models were used with an aim to reduce the computational cost as only a small discrete set of T sites can be used to represent the zeolite lattice and is terminated by H atoms or is embedded into classically treated larger model of the zeolite.\textsuperscript{156,207} Cluster models offer the advantage that the computational cost is not related to the size of the unit cell and rather the cluster size one chooses, therefore first principle or \textit{ab initio} techniques can be used at a reasonable computational cost. They are also well suited to studying the local chemical environments and bonding around the active site. However, over the last 15 years or so, PBC calculations using either plane wave or Gaussian basis sets have taken over as the most frequently used technique. Supercell models use a repeating unit cell in PBC to fully represent the three-dimensional nature of the zeolite framework, and it is therefore possible to vary the Si/Al an Cu/Al content in order to compare different Al distributions and sites in order to study the effect of the variation of the framework on the Cu site and mobility.\textsuperscript{140,208,209} In this work, solid state material systems are modelled by periodic boundary conditions (PBC), which are used to represent the crystal lattice. This allows for an infinite repeating unit cell which represents the system. This method exactly reproduces perfect crystal lattices, however when modelling intrinsic or extrinsic defects, which are often present in real life situations the distortion created in the crystal lattice needs to be accounted for and minimised. Due to the periodic nature of the unit cell in PBC calculations, defects will be infinitely repeated in all directions. This means that if the unit cell is too small then neighbouring identical defects and the distortion caused by them, can interact with each other causing spurious effects and unwanted contributions to the total energy, rendering results obtained unreliable. Therefore, it is necessary to make sure that when modelling defective systems such as Al in a zeolite framework with PBC that the unit cell used is large enough to negate unwanted periodic effects.

All density functional theory calculations were performed using the CRYSTAL17 software package.\textsuperscript{210} The catalyst is represented by the hexagonal unit cell of SSZ-13 which contains
108 framework Si, Al and O atoms and one Cu atom and any additional reacting molecules and ligands. In the calculations the unit cell is always constrained to parameters of a=13.514 Å, b=13.638 Å, c=14.646 Å, α=90°, β=90° γ=120°. Experimental values of the unit cell are found to be a=b=13.675 Å c=14.767.\(^{103}\) CRYSTAL uses a linear combination of Gaussian functions as the basis sets (BS), to represent electronic orbitals and Gaussian BS are generally accepted to be a better representation than the alternative plane waves to describe insulators such as zeolites. Each element is described using an all electron BS: H is represented by 3-1p1G BS, Al by 85-11G* BS, Si by split valence 6-21G BS, Cu by 86-4111(41D)G BS, N by 6-21G* BS and O by 6-31d1 BS. These basis sets are explicitly written in full in the example CRYSTAL17 input file listed at the bottom of this section.

The electronic exchange and correlation terms are represented by the hybrid exchange functional PBE0, which uses 25 % Hartree-Fock exchange and the D3 dispersion correction is added to better represent adsorption upon Cu\(^{2+}\).\(^{37-40,211}\) The sampling of the reciprocal space for the system was performed with a Pack-Monkhorst net with a shrinking factor 2 along each periodic direction, generating points 8 in the irreducible Brillouin zone. All geometry optimisations were performed using the Broyden-Fletcher-Goldfarb-Shannon (BFGS) algorithm as implemented in CRYSTAL17, where the convergence is determined by the default tolerances used for the values of displacement and forces.\(^{212}\) Activation barriers for each reaction step are calculated using the distinguished reaction coordinate method. It works by employing a sequence of constrained geometry optimisations along a chosen reaction coordinate. A distance is selected between two atoms which represents the reaction coordinate then this distance is reduced (or increased) by a specified amount and at each step a constrained geometry optimisation is performed with this specified distance not able to change and every other coordinate is able to relax. This optimisation is performed in internal redundant coordinates. The distance then sequentially changed for each step until a specified distance is reached. This produces an energy profile where a maximum point represents a transition state. Full unconstrained geometry optimisations are performed for the start and end geometries. For example, if a proton is being transferred from NH\(_3\) to OH, the O to H on NH\(_3\) distance is constrained for each step. Other methods such as the nudged elastic band (NEB) can also successfully find transition states, where each method has strengths and weaknesses. The NEB method finds a transition state by using a set of images created by
interpolating between the initial and final state and sometimes an intermediate state. The reaction pathway can be found by performing a simultaneous optimisation between all the images created, therefore meaning the optimisations of the images are not independent from one another. There is a force acting upon each of the images which is dictated by the neighbouring images and at each step the forces parallel to the reaction path are cancelled. A spring force is included which keeps each image in the middle of its neighbours along the path. Therefore, this does not let images optimise to the initial or final states and means that each image is evenly distributed along the reaction path. Finally, once the NEB path is found, a climbing image algorithm is employed from the highest-energy image along the path to find the transition state. The benefit of the distinguished reaction coordinate method compared to the NEB method is that it can allow the user more control over the transition state search. For example, the PES along the reaction path and in particular around the transition state can be very complex. The distinguished reaction coordinate method allows the user to finely sample the more complex areas such as the transition state only, whereas in the NEB method the image density along the path must be increased, which increases the computational cost hugely. Therefore, for example a distinguished reaction coordinate transition state search can give more detail about around the important transition state than a NEB and potentially find double maxima whereas a NEB may only find one.

All minima and transition states found in this work were confirmed via a vibrational analysis. The presence of true local minima and transition states can be confirmed via a phonon calculation. When the vibrational modes are calculated a true minimum will show exactly three vibrational modes with zero frequency which corresponds to the translations in three-dimensional space and importantly show no vibrational modes which have a negative frequency referred to as imaginary modes. Hence all vibrational modes for a true minimum must be positive. A transition state on a potential energy surface corresponds to a saddle point which is given by a negative frequency in the CRYSTAL17 output file. To be at a first order saddle point which is of the most chemical interest as it represents the transition state there must be only one imaginary mode. Therefore, it is possible to check if one has computed a local (or global) minimum or a transition state by calculating the vibrational modes and inspecting the number imaginary modes; 0 for a minimum and 1 for a transition state. This analysis was performed for the majority of the minima and transition states discussed in this
thesis in order to check their validity, but due to the very large computational cost of computing the vibrational modes it has not been possible to compute them all.

It should be noted that various tests have been performed to confirm the accuracy of the computational parameters. The basis sets were determined by investigating the adsorption energies of relevant adsorbates to Cu\(^{2+}\). It was found that values converge to approximately 1 kJ mol\(^{-1}\) at the all-electron level and Cu is modelled using the largest basis set offered by the CRYSTAL17 code, as reproducing Cu accurately is the most important aspect. Large band gap materials like zeolites converge quickly as a function of k-point sampling and all calculations on these type of materials are performed at the gamma point only. The choice of 2x2x2 sampling on cell with > 100 atoms is usually converged which indeed was the case for this system. The choice of cell size was decided by what was feasible on a basis needed to sample the entire cycle. The cell size used is close in value to experimental values, as previously discussed and also is observed when unconstrained optimisations are performed in both the oxidation and reduction half cycles. Furthermore, the basis sets and basis set superposition error has been tested in our groups previous works in alkane oxidation in MeAlPOs and shown to be negligible.\(^{213}\) As a further check for computational accuracy the Cu-O bond lengths of the hexaaqua Cu complex were compared to experimental values.\(^{214}\) Values are all within 5-10 % of the values stated for both the long axial and shorter equatorial bonds in the complex.

The reactants in adjacent cells are sufficiently separated to not interact directly with each other and are therefore chemically isolated from the periodic images. The cell is then fixed to prevent cooperative effects which exist under PBC. Under real conditions the framework will relax when a reaction occurs but here, we are only concerned about the local forces on the reacting atoms.

An example input file for the computation of a transition state has been included, to aid in the replication of data for future (Appendix). This input file builds upon a geometry optimisation calculation and can be easily edited for use as a geometry optimisation.
Results and Discussion

5 Equilibrium Speciation of Cu

We start the presentation of our results by discussing the structure and location of Cu in SSZ-13. In this section the energies of the different proposed active sites will be compared in order to understand if there is any clear energetic preference, as the local environment of Cu has been proposed to change with temperature and Al distribution.\(^{90,126,137,163,175}\) First, the form of ‘bare’ Cu in Cu-SSZ-13 will be investigated i.e. Cu in the catalyst with no reaction molecules or ligands present and an energetic comparison between Z\(_2\)Cu and ZCuOH will be made. The adsorption of single molecules present in the SCR gas mixture to Cu will then be studied followed by the adsorption of multiple water and ammonia molecules to Cu. We also investigate the relative adsorption strength of SCR-relevant molecules to Cu and probe the variation in the configurational space of these to Cu in SSZ-13. And finally, we inspect the dimeric form of Cu and run molecular dynamic simulations to further understand the mobility of Cu and the dynamics of the coordination environment.

5.1 Bare Cu

As discussed in section 3, when Cu\(^{2+}\) is in proximity to a single Al species the excess charge must be balanced, which is provided by a OH\(^-\) ion (ZCuOH), whereas no additional ion is need when Cu\(^{2+}\) is near 2 Al species (Z\(_2\)Cu). Here, the most favourable position and Al distribution for Z\(_2\)Cu and ZCuOH within SSZ-13 are investigated. For ZCuOH, geometry optimisations are performed with Cu\(^{2+}\) located in the 6MR, 8MR and 4MR in absence of adsorbates. For Z\(_2\)Cu there is the added layer of complexity of considering the Al distribution. It should be noted a full and exhaustive study into the position of Cu and the Al distribution is not practical as it would be too computationally demanding. Therefore, we select locations and distributions likely to give lower energies; the templates used in the zeolite synthesis direct Al distribution and this cannot be modified independently in response to the presence of Cu and gas phase composition.

5.1.1 Z\(_2\)Cu

A selection of optimised geometries for Z\(_2\)Cu is shown in figure 5.1 and the main structural parameters summarised in table 5.1. We perform geometry optimisations for Cu occupying
the 6-, 4- and 8-MR at a range of Al distributions. It is found that in the 6MR Cu$^{2+}$ ions exhibit 4-fold coordination, whereas they can only achieve a 3-fold coordination when in the 8MR as it has a larger diameter and forming a 4$^{th}$ bond is not possible due to there not being another framework oxygen species in proximity. In the 6MR there are different coordination modes accessible, even at the same Al distribution. The lowest energy configuration has a square planar coordination with Cu$^{2+}$ in the plane of the ring, and to 4 oxygen framework species (O$_{fw}$) which are also coordinated to Al in the framework (Fig. 5.1a). A configuration 33.8 kJ mol$^{-1}$ higher in energy shows a distorted square planar geometry in which Cu coordinates to 3 O$_{fw}$ bonded directly to Al and one O$_{fw}$ species directly coordinated to only Si (Fig. 5.1b). This shows that a Cu coordination to oxygen species directly coordinated to a Al species (O$_{fw}$-Al) is stronger than a Cu coordination to an oxygen species only directly to only Si atoms (O$_{fw}$-Si). When the Al distribution is at 2NN (Fig. 5.1c) the energy is 55.1 kJ mol$^{-1}$ higher in energy showing the favourable Al distribution in the 6MR is the 3NN. When Al and Cu occupy the 8MR the energy is significantly higher than in the 6MR. This is because Cu can only form three bonds to the framework rather than 4 like in the 6MR due to the diameter of the ring. The 2NN configuration (Fig. 5.1e) is 168 kJ mol$^{-1}$ higher in energy and the 3NN (Fig. 5.1d) is 210 kJ mol$^{-1}$ higher in energy. Cu occupying the 4MR is much higher in energy than the other areas with a 359 kJ mol$^{-1}$ increase in energy compared to the 6MR (Fig. 5.1f).

<table>
<thead>
<tr>
<th>ZCu Location</th>
<th>Al Distribution</th>
<th>Geometry</th>
<th>Energy / kJ mol$^{-1}$</th>
<th>Bond lengths / Å</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>6MR</td>
<td>3NN</td>
<td>Sq planar</td>
<td>0.0</td>
<td>1.94, 1.96, 1.98, 1.92</td>
<td>5.1.1a</td>
</tr>
<tr>
<td></td>
<td>3NN</td>
<td>Distorted sq planar</td>
<td>34</td>
<td>2.02, 1.92, 1.93, 1.97</td>
<td>5.1.1b</td>
</tr>
<tr>
<td></td>
<td>2NN</td>
<td>Distorted sq planar</td>
<td>55</td>
<td>1.92, 2.04, 1.994, 1.92</td>
<td>5.1.1c</td>
</tr>
<tr>
<td>8MR</td>
<td>3NN</td>
<td>Trigonal Planar</td>
<td>210</td>
<td>1.86, 2.00, 1.85</td>
<td>5.1.1d</td>
</tr>
<tr>
<td></td>
<td>2NN</td>
<td>Trigonal Planar</td>
<td>168</td>
<td>1.88, 1.93, 1.87</td>
<td>5.1.1e</td>
</tr>
<tr>
<td>4MR</td>
<td>3NN</td>
<td>Trigonal pyramidal</td>
<td>359</td>
<td>2.161, 2.021, 2.205</td>
<td>5.1.1f</td>
</tr>
</tbody>
</table>

Table 5.1 | A list of the different locations and Al distributions of the Z$_2$Cu site and their corresponding energies and both lengths.
83

5.1.2 ZCuOH

The variation in energy with Cu location around the zeolite cage is significantly less for the ZCuOH site compared to the Z2Cu site (Table 5.2). In the 6MR (Fig. 5.2a) there is a 3-fold coordination to framework oxygen and a coordination to the hydroxyl giving a total Cu coordination number of 4, but in the 8MR the framework coordination drops to 2 and retains the hydroxyl coordination giving total coordination of 3. However, in the 8MR there is an additional hydrogen bond formed from the hydroxyl to the 8MR, which stabilises the overall structure despite the lower coordination to the Cu ion. When Cu occupies the 8MR the overall coordination number to Cu falls from 4 to 3 as compared to the 6MR, which increases the energy. When Cu is coordinated to only one Ofw-Al (Fig. 5.2b) the energy is 64.2 kJ mol⁻¹, but when Cu bridges over the Al species and coordinates to 2 Ofw-Al species the energy is only 14.8 kJ mol⁻¹ higher than when Cu is in the 6MR (Fig. 5.2c). This set of results shows again that coordination to Ofw-Al is stronger than Ofw-Si, but different. Local minima of comparable energy exist in the PES, hence in real conditions Cu will be sampling a range of non-equal local configurations, even if the Al distribution and all other factors are identical for all sites. When Cu occupies the 4MR the energy is calculated to be 56.6 kJ mol⁻¹ higher in energy than the 6MR (Fig. 5.2d). The stability of Z2Cu in the 6MR compared the 4- and 8MRs is significantly
greater than the stability of ZCuOH in the 6 MR than compared to the 4- and 8MRs. This is because the OH⁻ on ZCuOH is able to form a hydrogen bond with the framework in the 4- and 8MR which isn’t accessible in the 6MR stabilising these positions relative to the Z₂Cu site. However, the loss of coordination number of Cu to O_{fw} upon moving from the 6MR to 4 or 8MR outweighs the energy gained by forming a hydrogen bond to the framework meaning the 6MR is still the most energetically favourable for the ZCuOH site.

<table>
<thead>
<tr>
<th>ZCuOH Location</th>
<th>Geometry</th>
<th>Energy / kJ mol⁻¹</th>
<th>Cu-O_{fw} Bond Lengths / Å</th>
<th>Cu-OH⁻ Bond Length / Å</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>6MR</td>
<td>Distorted Square Planar</td>
<td>0.0</td>
<td>2.27, 1.94, 2.23</td>
<td>1.76</td>
<td>5.2a</td>
</tr>
<tr>
<td>8MR</td>
<td>Trigonal Planar</td>
<td>64.2</td>
<td>1.91, 2.20</td>
<td>1.73</td>
<td>5.2b</td>
</tr>
<tr>
<td></td>
<td>Trigonal Planar</td>
<td>14.8</td>
<td>2.00, 1.92</td>
<td>1.73</td>
<td>5.2c</td>
</tr>
<tr>
<td>4MR</td>
<td>Trigonal Planar</td>
<td>56.6</td>
<td>2.05, 2.05</td>
<td>1.75</td>
<td>5.2d</td>
</tr>
</tbody>
</table>

*Table 5.2* | A list of the different locations and Al distributions of the ZCuOH site and their corresponding energies and both lengths.

*Figure 5.2* | The structure of ZCuOH at different locations and Al distributions in SSZ-13. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; gold=Cu
5.1.3 $Z_2Cu$ and $ZCuOH$ Comparison

It is not possible to directly compare the energy of $Z_2Cu$ and $ZCuOH$ sites as the computational unit cells have non-equal compositions, and therefore are on different energy scales. In order to compare the two sites, it is necessary to build a 2x1x1 supercell containing 2Al species, 1 Cu$^{2+}$, 2 hydrogens and 1 oxygen to compute a hypothetical exchange energy between the two sites, as this super cell contains two distinct chabazite cages. Mass balance requires the addition of 1 water molecule on the $Z_2Cu$ site, which can be either adsorbed on Cu or in the gas phase. Two different exchange energies represented by equations 5.1 and 5.2 are compared in order to understand if the adsorption of water onto Cu offsets the energy.

\[
[Z_2Cu(H_2O)] \rightarrow [ZCuOH] + Z/H 
\]  

5.1

\[
[Z_2Cu] + H_2O \rightarrow [ZCuOH] + Z/H 
\]  

5.2

In equation 5.1 water is directly adsorbed onto $Z_2Cu$ and the other cavity is empty, whereas in equation 5.2 $Z_2Cu$ is in one cavity and water occupies the other. $\Delta E$ for equation 5.1 is 174 kJ mol$^{-1}$ and for equation 5.2 $\Delta E$ is 126.5 kJ mol$^{-1}$. The corresponding geometries are shown in figure A5.1. Therefore, the $Z_2Cu$ site is found to be significantly more stable than the $ZCuOH$ sites independent on whether water is either adsorbed onto Cu or occupying the other cavity. It is, however, the SAR (the Al content) which will determine the distribution of Al and therefore the active site, and not just the thermodynamics of the Cu adsorption. The synthesis conditions also play a role in determining the proportion of paired Al to isolated Al too. Because the Al distribution is not only dependent upon the thermodynamics of the system, but the kinetics too, under high SARs and synthesis conditions conducive to 1Al sites prior to Cu ion exchange isolated Al sites will exist. The results do however signify that if both isolated and paired Al species are present, upon ion exchange of Cu the paired sites will be populated first due to the energetic preference of Cu located at paired Al sites compared to isolated Al sites. This also agrees with other works in literature.\textsuperscript{93}

5.2 Adsorption Study

To be able to fully understand the reaction mechanism, it is first necessary to understand how the molecules present in the reaction interact with the active Cu species and the effect of adsorption on Cu location. The species present in the SCR reaction cycle include NH$_3$, H$_2$O, NO, O$_2$ and N$_2$ that can all interact with Cu$^{2+}$ and Cu$^+$ and adsorb onto these ions. It is therefore
useful to understand the strength of the adsorption to provide a realistic simulation environment for the SCR reaction. First adsorption of single molecules is investigated in section 5.1, then water and ammonia sequential adsorption is studied in section 5.2.

5.2.1 Adsorption of Single Molecules
Geometry optimisations are performed in order to calculate the adsorption energy of H$_2$O, N$_2$, O$_2$, NO and NO$_2$, to both Cu$^{2+}$ and Cu$^+$ in proximity to 1Al and 2Al sites. Table 5.3 shows the adsorption energies of each molecule to Z$_2$Cu, ZCuOH, ZCu and ZCu-Z/NH$_4$ and table A5.1 shows more detail with the corresponding geometries and bond lengths. The equilibrium geometries are shown in figures A5.2-5.8. The geometry optimisations start from the stable position of bare Cu in the 6MR.

Adsorption energies ($E_{ads}$) are calculated using equation 5.1. $E_{zeo}$ represents the energy of the zeolite and Cu active site and $E_{mol}$ the energy of the absorbing molecule. The energy of the isolated adsorbing molecule is calculated in a non-periodic vacuum initially. In this case favourable adsorption is represented by negative adsorption energies.

$$E_{ads} = E_{zeo+mol} - (E_{zeo} + E_{mol})$$ \hspace{1cm} 5.1

| Molecule / Site | Z$_2$Cu | ZCuOH | ZCu | ZCu-Z/NH$_4$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>-167</td>
<td>-172</td>
<td>-158</td>
<td>-136</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-121</td>
<td>-127</td>
<td>-121</td>
<td>-114</td>
</tr>
<tr>
<td>N$_2$</td>
<td>-60</td>
<td>-49</td>
<td>-83</td>
<td>-75</td>
</tr>
<tr>
<td>O$_2$</td>
<td>-45</td>
<td>-32</td>
<td>-103</td>
<td>-119</td>
</tr>
<tr>
<td>NO</td>
<td>-60</td>
<td>-73</td>
<td>-106</td>
<td>-119</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>-157</td>
<td>-215</td>
<td>-278</td>
<td>-330</td>
</tr>
</tbody>
</table>

*Table 5.3 | The adsorption energy of H$_2$O, NH$_3$, N$_2$, O$_2$ and NO$_2$ to Z$_2$Cu, ZCuOH, ZCu and ZCu-Z/NH$_4$*

Water binds to Cu$^{2+}$ and Cu$^+$ sites similarly, with adsorption energies ranging from -114 to -127 kJ mol$^{-1}$, with coordination to Cu$^{2+}$ being slightly more energetically favourable than Cu$^+$. On each site water displaces an O$_{fw}$ bond to keep the overall coordination number at 4. Each Cu site exhibits a distorted square planar / tetrahedral apart from the ZCuOH site as it only
has two Cu-Ofw bonds because the OH\(^{-}\) ion displaces an additional framework bond with the adsorbate and therefore exhibits a square planar geometry.

NH\(_3\) out-binds H\(_2\)O on each site and has adsorption energies between -136 and -167 kJ mol\(^{-1}\). The adsorption behaviour mirrors that of water, where each ligand displaces a Ofw bond and pulls Cu out of the plane of the 6MR. The OH\(^{-}\) on the ZCuOH site also displaces an additional Ofw bond allowing the complex to access square planar geometry. Binding to Cu\(^{2+}\) is slightly stronger than to Cu\(^{+}\). Adsorption of both H\(_2\)O and NH\(_3\) do not change the oxidation state of Cu as the spin states on Cu before and after the adsorption are comparable.

NO binds weakly to Cu\(^{2+}\) with adsorption energies of -60 and -73 kJ mol\(^{-1}\) for Z\(_2\)Cu and ZCuOH respectively, and more strongly to Cu\(^{+}\) with adsorption energies of -106 and -119 kJ mol\(^{-1}\) for ZCu and ZCu-Z/NH\(_4\) respectively. Minimal change in electron spin states are observed on both Cu and NO upon adsorption for both Cu\(^{+}\) and Cu\(^{2+}\) and all exhibit NO coordinated to Cu in a bent configuration as would be expected when there is minimal π back donation from the metal centre.

N\(_2\) adsorption to both Cu\(^{+}\) and Cu\(^{2+}\) is weak, but stronger on Cu\(^{+}\) with adsorption energies on Z\(_2\)Cu and ZCuOH being -60 and -49 kJ mol\(^{-1}\) respectively and -83 and -75 kJ mol\(^{-1}\) on ZCu and ZCu-Z/NH\(_4\) respectively.

Upon oxygen adsorption, it is found that O\(_2\) behaves differently on Cu\(^{+}\) and Cu\(^{2+}\). With Cu\(^{2+}\), the adsorption strength is weak, and it is coordinated in an end-on fashion to Cu where Z\(_2\)Cu and ZCuOH sites have adsorption energies of -45 and -32 kJ mol\(^{-1}\) respectively. However, on Cu\(^{+}\) O\(_2\) adsorbs in a side-on configuration and has stronger adsorption energies of -103 and -119 kJ mol\(^{-1}\) on ZCu and ZCu-Z/NH\(_4\) sites respectively. The coordination of O\(_2\) to Cu has an important contribution to the reaction mechanism which is discussed further in section 9.

NO\(_2\) adsorbs strongly onto Z\(_2\)Cu and ZCuOH with adsorption energies of -157 and -215 kJ mol\(^{-1}\) respectively as a bidentate ligand. Both Cu and NO\(_2\) retain their unpaired electron and the electronic states are unaffected. On the ZCuOH site, a hydrogen bond is formed between OH\(^{-}\) and NO\(_2\) which is not present at the Z\(_2\)Cu and is a potential reason why the adsorption energy on ZCuOH is stronger compared to Z\(_2\)Cu. On Cu\(^{+}\) sites the adsorption of uncharged NO\(_2\) and NO\(_3\) induces electron movement in the form of oxidation of Cu to Cu\(^{2+}\), which is accompanied by a very large change in energy on the order of 300 kJ mol\(^{-1}\). The large adsorption energy is
due to the increased attraction between Cu and the adsorbing species after electron transfer. It should be noted that NO$_2$ is unlikely to exist as a neutral molecule during the SCR reaction and would rather form ammonium nitrite species. The adsorption energies were calculated to see how adsorption modes differ between different species and the adsorption energies of ions are beyond the scope of this thesis.

Both water and ammonia behave similarly upon adsorbing to the various Cu sites, but with ammonia out-binding water by 30-40 kJ mol$^{-1}$ consistently on each site. The adsorbed molecules, pulls Cu up out of the plane of the 6MR compared to its starting position, and for the ZCuOH a square planar geometry is observed due to the additional OH$^-$ coordination, which further pulls Cu out of the plane of the ring. For the other sites, a geometry somewhat between a square planar and tetrahedral geometry is observed, as Cu attempts to coordinate to 4 species if they are in close enough proximity. Furthermore, the O$_{nw}$ site adjacent to Al ions bind more strongly to Cu, therefore Z$_2$Cu sites hold Cu more strongly to the framework. Water and ammonia both adsorb to Cu$^{2+}$ more strongly than Cu$^+$. The behaviour of N$_2$ and NO is also similar. They coordinate in an end on manner and adsorb to Cu$^+$ more strongly than Cu$^{2+}$. O$_2$ however changes its behaviour as it coordinates to Cu$^+$ in a side-on mode whereas for Cu$^{2+}$ it coordinates end-on. The coordination mode of O$_2$ to Cu$^+$ is found to be a key aspect of the oxidation half cycle and will be further discussed in section 8. This gives a significantly higher adsorption energy in the side-on mode. These species show no change in spin states upon adsorption and therefore no change in oxidation state.

5.2.2 Adsorption of Multiple Water and Ammonia Molecules
In the Cu-SSZ-13 catalytic system, multiple molecules will absorb onto Cu, especially at lower temperatures. Water has the highest concentration in the exhaust gas feed, whereas ammonia is injected into it and adsorbs strongly onto Cu, so both will interact significantly with the Cu ions. Here, the adsorption of multiple water and ammonia molecules to Cu$^+$ and Cu$^{2+}$ sites is investigated. The investigation is extended to consider the configurational differences in the complex. Differences in the position and configuration of the complex, the interplay between the first and second solvation shells and Cu-O framework coordinations can all affect the energy of the system. It is not possible to complete an exhaustive study for all the possible adsorption configurations of water and ammonia to Cu active sites, as the
number of configurations would be too large to be computationally feasible. Therefore, a limited selection of geometries are taken in order to see how the energy of the system depends on the number and arrangement of molecules around the mono-Cu active site.

Figures 5.3 and 5.4 show the adsorption energies sequentially of water and ammonia respectively in different configurations to the 4 different active sites, Z₂Cu (black), ZCuOH (red), ZCu-Z/NH₄ (blue) and ZCu (green). Tables A5.2 and A5.3 report the same adsorption energies, but with added detail including the coordination environments and relative energies. The corresponding geometries of each complex in the different adsorption modes are shown in figures A5.9-A5.16. The adsorption energies are calculated from the lowest energy configuration, which has one fewer molecule adsorbed where each molecule is directly coordinated to Cu. The energy of the adsorbing molecule is calculated in the gas phase. The adsorption energy is calculated as in equation 5.2 where a positive adsorption energy denotes favourable adsorption in this case.

\[
E_{ads} = E_{zeo}(x + 1) - (E_{zeo}(x) + E_x)
\]

Figure 5.3 | The adsorption energies of water molecules to various different Cu active sites. The adsorption energy is calculated relative to a complex with one less molecule adsorbed to it. There are different adsorption configurations included, which adsorb at different strengths, the solid lines represent the strongest adsorption to each complex.
Adsorption of water and ammonia up to a coordination number of 6 (5 additional molecules for ZCuOH) is favourable, and there are multiple adsorption configurations accessible on the Cu sites. For both water and ammonia at Z2Cu, 6-fold coordination to Cu$^{2+}$ shows that the most favourable geometry is octahedral. This is not the case for the ZCuOH sites, however, as when 5 NH$_3$ molecules are in proximity to Cu the lowest energy configuration is not octahedral but trigonal bipyramidal with one NH$_3$ molecule in the second solvation shell. When a molecule occupies the second solvation shell a hydrogen bonding network is present and can lower the energy of the system to similar or lower than that of direct coordination. For both water and ammonia the removal of one adsorbate from direct coordination to Cu into the second solvation shell, hydrogen bonded to other molecules and O$_2$ or O$_{FW}$ species is of comparable energy to all species occupying the first solvation shell. This can be seen in figure 5.5. There is only a 0.6 kJ mol$^{-1}$ difference in energy between the hexaaqua complex on Z2Cu and 5 direct water coordinations to Cu$^{2+}$ and one water molecule occupying the second solvation shell (Fig. 5.5a) The same situation for ammonia is only 7 kJ mol$^{-1}$ higher in energy (Fig. 5.5b). In fact, it is more energetically favourable to have some molecules in the second solvation shell rather than all directly coordinated to Cu$^{2+}$ in some situations, which usually

Figure 5.4 | The adsorption energies of ammonia molecules to various different Cu active sites. The adsorption energy is calculated relative to a complex with one less molecule adsorbed to it. There are different adsorption configurations included, which adsorb at different strengths, the solid lines represent the strongest adsorption to each complex.
correspond to fuller chabazite cages with high levels of steric hindrance. For example, for water when 4 molecules are in the simulation with Z\textsubscript{2}Cu it is 38 kJ mol\textsuperscript{-1} more favourable to have three direct coordinations to water, two framework coordinations and a water molecule in the second solvation shell with hydrogen bond, compared to four direct coordinations in a square planar configuration (Fig. 5.5c). For ammonia adsorption this situation can be more predominant compared to water. On the ZCuOH site and with 5 ammonia molecules present, it is calculated to be 63 kJ mol\textsuperscript{-1} more favourable to have one molecule in the second solvation shell rather than all 5 directly coordinated to Cu\textsuperscript{2+} (Fig. 5.5d). There is also a different configuration shown to be 25 kJ mol\textsuperscript{-1} more energetically favourable than the octahedral configuration. These low energy configurations, however, show five coordinated Si species and only exists on the ZCuOH site as OH\textsuperscript{-} binds to a framework Si atom to yield the S-coordinaed geometry. This Si environment is unexpected and has only previously been reported in zeolites in the presence of F\textsuperscript{-}.\textsuperscript{215} The five coordinate Si is often present upon geometry optimisation and usually corresponds to low energy configurations and will be discussed further in section 5.4.5.
Figure 5.5 | Example configurations where molecules occupying the second solvation shell are either comparable in energy or lower in energy than a situation where all molecules are directly coordinated to Cu. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
Adsorption of water and ammonia to Cu$^+$ differs to that of Cu$^{2+}$. The first and second adsorptions to Cu$^{2+}$ are more exothermic than the rest, whereas for Cu$^+$ each adsorption is of similar energy. Coordination chemistry shows that Cu$^{2+}$ species favour a square planar coordination environment whereas Cu$^+$ species favour tetrahedral. Often, a complex tends to exhibit a different or distorted geometry, but at an energy penalty. Cu$^{2+}$ complexes have favourable direct adsorption of water and ammonia complexes up to coordination number 6 in an octahedral geometry. Cu$^+$ complexes however can only have a maximum coordination number of 5 in a square pyramidal geometry. Adsorption of water or ammonia into the second solvation shell of Cu$^+$ complex is also an exothermic process, and the formation of a hydrogen bond is comparable in energy to direct coordination to Cu. Adsorption of ammonia is consistently stronger to Cu$^+$ than water.

It is clear that there is a varied behaviour of ligands around Cu$^+$ and Cu$^{2+}$. For example, it has been calculated that water and ammonia configurations around Cu$^{2+}$ can vary by up to 55 kJ mol$^{-1}$ and 60 kJ mol$^{-1}$ respectively. For water and ammonia, the energy of configurations around Cu$^+$ can vary by 70 and 110 kJ mol$^{-1}$ respectively. This is a large range of energy considering there are no electronic changes only the spatial rearrangement of molecules. There are small differences in energy between bonding configurations which include different geometries, different numbers of molecules in the first and second solvation shells and various coordinations to framework oxygen species. This implies that at moderate temperatures a range of different configurations of molecules around Cu will be possible. As the temperature increases to SCR reaction conditions more configurations with higher energies will become available. It is possible that different configurations of Cu complexes with very similar energies could behave differently under reactions conditions.

Thus far adsorption energies have been calculated using equation 5.1, however there is a source of error due to the difference in calculated energy between a molecule in a pure vacuum and a non-interacting molecule in an SSZ-13 zeolite cavity. To understand the magnitude of the error we calculate the energy difference between a pure silica SSZ-13 zeolite and a water molecule in a vacuum, and a pure silica SSZ-13 with a water molecule with the oxygen atom fixed in the centre of the large chabazite cavity, so it doesn’t interact with the framework species. We calculate the difference to be 30 kJ mol$^{-1}$. As the method used for calculating adsorption energies in this section is consistent the results obtained above can be
compared to each other and our analysis holds, however, if comparing to experimentally calculated values the error should be considered. The most probable explanation for the source of this error is that the complex electrostatic field created by alternating point charges in the zeolite framework which creates a Madelung field that interacts with the water in the chabazite cage, changing the energy of the water molecule compared to that calculated in a pure vacuum with no interactions possible.

Li et al. also noticed this same phenomenon and devised an elegant but expensive and time-consuming scheme to adjust for the error. They propose a ‘potential of mean force’ method that involves sequentially moving the admolecule away from the adsorbent and subtracting the difference in energy of the admolecule in a pure vacuum and in a volume the same size as the zeolite cavity to adjust for errors.

5.2.3 Relative Strength of Ligand Interaction with Cu$^{2+}$
Here, an alternative method for combating the source of error highlighted in the previous section is proposed which differs to that demonstrated by Li et al. The method is based on the well-known Jahn Teller effect and allows the qualitative deduction of the order of adsorption strength of molecules to Cu$^{2+}$ within a zeolite, rather than a quantitative adsorption energy. Cu$^{2+}$ complexes are well known to exhibit Jahn-Teller distortion due to their d$^9$ electronic configuration, which causes a break in the degeneracy of the energy of the molecular orbitals, which subsequently lowers the overall symmetry and energy of the system. For an octahedral Cu d$^9$ complex the degeneracy is removed from t$_{2g}$ and e$_g$ orbitals by lowering the energy of 2 of the t$_{2g}$ orbitals and raising one, while one e$_g$ orbital is raised and the other lowered. This situation causes the lengthening of the two axial bonds and the contraction of the four equatorial bonds. It is also possible for the orbitals to split in the opposite way causing contraction of the axial bonds and lengthening of the equatorial bond, however this situation is less common.

If a strong ligand, such as H$_2$O or NH$_3$, occupies the weaker and therefore longer bonds of a Jahn Teller distorted octahedral complex the energy of the system will be stabilized more than if a weaker ligand, such as NO or N$_2$, is in the longer bonds as it will bond more strongly to the central Cu ion. These two effects of ligand strength and bond strength can be used to compare the adsorption energy of different molecules to Cu in a qualitative way. Therefore, when the
energies of two conformations of the ligand of interest in the long and short bond are taken relative to each other a small change in energy represents a strongest ligand. When this difference in energy is compared for different ligands an order of adsorption strength can be deduced. Calculations are performed for H₂O, NO, NO₂, N₂O, O₂ and N₂ on both Z₂Cu and ZCuOH sites, where all other ligands are NH₃, as NH₃ binds more strongly to Cu that all the other ligands. The bar charts in figure 5.6 a, b show the strength of adsorption, the images in figure 5.6 c, d show example geometries of water occupying the long and short bonds for both Z₂Cu and ZCuOH sites as a representative example. The equations in figure 5.6 represent the energy for the exchange of a ligand X in the long and short bonds of a Jahn-Teller distorted complex.

Figure 5.6 | The energy of exchanging a ligand between long and short bonds of a Cu²⁺ complex and equations representing this. a,c) the Z₂Cu site and b,d) the ZCuOH site with corresponding example geometries. Inside [ ] represents ligands in the 1st solvation shell and inside { } represents ligands in the short bonds of the complex, all ligands in [ ] but not in { } are in the long bonds of the complex. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu

These results indicate an order of adsorption strength to Cu²⁺ for admolecules relevant to the SCR in SSZ-13 as:

\[ NH_3 > H_2O > NO_2 > O_{fw} > N_2 \approx O_2 \approx NO \]
The smallest difference in energy for both Z$_2$Cu and ZCuOH sites is water, showing that it outbinds all other molecules except NH$_3$. The results obtained match the spectrochemical series reasonably well with the only obvious exception being NO$_2$, which is thought to be a better ligand than H$_2$O and NH$_3$, however this is not the case in our results. A possible explanation could be that NO$_2$ cannot access its preferred coordination mode in the equatorial bonds of the octahedral complex. Overall, there is a smaller energy difference between the long and short bond configurations for the ZCuOH site than the Z$_2$Cu site, despite similar geometries. This result highlights the complexity involved in sampling the configurational space of Cu-SSZ-13.

5.4 The Configurational Space
The Cu centres in SSZ-13 have been shown to have a complex configurational space in the presence of adsorbed molecules like water and ammonia where structurally different complexes can differ by a small amount of energy, which is shown in section 5.2. Complexes which have very high energies due to their molecular arrangement, are unlikely to be accessible at low to mid temperatures. The variation in energy depending on the arrangement of molecules in the configurational space is essential to understand, as it is possible that certain structures which are higher in energy than the ground state could give overall lower energy pathways for the reaction to proceed. Under typical SCR conditions where more than just a single type of molecule is present in the gas stream, the complexity in the configurational space is increased.

To further study the configurational space the [Cu$^{2+}$(OH$^-$)(H$_2$O)(NH$_3$)(NO)]$^+$ complex with four non-equal ligands has been chosen to be investigated further, as this allows for the extreme case of geometric isomerism. 23 different starting configurations of the complex were generated by varying the isomerism and geometry of the complex and also the position and orientation of the Cu complex relative to the zeolite cage. The structures are then fully relaxed via a geometry optimisation and the total energy calculated. The energy of each system relative the most stable geometry is shown in figure 5.7a. The overall energy of the system is seen to vary by over 100 kJ mol$^{-1}$. The highest and lowest energy structures are shown alongside the graph (Fig. 5.7a, b)
Figure 5.7 | a) the variation in energy of the system as a function of configurational space around the zeolite cage. b) lowest energy configuration c) highest energy configuration. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu

There are 7 distinct conformations which all have relative energy within 20 kJ mol$^{-1}$ and 18 within 60 kJ mol$^{-1}$ from the minimum energy case. There are two main similarities between the configurations of the lowest energy:

1) A square planar geometric feature is observed, as can be observed in figure 5.7b
2) The hydroxide ligand bonds to a framework Si species giving Si five-fold coordination.

The low energy case shown in figure 5.7 shows both these features. The high energy complexes often present a seesaw-like geometry including the highest energy complex as shown in figure 5.7 however, this is not necessarily the case for all coordination environments. When four bulky ligands like NH$_3$ coordinate to Cu$^{2+}$ the seesaw geometry becomes more comparable in energy to that of square planar structures.

5.4.1 5-Coordinate Si
The occurrence of pentavalent Si in the Cu-SSZ-13 system is an unexpected result. It has been previously shown that in zeolites only in the presence of fluoride ions, are reported to dynamically shift between Si sites fluctuating between 4 and 5 coordination.$^{215}$ This is also likely to happen in Cu-SSZ-13 with OH$^-$ ions as it is a dynamic system. Figure 5.8a shows example geometries of a five-coordinated Si and the difference in energy between the four and five coordinated versions of similar geometries and Figure 5.8b a closer view of the Si geometry. The energy gained upon formation of the five-coordinate Si ranges between 5 and 25 kJ mol$^{-1}$ depending upon the configuration, which is of low enough energy to be fluctuating dynamically between 4 and 5 coordination, or at low temperatures stable as the 5-coordinate
structure. The geometry around the Si atom is trigonal bipyramidal and the bond lengths range from 1.63 Å to 1.86 Å with the longer bonds corresponding to those bridging the Cu$^{2+}$ ion. The bond lengths are in line with those in the framework. The Cu-OH bond length is 1.93 Å and in line with other Cu-OH bond lengths where a 5 coordinate Si is not observed.

Figure 5.8 | Comparison between geometries and the energy of structures of the same ligation but with four and five coordinated Si. The 5-coordinate Si is circled in green. The lower panel shows another optimisation where 5-coordinate Si was present, showing each coordination around the Si atom in the plane of the 6MR. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu

The pentavalent Si is found to only occur when ZCuOH is in the presence of ammonia. It does not matter how many ammonia ligands are coordinated to Cu, but no 5 coordinated Si was found when no ammonia was present in the simulation cell. This is evident from analysis of a wide range of calculations. Furthermore, the presence of the five coordinated Si appears to be independent of the coordination number of Cu$^{2+}$ or the number of ligands in the simulation cell with the five-coordinated Si observed with only two ligands on Cu, or up to six. As this was an unexpected result, we investigated whether the five-coordinated Si was a symptom of the code, the use of a hybrid exchange functional or the dispersion correction used, however this is not the case as the five-fold coordination was present using the code CRYSTAL17 for functionals: PBE0+D3, PBE0 and PBE. Its presence was also confirmed using the code CP2K with functionals: PBE0+D3 and PBE. NMR would be a potential experimental validation of five-coordinate Si in Cu-SSZ-13 in the presence of ammonia. However, the paramagnetic Cu$^{2+}$ will dominate over any NMR signal from the five-coordinate Si as the Cu$^{2+}$
is in too close proximity to it. Also x-ray absorption techniques will not be able to detect the signal from 5 coordinated Si as it will be overwhelmed by 4-coordinated Si signals. Our interpretation is that the strong electron donor features of adjacent NH₃ molecules make the OH- ion a stronger nucleophile, able to interact strongly with the framework. Si therefore can behave in a similar way to F- resulting in the formation of a 5-coordinate framework Si intermediate.

5.4.2 Cu Dimer
Dimeric Cu species have also been proposed as a catalytically active centre for the SCR reaction. Here, supercell calculations are used to compare the energy between the monomeric form of Cu and the dimeric form. The dimeric form can exist as a true dimer with bridged OH⁻ between Cu²⁺ or as a proxemic form, where two monomers exist and interact within the same chabazite cavity, but without forming a true dimer. We use a 2x1x1 supercell with an isolated Al and 3NH₃ ligands coordinated to Cu²⁺. The lowest energy structure is found to be the true dimeric form where 2 OH⁻ species bridges Cu²⁺ (Fig. 5.9a). However, this is only 18 kJ mol⁻¹ lower in energy than two monomers situated in different chabazite cavities (Fig. 5.9b). Interestingly, another form of the dimer where only 1 OH⁻ species bridges Cu²⁺ can also be optimised and is 36 kJ mol⁻¹ higher in energy than the true dimer (Fig. 5.9c). The other OH⁻ is in a square planar bond to Cu²⁺. The proxemic form where two monomers are in the same cavity, shows one Cu in a square planar complex and the other in a distorted square planar geometry. The OH⁻ ligand does not bridge the two Cu ions but interacts weakly with the other Cu and a hydrogen bond forms between an NH₃ molecule and the other OH⁻. This configuration is 38 kJ mol⁻¹ less favourable than the true dimer. All the configurations generated are reasonably close in energy. This signifies that the monomeric species and dimeric species could both be present during the SCR reaction cycle and therefore both need to be considered as active sites. It should be noted that this short study into the dimer was completed in a later stage of the research project in order to see if under our computational details the Cu dimer forms could be energetically stable. Furthermore, the Cu dimer has only thus far been studied on the 1Al site rather than the 2Al site. The 2Al site has additional electrostatic attraction from the Al atoms to Cu which implies that Cu monomers which are less screened from the framework will be more stable at 2Al
sites than compared to 1Al site. However, this will need investigating to be confirmed. In this study the focus of the reaction cycle is exclusively on the Cu monomer.

**Figure 5.9** (a, c d,) The different forms of Cu dimer calculated. b) shows the two separate complexes in different respective chabazite cavities Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
6 Molecular Dynamics Simulations

Results discussed in chapter 5 show that Cu in the presence of gas phase molecules representative of SCR conditions has multiple accessible configurations of comparable energy that differ in the number, orientation and relative position of the admolecules interacting with Cu. It is important for the understanding of the SCR reaction mechanism to see if these configurations are dynamic or long-lived. It has also been seen that the energy of the system can vary by over 100 kJ mol\(^{-1}\) just depending upon the arrangement of molecules and Cu in the cage with no bond breaking process involved. The static study cannot provide information on the energetics required to transition between these configurations of molecules around Cu, or at what temperatures transitions can happen. It cannot be deduced whether a complex can undergo a certain rearrangement by inspection of static energies alone. Ab initio molecular dynamics (AIMD) simulations have been employed to probe possible rearrangements of molecules around the Cu complex. Low activation energy rearrangements can be investigated through molecular dynamics simulations. We have applied this technique to a selection of Cu complexes in SSZ-13 studied in the previous section, to understand whether ligand exchange or rearrangement reactions are possible under SCR conditions. Furthermore, molecular dynamics simulations can be used to follow the motion and migration of Cu through the zeolite and to understand differences between the Z\(_2\)Cu and ZCuOH sites. For example, the area of additional electrostatic charge created by an additional Al ion in the 6MR could more strongly anchor the Cu ion to the framework compared to the 1Al site. This could have important mechanistic implications. AIMD runs are performed on a range of different Cu complexes on both Z\(_2\)Cu and ZCuOH sites in order to understand the dynamics of the coordination environment and if the different sites affect the mobility of Cu.

CRYSTAL17 does not have the capability to perform molecular dynamics simulations, therefore the CP2K code is employed. CP2K like CRYSTAL17 uses DFT to calculate the electronic structure of a system, however CP2K can significantly cut computational costs by mixing the use of Gaussians and plane waves. This is employed by expanding the Kohn-Sham orbitals in Gaussians functions and representing the electronic density via an augmented planewave approach. This allows near linear scaling with the system size compared to conventional DFT techniques, that scale as \(n^3\) where \(n\) is the number of basis sets used. AIMD computes the Newtonian forces upon the individual atoms of a system numerically which
allows their motion of the system to be followed. In AIMD the finite-temperature dynamical trajectories are generated by using forces obtained directly from electronic structure calculations performed as the simulation proceeds.

AIMD runs were performed on six different complexes for both Z₂Cu and ZCuOH mono-Cu active sites and the species present at the end of the reduction half-cycle; [Cu⁺(NH₃)₂]⁺. The complexes used are:

- [Cu²⁺(OH⁻)(NO)(NH₃)]⁺ – (A)
- [Cu²⁺(OH⁻)(NO)(NH₃)₂]⁺ – (B)
- [Cu²⁺(OH⁻)(NO)(NH₃)(H₂O)]⁺ – (C)
- [Cu²⁺(OH⁻)(NO)(NH₃)₃]⁺ – (D)
- [Cu²⁺(OH⁻)(NO)(NH₃)(H₂O)₂]⁺ – (E)
- [Cu⁺(NH₃)₂]⁺ – (F)

These complexes are chosen as the Cu²⁺ complexes as they are relevant for the reduction half-cycle over a range of different gas compositions and temperatures. Previous literature has shown the state of the active complex changes as a function of temperature.⁹³,¹⁷⁵ The single Cu⁺ complex with two additional NH₃ molecules is chosen as it is generally accepted that this species is dominant at the beginning of the oxidation half cycle. MD runs are performed with an NVT ensemble, a time step of 0.5 fs, and ran for a total of 32500 steps with 2500 steps for equilibration of the system. All simulations have a production run of 15 ps. The simulations are conducted with the CSVR thermostat set to 100 °C to understand the dynamics of the more debated and less well quantified cold start of the diesel engine. The simulations here use the PBE functional and the DZVP-MOLOPT-SR-GTH basis set.

In the analysis of result we examine the positions of the Cu ion and the adsorbed molecules. Table 6.1 shows the root mean square distance of the Cu ion for the different complexes, separated into the x, y and z directions. This gives a measure of the displacement of the Cu ion along each axis. The greater the value of the root mean square distance, the higher the Cu mobility.
Table 6.1 | The RMSD of the position of the Cu ion in the x, y, and z directions for 6 different complexes in Cu-SSZ-13 for a 15 ps MD run.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Site</th>
<th>Cu RMSD / Å – x</th>
<th>Cu RMSD / Å – y</th>
<th>Cu RMSD / Å – z</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu²⁺(OH⁻)(NO)(NH₃)]⁺ – (A)</td>
<td>ZCuOH</td>
<td>0.28</td>
<td>0.21</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>Z₂Cu</td>
<td>0.31</td>
<td>0.23</td>
<td>0.24</td>
</tr>
<tr>
<td>[Cu²⁺(OH⁻)(NO)(NH₃)₂⁺ – (B)</td>
<td>ZCuOH</td>
<td>0.40</td>
<td>0.41</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>Z₂Cu</td>
<td>0.19</td>
<td>0.47</td>
<td>0.50</td>
</tr>
<tr>
<td>[Cu²⁺(OH⁻)(NO)(NH₃)₂⁺ – (C)</td>
<td>ZCuOH</td>
<td>0.29</td>
<td>0.36</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>Z₂Cu</td>
<td>0.20</td>
<td>0.47</td>
<td>0.46</td>
</tr>
<tr>
<td>[Cu²⁺(OH⁻)(NO)(NH₃)₂⁺ – (D)</td>
<td>ZCuOH</td>
<td>0.26</td>
<td>0.22</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>Z₂Cu</td>
<td>0.45</td>
<td>0.38</td>
<td>0.34</td>
</tr>
<tr>
<td>[Cu²⁺(OH⁻)(NO)(NH₃)₂⁺ – (E)</td>
<td>ZCuOH</td>
<td>0.48</td>
<td>0.32</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>Z₂Cu</td>
<td>0.77</td>
<td>0.33</td>
<td>0.75</td>
</tr>
<tr>
<td>[Cu⁺(NH₃)]₂⁺ – (F)</td>
<td>1Al</td>
<td>0.73</td>
<td>0.38</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>2Al</td>
<td>0.49</td>
<td>0.68</td>
<td>0.31</td>
</tr>
</tbody>
</table>

The x and y directions relate to the Cu ion moving across the 6MR in a plane and the z direction denotes up and down movement of the Cu ion with respect to the chabazite cage. For the Cu²⁺ ion on average the values of the RMSD increase with increasing numbers of ligands. Figures 6.1 and 6.2 show the trajectory that Cu (light blue) takes during the MD run and therefore the volume that it samples in a qualitative way for ZCuOH and Z₂Cu respectively, for each different complex represented by A-E as specified in the bullet points. The average of all the RMSD values for a complex with no additional ligands (A), with one additional ligand (B and C) and with two additional ligands (D and E) are 0.30, 0.41 and 0.46 respectively. This means that as the Cu ion is more solvated it is freed from the framework and samples more space in the chabazite cage. It can be seen visually that as the number of ligands to Cu²⁺ increases the overall space sampled also increases. For the ZCuOH and Z₂Cu sites there is little difference between the x and y values compared to each other. The stochastic nature of the MD run means that occasionally an energetic barrier can be overcome and the Cu ion samples a new area of space in the zeolite, which perhaps explains why the [Cu²⁺(OH⁻)(NO)(NH₃)(H₂O)₂]⁺ on the Z₂Cu site (Fig. 6.2,e) has a significantly increased RMSD. There is however, a clear increase of z component in the displacement when looking at the same
complex but on the different sites, where the only exception being the \([Cu^+(OH^-)(NO)(NH_3)(H_2O)_2]^+\) species which perhaps sampled a rare event during the simulation. The 1Al site shows an increased RMSD in the z direction compared to the 2Al site and this is therefore more mobile throughout the chabazite cage. This is because of the increased electrostatic attraction of Cu\(^{2+}\) to the two regions of negative charge in the 6MR. On the \([Cu^+(NH_3)_2]^+\) complex the scenario is similar with increased SD of Cu position along the z axis compared to the 2Al site with a value of 0.31 and 0.55 for 2Al and 1Al sites respectively.
Figure 6.1 | The trajectories for Cu and the atoms of NO, OH, water and ammonia directly coordinated to Cu over an AIMD run at 100°C for a production run of 15ps on ZCuOH sites for the complexes A–E. Light blue represents Cu, red an oxygen atom of either water or OH, blue N atom of either ammonia or NO. This colour scheme is different to the rest of this work as the software used to plot the trajectories would not allow colour changes. Each row down from complex A represent adding an additional molecule whereas the left-hand column adds additional ammonia molecules, and the right column represents adding additional water molecules. Colour scheme for elements: yellow=Si; pink=Al; small red=O; blue=N; pale blue=Cu
Fig 6.2 | The trajectories for Cu and the atoms of NO, OH, water and ammonia directly coordinated to Cu over an AIMD run at 100°C for a production run of 15ps on Z₄Cu sites for the complexes A-E. Light blue represents Cu, red an oxygen atom of either water or OH⁻, blue N atom of either ammonia or NO. Each row down from complex A represents adding an additional molecule whereas the left-hand column adds additional ammonia molecules, and the right column represents adding additional water molecules. Colour scheme for elements: yellow=Si; pink=Al; small red=O; blue=N; pale blue=Cu

The main events occurring in each of the MD trajectories were analysed with respect to the overall Cu speciation in the catalyst. In terms of rearrangement of the molecules around Cu²⁺ there are some rotations and the breaking of coordination to Cu observed over this short time
scale. For the \([\text{Cu}^{2+}(\text{OH}^-)(\text{NO})(\text{NH}_3)]^+\) (complex A), at both the ZCuOH and Z2Cu sites there is no rotation of the complex or re-orientations of molecules observed, although the ligands vibrate in place around Cu and sample a small area of space in their position (Fig. 6.1, 6.2). For \([\text{Cu}^{2+}(\text{OH}^-)(\text{NO})(\text{NH}_3)_2]^+\) (complex B) at the ZCuOH site there is no rearrangement of the molecules but the whole Cu complex performs a ridged rotation which allows the ligands to sample a greater area of space (Fig. 6.1). At the Z2Cu site an early desorption of NH3 is observed and it occupies the 8MR for the majority of the simulation (Fig. 6.2). For \([\text{Cu}^{2+}(\text{OH}^-)(\text{NO})(\text{NH}_3)(\text{H}_2\text{O})]^+\) (complex C) on the ZCuOH site no rigid rotation or rearrangements of ligands is observed and the ligands vibrate in place around Cu (Fig. 6.1), whereas on the Z2Cu site the water molecules desorb from Cu and occupies the second solvation shell and moves into the 8MR for a short time period (Fig. 6.2). The \([\text{Cu}^{2+}(\text{OH}^-)(\text{NO})(\text{NH}_3)_3]^+\) (complex D) at the ZCuOH site shows a rotation of the whole complex about 180° and also a reorientation of the molecules (Fig 6.1). The NO molecule in the axial bond were originally pointing upward whereas and at the end of the simulation it points towards the side of the chabazite cage. At the Z2Cu site one water molecule desorbs from Cu and occupies the second solvation shell, the Cu ion the coordinates to the framework, and the other molecules do not change their positions around the Cu complex significantly and vibrate in place (Fig. 6.2.). For the \([\text{Cu}^{2+}(\text{OH}^-)(\text{NO})(\text{NH}_3)(\text{H}_2\text{O})_2]^+\) (complex E) at the ZCuOH site there are no rearrangements of molecules but the Cu complex which is in a square pyramidal geometry does reorientate itself relative to the cage and rotates slightly (Fig. 6.1), whereas, at the Z2Cu site there is a rotation of the whole complex, and a change in the geometry of the complex (Fig 6.2).

The length of the simulations performed only allows for a qualitative analysis, the MD simulations show that Cu is more mobile at the ZCuOH site compared to the Z2Cu site and that even at a short timescale of 15ps it is possible to observe the reorientation of the Cu complex in relation to the cage, changes in geometry and the desorption of ligands directly coordinated to Cu and their occupation in the second solvation shell. Therefore, it is reasonable to assume that under real SCR conditions (such as higher temperatures and longer timescales) more rearrangements and desorption’s will be observed, with perhaps the formation of new coordinations to Cu. This shows that that it is indeed likely that the Cu complex in the real catalyst samples a variety of dynamically accessible geometries, rather than being in a static minimum energy configuration. This will undoubtedly affect the catalytic behaviour and must be appreciated for rationalisation of the mechanistic details.
Figure 6.3 shows the trajectory for the \([\text{Cu}^+(\text{NH}_3)_2]^+\) complex. There is a general literature consensus that at the end of the reduction half-cycle this is the most dominant species and that it is mobile throughout the chabazite cavity where it can migrate through the 8MR and visit other cavities.\(^{93,221-223}\) Due to the short scale of our simulations, no rare events such as a migration through the 8MR were observed in the simulation. However, we do find that on average, the \([\text{Cu}^+(\text{NH}_3)_2]^+\) complex is indeed more mobile though the chabazite cavity than the \(\text{Cu}^{2+}\) complexes. The average of all of the RMSD’s in all directions is 0.39 Å for the \(\text{Cu}^{2+}\) complexes whereas for \([\text{Cu}^+(\text{NH}_3)_2]^+\) the average is 0.52 Å, showing \([\text{Cu}^+(\text{NH}_3)_2]^+\) is more mobile than \(\text{Cu}^{2+}\) complexes in our simulations.

These results show that despite the short timescales involved in the reaction that the coordination environment of Cu is indeed dynamic and shifting even at low temperatures and that the Cu complex is mobile, especially in proximity to 1Al rather than 2Al. We observe translation and rotations of the entire Cu complex and desorption of molecules from Cu, which given longer timescales would likely re-coordinate to the Cu. Therefore, it is likely that especially at temperatures > 100 °C the Cu complex can sample numerous configurations of similar energies, but different geometries as highlighted in chapter 5.
Fig 6.3 | The trajectories for Cu\(^{(NH_3)}_2\) over an AIMD run at 100°C for a production run of 15ps. Light blue represents Cu, blue N atom of either ammonia or ammonium. a) represents the trajectory on 1Al site and b) on the 2Al site. Colour scheme for elements: yellow=Si; pink=Al; small red=O; blue=N; pale blue=Cu.
The Reaction Mechanism

As highlighted in section 3.6.3 the exact reaction mechanism for the SCR reaction over Cu-SSZ-13 is still unresolved. The different active sites, which are governed by Al and Cu content mean there are potentially multiple different speciations of active site on which the reaction can proceed. Furthermore, the seagull feature of the SCR light-off curve corresponding to a slight dip in activity at ~300 °C implies temperature has a significant role in the reaction and changes how it proceeds or changes an intrinsic property of the zeolite which governs the reaction mechanism. In addition, it has been shown in chapter 5 that monomeric Cu complexes can vary significantly in their structure while being comparable in energy. This could have important consequences in regard to how the reaction proceeds. Here, the formation of key reaction intermediates for the reduction and oxidation half cycles of the SCR reaction on Cu-SSZ-13 mono-Cu active sites are modelled computationally. Recently there is a shifting consensus in the literature that Cu dimers are the dominant form of the active site in Cu mainly due to second order reaction kinetics dependent upon Cu loadings. However, this quadratic dependence of SCR rate on Cu loading is only visible after a certain, albeit low level of Cu is exchanged into SSZ-13, which is approximately 0.01wt% Cu. Furthermore at high temperatures (> 250 °C) the second order rate dependence on Cu is no longer observed and the SCR rate increases linearly with Cu loading. The ‘cold-start’ of a diesel engine emits a significant proportion of NOx and is therefore a reason why literature focus recently has shifted from research on mono-Cu active sites to dimeric Cu species as this form of the active site is thought to dominate at low temperatures. However, it is first crucial to understand the reaction mechanism over mono-Cu active sites while the reaction is performing well at low-mid Cu loadings and at moderate to high temperatures. Here we examine the SCR reaction mechanism over mono-Cu active sites for a range of different Cu complexes which exhibit different coordination environments, position, orientation and isomerism for Cu in proximity to both 1Al and 2Al is studied. Figure i sums up the leading literature proposals for the mono-Cu active site which includes multiple routes for the reduction half cycle shown in red and the best recognised, but non-elementary route for the oxidation half cycle. The reduction half-cycle and oxidation half-cycles are considered in sections 7 and 8 respectively.
Figure 1 | A summary of the leading proposals for the SCR reaction mechanism. The right hand side in red summarises the three leading proposed reaction mechanisms for the reduction half-cycle over monomeric Cu. The left-hand side summarises the leading proposal for the oxidation half-cycle over monomeric Cu. The cycle assumes that there is an intrinsic OH- species present.
7. The Reduction Half-Cycle

In this chapter the reduction half-cycle will be studied. First the activation of ammonia, the reductant in the SCR reaction is investigated. We then study a transformation or equilibrium between $\text{Z}_2\text{Cu}$ and $\text{ZCuOH}$ sites. The SCR reduction half-cycle is proposed to proceed via several potential different routes (Fig. 7.1), we compute the energy barriers for these routes and provide a comparison between them and also deduce the elementary reaction steps involved in each pathway. It has been observed in chapters 5 and 6 that there is a complex and dynamic configurational space, we therefore investigate if and how this has an impact upon the activation barriers for the SCR cycle. Furthermore, as it is generally accepted that as the temperature increases the Cu complex loses solvation, we investigate how the number and type of ligand can affect the activation barriers for the reaction. Nitrosamine ($\text{H}_2\text{NNO}$) is shown to be a key reaction intermediate for the reduction half-cycle and here, we calculate the activation barriers for its dissociation.

7.1 The Activation of Ammonia

For the SCR reaction to proceed, $\text{NH}_3$ first needs to be activated. $\text{NH}_3$ activation has previously been thought to be the rate-limiting step of the SCR reaction; however, it has more recently been proposed by Gao et al. that the rate limiting step is in the low-temperature oxidation half cycle, in-particular the migration of $[\text{Cu}^\prime(\text{NH}_3)_2]^+$ species to form Cu dimers. Other works for the mid to high temperature oxidation and reduction half-cycles suggest that these two half-cycles have very similar rates, meaning neither is exclusively rate limiting. Nonetheless, $\text{NH}_3$ activation is still an integral part of the reaction mechanism and it is likely to be the rate limiting step of the reduction half cycle.

Ammonia activation is plausibly achieved via a proton or hydrogen transfer after a heterolytic or homolytic cleavage of an N-H bond respectively. The likely acceptors are either OH$^-$ ions or framework acid sites, i.e. oxygen species nearest neighbour to Al dopants. However, other potential acceptor species in the SCR gas mixture include HONO, $\text{H}_2\text{O}$ and $\text{NH}_3$. Ab initio calculations have been performed to determine the energetic barriers necessary to transfer a proton/hydrogen atom to either OH$^-$, $\text{NH}_3$, $\text{H}_2\text{O}$, HONO or a framework oxygen species to form a Brønsted acid site, represented by equations 7.1-7.5.
\[ \text{OH}^- + \text{NH}_3 \rightarrow \text{H}_2\text{O} + \text{NH}_2^- \]  
\[ \text{NH}_3 + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{NH}_2^- \]  
\[ \text{H}_2\text{O} + \text{NH}_3 \rightarrow \text{H}_3\text{O}^+ + \text{NH}_2^- \]  
\[ \text{HONO} + \text{NH}_3 \rightarrow \text{H}_2\text{O} + \cdot\text{NH}_2 + \cdot\text{NO} \]  
\[ \text{Z} + \text{NH}_3 \rightarrow \text{Z}/\text{H}^+ + \text{NH}_2^- \]

Activation barriers and transition states are calculated via the distinguished reaction coordinate method, where the reaction coordinate is explicitly defined as the distance between two atoms and sequentially reduced and constrained while all other parameters are optimised. For each reaction 7.1-7.5 the reaction coordinate is constrained and the distance between the proton on the dissociating NH\(_3\) molecules and the basic species accepting the proton is reduced. These reaction profiles are shown in figures 7.1 and 7.2. Only proton transfers to OH\(^-\) and HONO species from NH\(_3\) lead to stable intermediates with reaction barriers of 52 and 111 kJ mol\(^{-1}\) respectively, showing the successful activation of ammonia. (Fig. 7.1). Proton transfer to any of the other potential H acceptors does not yield a minimum on the PES corresponding to a H species (Fig. 7.2), whereas successful transfers show a shallow minimum corresponding to forming a new bond to H species (Fig. 7.1). We find this transfer to be a heterolytic bond cleavage where the H is transferred as a proton and NH\(_2^-\) is formed after the N-H bond is broken. It should be noted that multiple calculations at different orientations, positions and ligations were performed to try to achieve proton transfers to species other than OH\(^-\) and HONO. None were able to form a stable Brønsted acid site, H\(_3\)O\(^+\), or NH\(_4^+\) upon optimisation. The failed reaction profiles show the same shape and similar energies as the graphs shown in figure 7.2. It is therefore found at this level of theory that only OH\(^-\) and HONO are basic enough to abstract a proton from NH\(_3\) in Cu-SSZ-13, whereas other species like framework acid sites are not. Other computational papers found that proton transfer to a O\(_{FW}\) species does provide a metastable intermediate, but this was not the case in our work.\(^{224}\) Any calculation starting from NH\(_2^-\) in proximity to a framework Brønsted acid site reverses to NH\(_3\) upon full geometry optimisation.
Figure 7.1 | Successful proton transfers from NH$_3$ to a) OH$^-$ and b) HONO. The insets show the starting and ending geometries. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu

Figure 7.2 | The unsuccessful protons transfers from NH$_3$ to: a) NH$_3$ b) H$_2$O c) Brønsted acid site. The inset shows the starting geometry. The steep rise in energy as H approaches the receiver shows there is no PES corresponding to a new H-X bond formed. The drop in energy in figure 7.2a corresponds to NH$_3$ desorbing from Cu. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu

The CRYSTAL17 code at the PBE0-D3 level of theory could not find a minimum on the PES for the transfer of a proton/hydrogen to a framework oxygen to form a Brønsted acid site and NH$_2^\cdot$. This is in contrast to the work of Wang et al. who calculate the barrier to be 122 kJ mol$^{-1}$ and the Brønsted acid site and an NH$_2^\cdot$ as a stable reaction intermediate.$^{224}$ The disagreement of results is likely due to differences in computational set up. Wang et al. use a 12 T site cell whereas here, a PBC cell with 36 T sites is used here, which reduces unwanted periodic effects and gives a better representation of Si/Al ratio to commercial catalysts. Wang et al. use the VASP code with a PBE-D3 functional, which is a GGA functional whereas here PBE0-D3, a hybrid exchange functional is used, which is generally accepted to be a higher level
These results are also in disagreement to the reduction half cycle proposed by Paolucci et al. where they suggest activation of ammonia on Z2Cu can proceed via a proton transfer to framework oxygen species and perform hybrid DFT calculations with the VASP code to find a barrier of 74 kJ mol$^{-1}$. This simulation, however, includes NO and uses a nudged elastic band calculation to find the activation barrier for the process which could explain the differences found. The results here, indicate that in order for NH$_3$ to be activated in the reduction half cycle an OH$^-$ ion must be present. The HONO species, which participates in the reduction half-cycle and will be discussed in more detail in section 7.3, is formed by the reaction of OH$^-$ and NO and is an important intermediate in the reduction half-cycle (RHC). Therefore, it is found here that ammonia can only be activated in the presence of OH$^-$, by either OH$^-$ forming water, or after OH has reacted with NO forming the HONO SCR intermediate, which can then activate NH$_3$ forming H$_2$O and NO. This result implies that the SCR reaction can only proceed on the 1Al or ZCuOH site. However, it is well known that zeolite samples which are thought to contain majority Z2Cu still show SCR catalytic activity.

7.2 Transformation of Active Site
Calculations in section 7.1 indicate that OH$^-$ is needed for the activation of ammonia, and the initiation of the reduction half cycle. The Z2Cu site does not have intrinsic OH$^-$ present like ZCuOH does. The implication of the different active sites containing an intrinsic and strongly basic OH- species on the SCR mechanism needs to be considered and explored for a greater understanding of the full reaction cycle. This is taken into account when simulating the full RHC in section 7.3. However, on zeolite samples which are thought to contain a majority of Z2Cu the reaction proceeds without the intrinsic OH- species present.$^{93,103,162,184,189,221,226}$ Therefore, it is important to explore the possibility of a reaction between Cu species containing water which dissociates via a proton transfer into OH- species and a proton acceptor. It is possible that an initial transformation of active site or an equilibrium between Z2Cu and ZCuOH, represented in equation 7.6 could be responsible for the formation of OH$^-$ on Z2Cu which allows the reduction half-cycle to proceed on the Z2Cu site.

$$[Z_2Cu(H_2O)(NH_3)] \rightarrow Z/NH_4^+ + [ZCuOH]$$ 7.6
In this reaction a proton is transferred from $\text{H}_2\text{O}$ to $\text{NH}_3$ creating $\text{OH}^-$ coordinated to $\text{Cu}^{2+}$ and $\text{NH}_4^+$ adsorbed on a Brønsted acid site. This transformation of active site has been investigated over three different Al distributions to understand how and if it affects activation barriers for the dissociation of water according to reaction 7.6 and if this process is stable across different forms of the zeolite. It is possible that an increased separation of Al ions in the framework could assist the dissociation of water and subsequent formation of $\text{NH}_4^+$ and $\text{OH}^-$. Reaction barriers were successfully calculated for three different Al distributions with one $\text{H}_2\text{O}$ and one $\text{NH}_3$ molecule present and initially coordinated to $\text{Cu}^{2+}$, to investigate if a certain Al distribution can lower the energy barrier for the reaction. The three Al distributions used are:

1) Al in 6MR at the 3rd nearest neighbour (NN) position – the global minimum for Al distribution and Cu location (Fig. 7.3 black).

2) Al in the 8MR at the 2NN position (Fig. 7.3 red).

3) Al in 8MR at the 4NN position (Fig. 7.3 blue)

In all of the simulations $\text{Cu}^{2+}$ is situated in the plane of the 6MR for consistency. The 6MR 3NN configuration initially is the most stable as expected, with the 8MR 2NN configurations starting energy being 93 kJ mol$^{-1}$ higher in energy and the 8MR 4NN configuration being 118 kJ mol$^{-1}$ higher in energy. Reaction profiles are plotted relative to the energy of initial geometry for each reaction (Fig. 7.3).
Figure 7.3  

We find that it is possible to form ZCuOH from Z2Cu with reasonable activation energies of between 60-80 kJ mol⁻¹. In fact, for the 2NN in the 8MR configuration and 4NN in the 8MR configuration the product of ZCuOH and Z/NH₄⁺ is more stable than the reactants of [Z₂Cu(H₂O)(NH₃)], whereas for the 3NN in the 6MR configuration the reactants are more stable than the products, but only slightly. This means that for some Al distributions the equilibrium of this reaction will be shifted more to ZCuOH and Z/NH₄⁺ than Z₂Cu and for the most stable Al distribution of 3NN in the 6MR there will be a near equal split between ZCuOH and Z/NH₄⁺ compared to Z₂Cu. This result strongly suggests that OH⁻ which we find to be vital for the activation of NH₃ in the RHC can be easily generated from Z₂Cu in the presence of water and ammonia and is a stable product.

A study by Greenaway et al. may have found evidence for the production and consumption of OH⁻ as a transformation of active site. The authors use modulation excitation IR spectroscopy techniques to understand the production and consumption of species key to the SCR reaction. Modulation excitation techniques allow for the detection of short-lived transient species as DRIFTS spectra for in-situ study of the SCR reaction are dominated by species with high molar extinction coefficient such as NH₃, NH₄⁺, and NO₃⁻. Other spectroscopic techniques such as XANES which can probe the oxidation state and coordination number of Cu find it difficult to deconvolute the signals relevant to the reaction.
mechanism to those from non-active sites. Modulation excitation techniques allows the detection of species directly involved in a reaction by using a pulse sequence of reactant into the reaction bed. This allows the removal of spectroscopic signals from species not participating in the reaction as their signal will not be pulsating or oscillating at the same frequency as the reactant. Therefore, reaction intermediates can be studied with greater resolution. The study by Greenaway et al uses NO as the pulsed species and a zeolite sample containing a mix of 1Al and 2Al sites. The results show that Cu$^{2+}$ OH$^{-}$ is affected over the whole NO pulse and is clear evidence that Cu$^{2+}$ OH$^{-}$ is consumed and regenerated in SCR conditions. This adds evidence to the postulation that dissociation of H$_2$O must take place for the reaction to proceed upon a Z$_2$Cu site as this corresponds to the generation of OH$^{-}$. Furthermore, the study shows that NH$_4$$^+$ ions are not particularly reactive in the SCR reaction and act as a ‘reservoir’ of NH$_3$ and are abundant in the zeolite. The proposed transformation of active site could account for the generation and subsequent storage of NH$_4$$^+$ found in modulation excitation experiments. It is plausible that the NH$_4$$^+$ could eventually react with NO$_2^-$ present in the SCR gas mixture forming ammonium nitrite which is known to decompose into N$_2$ and H$_2$O only and could be a side route in the SCR reaction. However, NH$_4$$^+$ is shown to react slowly with NO and O$_2$ in Cu-SSZ-13 meaning the reservoir hypothesis is more likely.

7.3 Elementary Reaction Steps of The Reduction Half-Cycle
As discussed in section 3.3 the exact mechanism of the reduction half cycle is still debated, with the leading proposals from Janssens, Gao and Paolucci.$^{93,135,189}$ In order for N$_2$ to be produced, an N-N bond needs to form. The mechanisms proposed by Paolucci and Janssens suggest the first occurrence of the N-N bond when H$_2$NNO is formed, however, they propose it is formed via different routes. Gao et al. postulate that the reduction half cycle is closed by the decomposition of NH$_4$NO$_2$, however the N-N bond still needs to form, and a pathway is not explicitly outlined in their work. The eventual formation of the N-N bond is likely to form via the decomposition of NH$_4$NO$_2$ which is thought to proceed via H$_2$NNO in the gas phase making this the key reduction half cycle intermediate.$^{229}$ In fact this process requires Brønsted acidity which initiates the proton transfers and therefore the highlights that Brønsted acidity and hence a mix of zeolitic sites are required for the SCR reaction to proceed.
For the reduction half cycle, there are three feasible routes which have been proposed. Paolucci et al propose that \( \text{H}_2\text{NNO} \) is directly formed by the reaction of NO, \( \text{NH}_3 \) and a proton acceptor, either OH\(^-\) or a Brønsted acid site. Gao et al and Janssens et al both propose the reduction half cycle is initiated by the formation of HONO. Gao et al postulate that \( \text{NH}_4\text{NO}_2 \) is then formed whereas Janssens proposes \( \text{H}_2\text{NNO} \) is formed. Upon analysis of the different proposed mechanisms 3 different complete routes for the reduction half cycle can be deduced:

1) The direct formation of \( \text{H}_2\text{NNO} \) via a metastable \( \text{NH}_2^- \) intermediate:

\[
[Cu^{2+}(OH^-)(NO)(NH_3)]^+ \rightarrow [Cu^{2+}(H_2O)(NH_2^-)(NO)]^+ \rightarrow [Cu^+(H_2O)(H_2NNO)]^+ \quad 7.7
\]

2) Formation of \( \text{H}_2\text{NNO} \) via HONO:

\[
[Cu^{2+}(OH^-)(NO)(NH_3)]^+ \rightarrow [Cu^+(HONO)(NH_3)]^+ \quad 7.8
\]

\[
[Cu^+(HONO)(NH_3)]^+ \rightarrow [Cu^+(H_2O)(NH_2)(NO)]^+ \rightarrow [Cu^+(H_2O)(H_2NNO)]^+ \quad 7.9
\]

3) Formation of \( \text{NH}_4\text{NO}_2 \) via HONO:

\[
[Cu^{2+}(OH^-)(NO)(NH_3)]^+ \rightarrow [Cu^+(HONO)(NH_3)]^+ \rightarrow [Cu^+(NH_4\text{NO}_2)]^+ \quad 7.10
\]

Additional spectator ligands may be coordinated or interacting with Cu, without taking part in the reaction. We consider these steps over both ZCuOH and Z\(_2\)Cu. It is assumed here the reduction half cycle takes place over ZCuOH, or that on the Z\(_2\)Cu site an OH\(^-\) ion has originally been generated by water dissociation as discussed in section 7.2. The potential reaction mechanisms can be considered as a succession of either proton or hydrogen transfers, electron movement, and the formation of new bonds. The direct formation of \( \text{H}_2\text{NNO} \) is initiated by the activation of ammonia forming a metastable \( \text{NH}_2^- \) ion, which then reacts with NO forming \( \text{H}_2\text{NNO} \) (equation 7.9). The \( \text{H}_2\text{NNO} \) via HONO route, is initiated by the reaction of NO and OH\(^-\) forming HONO, which reduces Cu\(^{2+}\) and then activates ammonia by accepting a hydrogen forming NO and \( \text{NH}_2^- \) which can combine to form \( \text{H}_2\text{NNO} \) (equations 7.8, 7.9). The \( \text{NH}_4\text{NO}_2 \) route is initiated by the formation of HONO, but then there is a proton transfer from HONO to \( \text{NH}_3 \), in the opposite direction required to form \( \text{H}_2\text{NNO} \) from HONO. The exact elementary reaction steps are yet to be resolved in literature. These routes are summarised in figure 7.4 in the reduction half-cycle section (right, red). The subsequent intermediates
formed, are well known to dissociate into water and nitrogen only, completing the reduction half cycle.

Fig. 7.4 | The red or right-hand side of the figure shows the three potential different routes for the reduction half cycle. The left-hand side shows the oxidation half-cycle and will be discussed later. This is identical to figure i

In order to study the differences between the three proposed reaction routes, we simulated each reaction step involved using a form of the Cu complex with a similar geometry on both Z₂Cu and ZCuOH sites. This will act as an exemplar complex, on which the three different pathways will be simulated to allow them to be compared to one another and analyse any differences between the two different forms of the active site. This complex has the three reacting molecules NO, OH⁻ and NH₃ adsorbed onto Cu²⁺ in the chabazite framework with an additional NH₃ molecule present, creating an exemplar complex for the reaction pathways. Different coordination environments and ligand configurations will be considered later in this chapter.
An initial geometry is found by performing a geometry optimisation on the \([\text{Cu}^{2+}(\text{OH}^-)(\text{NO})(\text{NH}_3)_2]^{2+}\) complex (Fig. 7.5), for both the ZCuOH site and the Z\(_2\)Cu after an initial generation of \(\text{OH}^-\) ion. The geometries on ZCuOH (a) and Z\(_2\)Cu (b) are kept as similar to one another as possible in order to provide a good comparison of the reactions over the different sites. The geometries show a square pyramid geometry with NO in the axial position oriented into the chabazite cavity, two \(\text{NH}_3\) molecules in a cis arrangement, one \(\text{O}_{\text{fw}}\) bond and a bond to \(\text{OH}^-\). Cu has an overall coordination number of 5 at both sites. Both complexes also show the 5-coordinate Si atom discussed in section 5.4.1, although this bond is not shown in the illustration. These complexes are almost identical apart from the additional Al and \(\text{NH}_4^+\) for the Z\(_2\)Cu site, which occupies an 8MR and is not part of the Cu coordination sphere.

**Figure 7.5 |** The base geometries used for the exemplar reactions in order to study the three different potential reduction half-cycle routes. The geometries on ZCuOH (left) and Z\(_2\)Cu (right) are kept as similar to one another in order to provide a good comparison of the reactions over the different sites.

Barriers for the formation of the \(\text{H}_2\text{NNO}\) intermediate were obtained by constraining the O-H distance between the transferring proton of \(\text{NH}_3\) and the \(\text{OH}^-\) species until its equilibrium value of 0.96 Å at steps of 0.1-0.2 Å, then performing an unconstrained geometry optimisation to find the metastable \(\text{NH}_2^-\) intermediate. In a second series of calculations the N-N distance between \(\text{NH}_2^-\) and NO is constrained until 1.33 Å at steps of ~0.1 Å, then performing an unconstrained geometry optimisation to find the final state. Barriers for the formation of HONO are calculated by constraining the N-O distances between O in \(\text{OH}^-\) and N in NO at steps of ~0.1 Å up to 1.3 Å and then performing an unconstrained geometry optimisation to let the system fully relax. Furthermore, barriers for the formation of \(\text{NH}_4\text{NO}_2\) were calculated by constraining the N-H distance between the proton being transferred down to 0.96 Å at steps
of ~0.1 Å, then fully relaxing the system to find the geometry and energy of the NH₄NO₂ intermediate.

Figures 7.6 and 7.7 show the reaction profile for Z₂Cu and ZCuOH respectively, including transition and stable intermediate state energies and intermediate geometries. There are significant differences for the ZCuOH and Z₂Cu but the lowest route for both sites is via NH₄NO₂. The first step corresponding to the formation of the HONO intermediate has a barrier of 33 and 40 kJ mol⁻¹ respectively for Z₂Cu and ZCuOH (Fig. 7.6, 7.7 black). Both sites exhibit similar intermediate geometries where HONO is bound to Cu by the N atom. The activation barrier for the formation of NH₄NO₂ from HONO is calculated to be 38.6 and 44.8 kJ mol⁻¹ for Z₂Cu and ZCuOH respectively (Fig. 7.6, 7.7 blue). This reaction step is significantly more exothermic over the Z₂Cu site than the ZCuOH site as the final geometry for Z₂Cu shows additional hydrogen bonds, which lower the overall energy of the system. The other pathways both proceed via H₂NNO formed directly, or via HONO. Direct formation of H₂NNO has an initial barrier of 80.7 and 100.2 kJ mol⁻¹ when forming NH₂⁻ at Z₂Cu and ZCuOH respectively and exhibits a very shallow minimum (Fig. 7.6, 7.7 red). The subsequent step corresponding to the N-N bond formation for H₂NNO has small barriers of 13.8 and 9.4 kJ mol⁻¹. The formation of H₂NNO via HONO first proceeds as previously mentioned with barriers of 33 and 40 kJ mol⁻¹ respectively for Z₂Cu and ZCuOH. Formation of H₂NNO from HONO is found to be a 2-step process. The first step which corresponds to the formation of H₂O, NO and NH₂⁻ from NH₃ and HONO has barriers of 61.6 and 118.2 kJ mol⁻¹ for Z₂Cu and ZCuOH. H₂NNO is then formed upon the creation of N-N bond by NO and NH₂ reacting, with barriers of 26.9 and 23.1 kJ mol⁻¹ respectively (Fig. 7.6, 7.7 green). The route via NH₄NO₂ is the lowest energy pathway for both sites, however the other pathways will be accessible at higher temperatures present in exhaust flues of diesel engines. This implies that over a range of temperatures there will be distribution of different pathways that the reduction half cycle can take despite the NH₄NO₂ dominating. The Z₂Cu site has lower barriers for each potential reaction route compared to that of ZCuOH. This is likely due to it already being in an activated or high energy state due to the proton transfer from H₂O to NH₃. However, the reduction in activation energies for Z₂Cu is not less than the initial ~70 kJ mol⁻¹ needed in order to form the OH⁻ ion, which initiates the reduction half cycle. Interestingly, the route for H₂NNO formation via HONO is significantly reduced in energy on the Z₂Cu compared to the ZCuOH site. This implies that at moderate
temperatures there is an additional pathway for the SCR reaction to proceed via on the \( Z_2Cu \) site compared to the \( ZCuOH \) site.

*Figure 7.6* | The reaction profiles for the direct formation of \( H_2NNO \) (red), formation of HONO (black), the formation of \( NH_4NO_2 \) from HONO (blue), and the formation of \( H_2NNO \) from HONO, over the \( Z_2Cu \) site. The metastable intermediate geometries are also shown with matching colours as the border. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
It is possible to compare the rate constants of two reaction pathways at the same temperature using the Arrhenius equation:

\[
k(T) = Ae^{-\frac{E_a}{RT}}
\]

\(k\) gives the rate constant, \(A\) is the pre-exponential factor, \(E_a\) is the activation energy, \(T\) is the temperature and \(R\) is the universal gas constant. The rate constant gives a quantifiable rate of a chemical reaction meaning it is possible to compare how fast different SCR pathways proceed. The ratio of the rates will give the how many times faster one pathway is compared to the other. When the temperature is constant the pre-exponential factors will cancel and the activation energy which has been calculated using DFT can be used to find the ratio of the rates. On the ZCuOH site the HONO via NH₄NO₂ pathway has a maximum activation energy of 43.1 kJ mol⁻¹ and the direct H₂NNO pathway has an activation energy of 108.4 kJ mol⁻¹. Using the Arrhenius equation it is found that at 200 °C the NH₄NO₂ pathway will be approximately 20,000 times faster whereas at 400 °C it will be 20 times faster and at 500 °C only 5 times
faster. Therefore, it can be shown that for the complexes in the low temperature regime (<200 °C) the NH₄NO₂ pathway will be extremely dominant and at 500 °C the direct H₂NNO pathway will become comparable in rate despite NH₄NO₂ still dominating over H₂NNO. However, by 600 °C the rates are virtually indistinguishable. Diesel exhaust catalytic systems generally operate over a very wide range of temperatures (200-700 °C) depending upon various factors, meaning depending upon driving conditions and engineering a range of reactions could be observed. It should be noted that activation energies vary, and this analysis is to show the difference in one scenario.

One aspect missing in the literature of the SCR reaction, is a full description of the elementary reaction steps involved in the formation of the key reaction intermediates. Cu²⁺ has a d⁹ electron configuration and therefore has one unpaired electron possessing spin. Furthermore, NO has an unpaired electron due to its bonding configuration meaning both Cu²⁺ and NO are open shell systems. In our calculations we can monitor the evolution of the unpaired electrons over the reaction profile and characterise the features of any electron transfer by performing a Mulliken population analysis. When Cu²⁺ is reduced to Cu⁺ (d¹⁰) it becomes a closed shell system. OH⁻, H₂O, NH₃, NH₄⁺, HONO, NO₂⁻ and H₂NNO are closed shell molecules and possess no electron spin density. NH₂⁻ is closed shell, but the NH₂ neutral molecule is an open shell radical.

Figure 7.8a, b shows the electron spin density on Cu and the N atom of NO as a function of reaction coordinate for the two stages of the direct formation of H₂NNO reaction; NH₂⁻ formation, and H₂NNO formation. The unpaired electrons on Cu²⁺ and N must have opposite spin polarisation for the reaction to proceed. The starting spin density for Cu and NO is approximately 0.75 and -0.75 electrons respectively. This corresponds to Cu²⁺ and a neutral NO radical. The reaction leading to the direct formation of H₂NNO is initiated by the transfer of H⁺ from ammonia to OH⁻ forming NH₂⁻ and H₂O. There is no spin density gained for the migrating H species, N of ammonia or the O on OH⁻, all values stay at 0 throughout the reaction. This is therefore a heterolytic proton transfer. There is no change of spin density on NO and a slight reduction in spin density on Cu, likely due to some electron density being delocalised around the ligands but not enough to signify Cu has been reduced. Therefore, the direct formation of H₂NNO is initiated by a heterolytic bond cleavage where NH₃ retains both
electrons in the covalent N-H bond and proceeds via a proton transfer to OH\(^-\). The next reaction step is calculated by constraining the N-N distance between the NH\(_2\) species which has just formed, and NO, and reducing it stepwise. We observe a clear reduction of Cu\(^{2+}\) to Cu\(^+\) upon formation of the N-N bond in H\(_2\)NNO. Both spin densities on Cu and N of NO tend toward zero at approximately 2 Å, which is also when the energy begins to drop significantly and correspond to the transition state of this reaction step. This energy drop is also when the N-N bonds starts to form and is a clear indication that during the formation of H\(_2\)NNO Cu\(^{2+}\) is only reduced to Cu\(^+\) upon the formation of the N-N bond. During the calculation no other species gain or lose significant spin density, and upon the final optimisation of the system all species are closed shell with zero spin. Therefore, we can deduce that one electron from the lone pair on the NH\(_2\) species reduces Cu, and another forms a single bond with the unpaired electron on NO. This reaction mechanism is represented in figure 7.8c and the elementary reaction steps have been resolved.
Figure 7.8 | The spin states on Cu and N of NO with the corresponding energy, as a function of the reaction coordinate for the direct formation of H₂NNO. **a)** the first step corresponding to a proton transfer from NH₃ to OH⁻. **b)** the second step corresponding to the formation of the N-N bond and the reduction of Cu²⁺ to Cu⁺. **c)** The elementary reaction steps and electron movement involved in the direct formation of H₂NNO.

Figure 7.9a shows the electron spin density on Cu and the nitrogen atom of NO and its corresponding energy as a function of reaction coordinate for formation of the HONO intermediate. For the formation of the HONO intermediate the distance between O on OH⁻ and N on NO is constrained. It is observed that at ~2 Å the spin density on Cu and NO decreases towards zero, this corresponds to the transition state of the reaction, which can therefore be classified as a redox reaction with electron transfer to Cu²⁺, and reduction of Cu to 1⁺ oxidation state. Upon formation of HONO and a full geometry optimisation at the end of the reaction, all species are closed shell and no spin density is observed. Therefore, it is found that upon formation of HONO Cu²⁺ is reduced to Cu⁺. No other species during the reaction gain or lose spin, therefore the HONO intermediate is created upon bond formation from the unpaired electron on the NO radical and one electron from a lone pair from OH⁻.
reacting, and the other electron from the lone pair on OH\(^-\) moves into the d orbitals of Cu. The elementary reaction step involved in the formation of HONO is represented in figure 7.9,b.

![Figure 7.9](image)

**Figure 7.9** | **a)** The spin states on Cu and N of NO with the corresponding energy, as a function of the reaction coordinate for the formation of HONO. **b)** The elementary reaction steps involved in the direct formation of HONO and the corresponding electron movements.

Once HONO is formed, either NH\(_4\)NO\(_2\) or H\(_2\)NNO can form on addition of NH\(_3\) (reactions 7.9 and 7.10) depending upon the direction of the proton transfer. For either proton transfer, no change of spin density is observed for any species involved with the reaction and all spins states stay at zero, despite initiating some calculations with spin density on Cu and N atoms in order to test this. The formation of NH\(_4\)NO\(_2\) is calculated by constraining the distance between H on HONO and N on ammonia and sequentially reducing it. Therefore, it can be deduced that NH\(_4\)NO\(_2\) is formed upon a heterolytic bond cleavage of the O-H bond on HONO, where ONO\(^-\) retains the electrons, and then via a proton transfer to NH\(_3\) forming NO\(_2^\cdot\) and NH\(_4^+\) species as ammonium nitrite. The elementary reaction steps involved in the formation of NH\(_4\)NO\(_2\) is represented in figure 7.10.
H$_2$NNO can also be formed via HONO (reactions 7.8, 7.9). After HONO has formed a proton can be transferred from ammonia to HONO forming NH$_2$ and H$_2$O. Next NH$_2$ and NO react to form H$_2$NNO. We simulate this reaction by first constraining the distance between H on ammonia and O on HONO, then N of NH$_2$ and N of NO. After the initial formation of HONO no species possess any spin density despite the partial geometry optimisations starting with spin density on N of NH$_2$ and N of NO. This makes the determination of the exact elementary steps difficult. Assuming the Cu active centre stays as Cu$^+$ as the spin density indicates throughout this process, there is only one likely way this reaction proceeds; two simultaneous heterolytic bond cleavages of the N-O bond on HONO and the N-H bond on ammonia and the subsequent homolytic OH bond formation making water. Another heterolytic bond formation then occurs between N of NO and N of NH$_2$. However, after the first hydrogen transfer, we observe no spin density on any species in the simulation. DFT calculations are known to have electron delocalisation issues where electrons which are known to be localised in the physical system are in fact unphysically delocalised in the simulation. Hybrid exchange-correlation DFT can somewhat improve this known issue, however it is still a significant problem.$^{233}$ It is possible that here, electrons which should be localised on N of NO and N of NH$_2$ as radicals are actually unphysically delocalised throughout the system. Therefore, the likely route of formation of H$_2$NNO via HONO is through NO and NH$_2$ radicals, despite results from our DFT simulations showing closed shell systems. Figure 7.11 shows the likely elementary reaction steps involved in the formation of H$_2$NNO via HONO.
Figure 7.11 | The potential elementary reaction steps involved in the direct formation of NH₄NO₂ and corresponding likely electron movement.

7.4 Configuration Dependent Activation Barriers in the Reduction Half-Cycle

As supported by literature and chemical intuition, upon increasing temperature the active Cu complex loses solvation. Therefore, the Cu complexes selected are chosen to represent the SCR reaction proceeding under different temperatures. In addition, it has been shown in sections 5 and 6 that the Cu complex has a complex configurational space with many structurally different Cu complexes that have a very similar energy. For each individual Cu complex, we take a range of different geometries, positions, and orientations of the complex around the chabazite cavity in order to understand whether a higher energy starting configuration gives an overall lower activation barrier. Some molecules are placed in the second solvation shell to sample as broad a range of geometries as possible. The simulations on a Z₂Cu site which has undergone an initial transformation of active site forming OH⁻ and NH₄⁺ are also performed. NH₄⁺ is not active during the reaction. We use the same Cu complexes as listed on the Z₂Cu site as the ZCuOH, but there is an additional NH₄⁺ species present in the reaction cell next to a second framework Al ion.

So far, the three potential routes for the reduction half cycle have been considered from the perspective of one complex with a very similar geometry on both Z₂Cu and ZCuOH sites. However, as previously discussed in sections 5 there are multiple accessible conformations and configurations of a complex and furthermore, the active Cu species can have different types and numbers of ligands due to the variation and complexity of the diesel exhaust gas stream. It is therefore important to understand if and how different coordination environments affect the activation barriers and reaction routes.
The three different reduction half-cycle reaction schemes are compared for a range of coordination environments. These include 5 different starting complexes for both $Z_2$Cu and ZCuOH and in non-equal conformations:

- $[\text{Cu}^{2+}(\text{OH}^-)(\text{NO})(\text{NH}_3)]^+$;
- $[\text{Cu}^{2+}(\text{OH}^-)(\text{NO})(\text{NH}_3)_2]^+$;
- $[\text{Cu}^{2+}(\text{OH}^-)(\text{NO})(\text{NH}_3)_3]^+$;
- $[\text{Cu}^{2+}(\text{OH}^-)(\text{NO})(\text{NH}_3)(\text{H}_2\text{O})]^+$;
- $[\text{Cu}^{2+}(\text{OH}^-)(\text{NO})(\text{NH}_3)(\text{H}_2\text{O})_2]^+$

In this analysis the temperature is not considered for the energy of activation barriers as all reaction schemes are calculated at 0 K. However, it is generally accepted that under SCR reaction conditions as the temperature increases, solvation is lost from the Cu complex, and it coordinates to the zeolite framework. Therefore, the different complexes can be loosely used as a representation of different temperature ranges in order to see if and how activation barriers range for the three identified pathways over the mono-Cu active sites, $Z_2$Cu and ZCuOH.

A larger number of reaction simulations were successful on the ZCuOH site compared to the $Z_2$Cu site. Even under constrained conditions, upon optimisation of certain intermediate geometries a proton from NH$_4^+$ or other species would migrate to a negatively charged species like NH$_2^-$ or OH$^-$ preventing the formation of the intended product.

A selection of different geometries of the mono-Cu active site are taken in order to see if and how different configurations and conformations affect reaction barriers for the three different pathways for the reduction half cycle. It is computationally intractable to study the reaction mechanism upon all the different potential configurations and conformations, so a selection for each complex is taken to provide an overview. Analysis of the activation barriers for the three different reaction pathways over the five different complexes for both active sites taking into account the difference in energies of the starting complexes due to their different geometries is undertaken. In addition, a comparison of the activation barriers for each pathway depending upon the type and number of ligands are present in the simulation is considered later.

7.4.1 $[\text{Cu}^{2+}(\text{OH}^-)(\text{NO})(\text{NH}_3)]^+$

At the ZCuOH site, with just the reacting ligands (OH$^-$, NO, NH$_3$) present in the simulation, four starting geometries have been employed, shown in figure 7.12. They are separated by 48.6 kJ
The lowest energy configuration exhibits a square pyramidal geometry with Cu coordinated to two framework oxygen species bridging the Al in the 6MR, with NH$_3$ and OH$^-$ in the other equatorial positions and NO in the longer axial position (Fig. 7.12a green). This geometry also shows a five-coordinate Si species with the extra bond to the OH$^-$ ligand. The second lowest geometry is similar to the first, but with the position of the OH$^-$ and NH$_3$ swapped around and is 20.4 kJ mol$^{-1}$ higher in energy (Fig. 7.12a red). The OH$^-$ ligand is now not in proximity to the framework, and therefore cannot coordinate to the framework. The third geometry has the same equatorial coordination environment as the first but does not have the five-coordinate Si and NO is in the second solvation shell, hydrogen bonded to NH$_3$ (Fig. 7.12a blue). This geometry is 30.4 kJ mol$^{-1}$ higher in energy compared to the lowest. The highest energy geometry is orientated differently compared to the other complexes and bridges across the 6MR, with OH$^-$ and NH$_3$ creating a square planar geometry with NO in the second solvation shell (Fig. 7.12a black). This geometry is 48.6 kJ mol$^{-1}$ higher in energy than the lowest.

Fig. 7.12b shows the reaction profile for the direct formation of H$_2$NNO (reaction 7.7) which proceeds from centre to the right, and the formation of HONO from centre to left. Figure 7.12c shows the formation of H$_2$NNO from HONO centre to right and the formation of NH$_4$NO$_2$ from HONO centre to left. The colour of the border of starting geometry image in Figure 7.12c corresponds to the colour of the line representing the reaction profile. The subsequent figures which outline the reaction profile over the other complexes mentioned follow the same structure described here. The zero of energy used, for all intermediates and transition states is the lowest energy starting complex. Interestingly, it is found that the lowest starting geometry does not provide the overall lowest route of reaction for the three pathways on ZCuOH for this complex.

For the direct formation of H$_2$NNO on [ZCuOH(NO)(NH$_3$)] the third highest energy starting geometry gives the lowest route overall (Fig. 7.12b right blue pathway). This pathway has an overall activation barrier of 87.3 kJ mol$^{-1}$ and is 117.7 kJ mol$^{-1}$ higher in energy than the lowest energy starting geometry, whereas the initial geometry with the lowest energy has an activation barrier of 129.3 kJ mol$^{-1}$ (Fig. 7.12b green). All reaction paths found for the direct formation of H$_2$NNO on [ZCuOH(NO)(NH$_3$)] are between 117.7 and 130 kJ mol$^{-1}$ relative to the
lowest energy complex. The formation of H₂NNO is also slightly exothermic with a range of energies for H₂NNO configurations possible.

The reaction routes for formation of HONO (reaction 7.8) on [ZCuOH(NO)(NH₃)] have energies ranging between 47.5 and 72.7 kJ mol⁻¹ relative to the lowest energy stating complex (Fig. 7.12b left). The starting geometry with the second lowest energy has the lowest overall transition state energy for the formation of HONO, being 10 kJ mol⁻¹ lower in energy than the pathway from the lowest energy starting complex (Fig. 7.12b left red pathway). The fact that OH⁻ has an additional coordination to the framework on the lowest energy starting complex could be a potential hindrance in the formation of HONO and the acceptance of a proton during the formation of NH₂⁻ and H₂NNO as to form these species an additional bond must be broken compared to the other geometries.

The formation of NH₄NO₂ via HONO is the pathway with the lowest energy and on average it is a lower energy process than the formation of HONO, as the transition state energy between HONO and NH₄NO₂ is lower than that of the starting geometry to HONO (Fig. 7.12c left). The energy of the transition states are between 39.7 and 56.1 kJ mol⁻¹ compared to the lowest energy starting geometry. The lowest energy starting complex for this reaction also does not provide the lowest route overall. As the transition state energies are lower for the second stage of the reaction, the formation of NH₄NO₂ from HONO, it is an easier process than the first stage in the reaction meaning NH₄NO₂ will form faster than HONO, which will be a metastable intermediate.

Only two routes of reaction were found for the formation of H₂NNO via HONO, with the highest energy transition state values of 116.1 and 118.8 kJ mol⁻¹ over the whole three step process (Fig. 7.12c right). Here, the lowest energy starting geometry does provide the lowest route of reaction overall. The energy of the transition states for the formation of H₂NNO via HONO is comparable to the transition state energy for the direct formation of H₂NNO, but both are significantly higher in energy compared to the formation of NH₄NO₂. However, at temperatures over 500 °C either route for H₂NNO formation becomes comparable in rates and competes with the NH₄NO₂ pathway as implied by the Arrhenius equation.
Figure 7.12 | The reaction profiles for the three different reduction half cycle potential routes on \( \text{[ZCuOH(NO)(NH}_3\text{)]} \). a) The initial geometries for the reaction pathways. b) direct \( \text{H}_2\text{NNO} \) (right) and HONO (left) pathways. c) \( \text{H}_2\text{NNO} \) from HONO (right) and \( \text{NH}_2\text{NO}_2 \) from HONO (left). Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
On the $\text{Z}_2\text{Cu}$ site, the energy of the starting complexes are separated by 29.4 kJ mol$^{-1}$ (Fig. 7.13a). The lowest energy complex has two Cu coordinations to framework oxygen species which bridge the 6MR and where $\text{NH}_3$ and $\text{OH}^-$ complete the distorted square planar geometry, with NO occupying the second solvation shell (Fig. 7.13a blue). The second and third lowest energy geometries are 18.4 and 19.1 kJ mol$^{-1}$ higher in energy respectively but despite the similar energies, the geometries are different. The 18.4 kJ mol$^{-1}$ geometry bridges the 6MR (Fig. 7.13a red) whereas the 19.1 kJ mol$^{-1}$ geometry bridges a single aluminium species (Fig. 7.13a black), both do however have NO in the axial bond and show a 5 coordinate framework species. The highest energy geometry is similar to the lowest energy geometry but has NO in a different position relative to the Cu complex (Fig. 7.13a green).

Performing the simulation for direct formation of $\text{H}_2\text{NNO}$ on the $[\text{Z}_2\text{Cu(OH)}(\text{NO})(\text{NH}_3)](\text{NH}_4^+)$ complex was more difficult compared to that of the equivalent ZCuOH site. Out of the 4 geometries tried only one route was successful in the direct formation of $\text{H}_2\text{NNO}$. The three other routes exhibited unstable $\text{NH}_2^-$ intermediates where upon unconstrained optimisation a proton would migrate from either the water species or the $\text{NH}_4^+$, reforming $\text{NH}_3$. The one successful simulation did not have stable $\text{NH}_2^-$ intermediate and upon unconstrained optimisation after the first proton transfer $\text{H}_2\text{NNO}$ was formed directly, with a barrier of 79.5 kJ mol$^{-1}$ from the lowest energy configuration (Fig. 7.13b blue, right).

The transition state energy for the formation of HONO ranges between 12.8 and 64.2 kJ mol$^{-1}$, where the transition state energy for this process from the lowest energy initial complex is significantly lower in energy than the other transition states found (Fig. 7.13b blue, left). The highest energy complex has the second lowest transition state energy (Fig. 7.13b green). The two complexes which have the middle energies of the starting geometry both have high transition state energies of 60.0 and 64.2 kJ mol$^{-1}$ (Fig. 7.13b red, black). Both exhibit an additional bond from $\text{OH}^-$ to the framework which needs to be broken in order for HONO to form, therefore adding additional energy to the process compared to just $\text{OH}^-.$

The formation of $\text{H}_2\text{NNO}$ via HONO on the $[\text{Z}_2\text{Cu(OH)}(\text{NO})(\text{NH}_3)](\text{NH}_4^+)$ complex shows lower energy transition states compared to that on the ZCuOH site, and are in fact at a lower energy than the transition state geometry for the formation of HONO. However, the transition state energies of 33.3 and 59.4 kJ mol$^{-1}$ are not lower than the corresponding route for $\text{NH}_4\text{NO}_2$
formation making this consistently the most favourable route. There is an indication that the $Z_2Cu$ site lowers barriers especially for the formation of $H_2NNO$ via HONO.
The reaction profiles for the three different reduction half cycle potential routes on $[Z_2Cu(OH)(NO)(NH_3)](NH_4^+)$.  

- **a)** The initial geometries for the reaction pathways. 
- **b)** direct $H_2NNO$ (right) and HONO (left) pathways. 
- **c)** $H_2NNO$ from HONO (right) and $NH_4NO_2$ from HONO (left). 

Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
7.4.2 \([\text{Cu}^{2+}(\text{OH}^-)(\text{NO})(\text{NH}_3)_2]^+\)

In this section we consider the reduction half cycle routes where the Cu active sites \(Z_2\text{Cu}\) and \(Z\text{CuOH}\) is in proximity to the three reacting molecules (\(\text{OH}^-, \text{NO}\) and \(\text{NH}_3\)) and an additional ammonia molecule are considered. i.e. the same as discussed in section 7.4.1, but in which there is an additional \(\text{NH}_3\) molecules adsorbed on Cu. Again, we consider 4 non-equal arrangements of the ligands for both \(Z\text{CuOH}\) and \(Z_2\text{Cu}\) sites.

On the \(Z\text{CuOH}\) site the four starting geometries are separated by 21.1 kJ mol\(^{-1}\) (Fig. 7.14a). The two geometries with the lowest energy are somewhat similar and are only separated by 2.1 kJ mol\(^{-1}\) (Fig. 7.14a black, blue). They both have a distorted square pyramidal geometry with NO in the longer axial bond and one coordination to the framework and exhibit a five-coordinate Si, however the orientation of the axial bond is in opposite directions for the two complexes. The third lowest energy complex shows a see-saw like geometry and has NO and \(\text{OH}^-\) to one another and are therefore in close proximity (Fig. 7.14a green). The highest energy complex is also see-saw like in geometry but with NO and \(\text{OH}^-\) trans to one another (Fig. 7.14a red).

The energy of the transition states for the formation of HONO are between 21.1 and 64.4 kJ mol\(^{-1}\), with the lowest energy transition state coming from the geometry with the third lowest initial energy (Fig. 7.14b green, left). It follows that as NO and \(\text{OH}^-\) are already in close proximity to one another in this geometry as they are in cis arrangement there is a very low activation barrier of 14.6 kJ mol\(^{-1}\) for them to react and form the HONO intermediate. Similar to the \([\text{Cu}^{2+}(\text{OH}^-)(\text{NO})(\text{NH}_3)]^+\) complex, the two geometries which present a five-coordinate Si species exhibit high transition state energies (Fig. 7.14b blue and red, left).

The transition states for the formation of \(\text{H}_2\text{NNO}\) have energies between 79.3 and 118.6 kJ mol\(^{-1}\), relative to the lowest energy starting complex. As for the formation of HONO the third lowest energy starting geometry has the lowest overall transition state energy which is at least 20 kJ mol\(^{-1}\) lower in energy than other transition state energies (Fig. 7.14b green, right).

The energy of the transition states for the formation of \(\text{NH}_4\text{NO}_2\) from HONO ranges between 43.1 and 53.6 kJ mol\(^{-1}\), which is comparable to the energy needed to form HONO from the starting geometries. Therefore, it is likely that \(\text{NH}_4\text{NO}_2\) forms easily after HONO is formed. This route is on average the lowest energy pathway out of the three possible reduction half cycle routes. The lowest overall route for \(\text{NH}_4\text{NO}_2\) formation is from the geometry which has
the third lowest initial energy and is also the lowest energy route for HONO and direct H$_2$NNO formation (Fig. 7.14c green, left).

Only one successful route was found for the formation of H$_2$NNO via HONO for the [ZCuOH(NO)(NH$_3$)$_2$] complex which is from the third lowest energy starting geometry (Fig. 7.14c green, right). It has the highest transition state geometry of 126.7 kJ mol$^{-1}$ and is higher than any transition state for HONO formation, the direct formation of H$_2$NNO or formation of NH$_4$NO$_2$. 

Figure 7.14 | The reaction profiles for the three different reduction half cycle potential routes on ZCuOH(NO)(NH₃)₂. a) The initial geometries for the reaction pathways. b) direct H₂NNO (right) and HONO (left) pathways. c) H₂NNO from HONO (right) and NH₄NO₃ from HONO (left). Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
On the Z₂Cu site, two different geometries overall of the \([\text{Cu}^{2+}(\text{OH}^-)(\text{NO})(\text{NH}_3)_2]^+\) complex provided successful reduction half cycle reactions and are separated by 23.9 kJ mol\(^{-1}\). Both complexes have a square pyramidal geometry and a five coordinate Si, with the additional bond to the OH\(^-\) species. However, they have a different position and orientation in the chabazite cavity which accounts for the different energy (Fig. 7.15a).

The transition states for the formation of HONO have energies of 33.8 and 56.7 kJ mol\(^{-1}\) where the lowest energy transition state corresponds to the initial geometry with lower energy. (Fig. 7.15b red, left).

The direct formation of H₂NNO is found to proceed with transition state energies of 110 and 116 kJ mol\(^{-1}\) (Fig. 7.15b right). The lowest energy initial complex corresponds to the lowest energy pathway for this complex (Fig. 7.15b red, right).

As with the other complexes investigated thus far, the NH₄NO₂ route is significantly lower in energy compared to the H₂NNO routes. The energy of the transition states for NH₄NO₂ formation are 21.4 and 8.9 kJ mol\(^{-1}\) and are both lower in energy than the transition states for HONO (Fig. 7.15c left). Therefore, it is expected that this step in the reaction would proceed faster and more easily compared to the formation of HONO.

Only one route for the formation of H₂NNO via HONO was found with a maximum transition state energy of 57.9 kJ mol\(^{-1}\), which is significantly lower in energy compared to the direct formation of H₂NNO and comparable in energy to the transition state of HONO. Therefore, it follows that on the Z₂Cu site once HONO is formed the pathway for both H₂NNO and NH₄NO₂ are active.
Figure 7.15 | The reaction profiles for the three different reduction half cycle potential routes on $[\text{ZCu(OH)}(\text{NO})(\text{NH}_3)_2](\text{NH}_2^+)$.

a) The initial geometries for the reaction pathways. b) Direct $\text{H}_2\text{NNO}$ (right) and HONO (left) pathways. c) $\text{H}_2\text{NNO}$ from HONO (right) and $\text{NH}_2\text{NO}$ from HONO (left). Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu.
7.4.3 [Cu$^{2+}$(OH$^-$)(NO)(NH$_3$)(H$_2$O)]$^+$

This section considers a new complex with 4 ad-molecules, where one of the NH$_3$ molecules from the complex modelled in the previous section is replaced with H$_2$O. Although H$_2$O is not a reactant of the SCR cycle, it is present in the catalytic system since it is a product of the de-NO$_x$ cycle, hence considering the effect of its presence next to Cu is relevant. Here, the transition state energies relative to the lowest energy starting geometry found for the both the ZCuOH and Z$_2$Cu sites with the reacting molecules and an additional water molecule are analysed.

On the ZCuOH site, the initial geometries found are separated by 56.4 kJ mol$^{-1}$. The lowest energy starting geometry presents an octahedral geometry with two O$_{fw}$-Cu bonds, one axial and one equatorial, with NO occupying the other axial bond (Fig. 7.16a black). There is also a five-coordinated Si bonded to OH$^-$ which is a common feature for low energy complexes. The second lowest energy complex is 38.1 kJ mol$^{-1}$ higher in energy and shows a square pyramidal geometry with NH$_3$ in the axial bond, two O$_{fw}$ coordinations which bridge over the Al species and the water molecule occupying the second solvation shell not directly coordinated to Cu, and NO and OH$^-$ cis to one another (Fig. 7.16a blue). The third lowest energy complex has all ligands directly coordinated to Cu in a distorted square pyramid like geometry, with O$_{fw}$ as the axial bond and NO and OH$^-$ trans to one another, with an energy of 42.0 kJ mol$^{-1}$ (Fig. 7.16a red). The highest energy complex found, is centred more in the 8MR than the 6MR and has a trigonal bipyramidal geometry, with NO and OH$^-$ in the axial bonds and 1 O$_{fw}$ coordination in the equatorial bonds with water and ammonia in the remaining bonds (Fig. 7.16a green).

The energy of the transition states for the formation of HONO range from 26.3 to 75 kJ mol$^{-1}$, with the lowest energy starting complex corresponding to the lowest energy transition state (Fig. 7.16b black, left). In fact, the energy of this transition state is lower in energy than the other starting configurations, which highlights how strong the variation in energy can be for different complexes and the low barrier nature for the formation of HONO. Furthermore, the highest energy initial complex has a transition state energy exactly the same as the transition state energy from the second lowest complex, despite the initial geometries being different further highlighting the complexity in the configurational space and how it can impact upon activation barriers.
Two successful simulations were found for the direct formation of H$_2$NNO, but with high transition state energies of 163.8 and 179.3 kJ mol$^{-1}$. The lowest energy initial geometry corresponds to the lowest energy transition state (Fig. 7.16b black, right). These are high energy processes and would possibly only proceed at high temperatures.

Transition state energies for the formation of NH$_4$NO$_2$ are calculated to be 46.1, 87.3 and 89.4 kJ mol$^{-1}$ relative to the lowest energy starting geometry. The lowest energy transition state also corresponds to the lowest energy initial geometry (Fig. 7.16c black, left). This is also the overall low energy pathway for this complex as both HONO and NH$_4$NO$_2$ transition state geometries stem from the same low energy initial geometry.

Only one pathway for H$_2$NNO via HONO is found for this complex which an energy of 156.4 kJ mol$^{-1}$, which is lower than that for the direct formation of H$_2$NNO (Fig. 7.16c blue, right).
The reaction profiles for the three different reduction half cycle potential routes on ZCuOH(NO)(NH\textsubscript{3})(H\textsubscript{2}O). a) The initial geometries for the reaction pathways. b) direct H\textsubscript{2}NNO (right) and HONO (left) pathways. c) H\textsubscript{2}NNO from HONO (right) and NH\textsubbox{4}NO\textsubbox{2} from HONO (left). Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
On the Z\textsubscript{2}Cu site with the reacting molecules and an additional water molecule, the energy of the four different initial geometries is found to be separated by 81.4 kJ mol\textsuperscript{-1}. The lowest energy complex shows a square pyramidal with two Cu to framework oxygen coordinations which bridges over an Al, OH\textsuperscript{-} and NH\textsubscript{3} are in the other equatorial bonds whereas NO is in the axial bond (Fig. 7.17a red). The water molecule occupies the second solvation shell hydrogen bonded to OH\textsuperscript{-}. This shows that not all ligands have to be directly coordinated to Cu in order to show a low energy geometry and that Cu coordinations to the framework are of a similar strength to framework oxygen coordinations. The hydrogen bond network lowers the overall energy of the system. The higher energy complexes all show a five-coordinate Si species. This is the opposite trend observed for the other complexes where the low energy geometries show the five-coordinate Si feature. This highlights not only the complexity of the configurational space but that complexes with different ligations can behave differently. The second lowest energy geometry is 26.6 kJ mol\textsuperscript{-1} higher in energy and shows a similar square pyramidal geometry but orientated differently with respect to the 6MR, and only has one framework coordination with NO in the axial bond (Fig. 7.17a blue). The third lowest energy geometry is similar to the second, but NH\textsubscript{3} and H\textsubscript{2}O have swapped positions which increases the energy to 63.6 kJ mol\textsuperscript{-1} higher in energy relative to the lowest energy complex (Fig. 7.17a black). This is a surprising increase for a relatively small change in geometry. The highest energy starting complex is 81.4 kJ mol\textsuperscript{-1} higher in energy and has the same orientation in the cage to the lowest energy complex, but only has one framework coordination and H\textsubscript{2}O is in the first coordination shell in the long axial bond and NO is the equatorial plane (Fig. 7.17a green). The fact that the weak ligand, NO, is in a shorter, stronger equatorial bond could be a reason for such a high energy.

The energy of the transition states for the formation of HONO are 52.6, 76.8, 89.6 and 130.0 kJ mol\textsuperscript{-1} relative to the lowest energy starting complex. It is the second lowest energy initial geometry, which corresponds to the lowest energy transition state and is 24.2 kJ mol\textsuperscript{-1} lower in energy, a significant difference (Fig. 7.17b blue, left). Here, another example where the lowest energy starting geometry does not correspond to the lowest energy route of reaction is observed.

Of the four starting geometries, only one was able to directly form H\textsubscript{2}NNO, with a high energy transition state of 133.7 kJ mol\textsuperscript{-1} (Fig. 7.17b blue, right). This is the same geometry which has
the lowest route of reaction for HONO formation and the direct formation of H$_2$NNO is the unfavourable route in comparison.

For the formation of HONO after NH$_4$NO$_2$ we find transition state energies of 40.1, 49.5 and 95.1 kJ mol$^{-1}$ where the lowest energy route from HONO continues to be the lowest energy pathway for NH$_4$NO$_2$ formation (Fig. 7.17c blue, left).

One successful pathway was found for the formation of H$_2$NNO via HONO with a transition state energy of 175 kJ mol$^{-1}$ (Fig. 7.17b green, right). This reaction displayed no stable NH$_2$ intermediate and upon optimisation after the proton transfer from NH$_3$ to HONO H$_2$NNO was formed, rather than NH$_2$. 
Figure 7.17 | The reaction profiles for the three different reduction half cycle potential routes on \([Z_2Cu(OH)(NO)(NH_3)(H_2O)](NH_4)^+\). a) The initial geometries for the reaction pathways. b) Direct \(H_2NNO\) (right) and HONO (left) pathways. c) \(H_2NNO\) from HONO (right) and \(NH_4NO_2\) from HONO (left). Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
7.4.4 $[\text{Cu}^{2+}(\text{OH}^-)(\text{NO})(\text{NH}_3)(\text{H}_2\text{O})_2]^+$

The reaction for the formation of $\text{H}_2\text{NNO}$ and $\text{NH}_4\text{NO}_2$ was performed on $\text{Z}_2\text{Cu}$ and $\text{ZCuOH}$ sites on a range of different geometries for a complex with the reacting molecules and two additional water molecules.

On the $\text{ZCuOH}$ site, four starting complexes which have energies 14.2, 25.6 and 41.3 kJ mol$^{-1}$ relative to the lowest energy geometry are found, but all show similar traits. All show a clear square planar feature and NO coordinated to Cu in a long axial bond. Upon optimisation Cu is pulled toward the 6MR framework forming what could be constituted a bond with distances ranging from 2.2 to 2.6 Å. The two lowest energy geometries have the Cu complex close to the Al species and are in the proximity of the 8MR (Fig. 7.18 green, blue). They also show a five coordinated Si. On the lowest energy geometry $\text{NH}_3$ is pointing into the chabazite cavity whereas for the second lowest $\text{NH}_3$ is in the face of the 8MR. The 3rd lowest, and highest energy geometries are situated away from the Al species in the 6MR (Fig. 7.18a black, red). The highest energy geometry has $\text{NH}_3$ pointing into the chabazite cavity whereas the 3rd lowest energy geometry has $\text{NH}_3$ pointing toward the framework.

For the formation of HONO transitions state energies of 64.5, 77.9, 95.0 and 99.8 kJ mol$^{-1}$ are found. It is evident that the lowest energy initial geometry does not provide the lowest overall pathway for the formation of HONO, just as observed on other complexes with different ligation. The second lowest initial energy actually provides the lowest overall route for the formation of HONO (Fig. 7.18b blue, left). It is interesting to see that despite the geometrical similarities of the two lowest energy complexes they show different energetic behaviour.

The transition state energies found for the formation of $\text{NH}_4\text{NO}_2$ have energies of 74.5, 89.0 and 104.5 kJ mol$^{-1}$, relative to the lowest energy starting complex. It is also observed that the lowest energy transition state is not the lowest energy starting complex, the third highest energy starting geometry provides the lowest energy transition state for the formation of $\text{NH}_4\text{NO}_2$ (Fig. 7.18c black). One of the attempted reactions was unsuccessful.

The direct formation of $\text{H}_2\text{NNO}$ exhibits a high energy transition state of 179 kJ mol$^{-1}$ and only one of the attempted reaction simulations was successful. For the formation of $\text{H}_2\text{NNO}$ via HONO none of the attempted reactions were successful and no transition states were found.
The reaction profiles for the three different reduction half cycle potential routes on $[\text{ZCuOH(NO)}(\text{NH}_3)(\text{H}_2\text{O})_2]$. a) The initial geometries for the reaction pathways. b) direct $\text{H}_2\text{NNO}$ (right) and HONO (left) pathways. c) $\text{H}_2\text{NNO}$ from HONO (right) and $\text{NH}_4\text{NO}_2$ from HONO (left). Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
On the $Z_2$Cu site for the $[\text{Cu}^{2+}(\text{OH}^-)(\text{NO})(\text{NH}_3)(\text{H}_2\text{O})_2]^+$ complex it was difficult to perform successful reaction simulations for each of the pathways. Four initial geometries were used, however only two of them were able to form stable reaction intermediates, so the others will not be discussed. The lowest energy starting complex has an octahedral geometry with water and a framework oxygen in the longer axial bond with $\text{H}_2\text{O}$, $\text{NH}_3$, $\text{OH}^-$ and a framework oxygen species in the equatorial bonds and NO in the second solvation shell (Fig. 7.19a red). The highest energy complex is 60.3 kJ mol$^{-1}$ higher in energy and is located more toward the 8MR, with oxygen framework and NO in the axial bonds and both water molecules, $\text{OH}^-$ and $\text{NH}_3$ in the equatorial plane (Fig. 7.19a black). Both complexes have a 5 coordinate Si species.

One barrier for the HONO is formed from the lowest energy complex with a transition state energy of 50.3 kJ mol$^{-1}$. After HONO is formed $\text{NH}_4\text{NO}_2$ can then form with a transition state energy of 93.3 kJ mol$^{-1}$. The highest energy complex was found to only form $\text{H}_2\text{NNO}$ directly without a stable $\text{NH}_2^-$ intermediate with a transition state energy of 127.4 kJ mol$^{-1}$ and could not form the HONO intermediate.
Figure 7.19  | The reaction profiles for the three different reduction half cycle potential routes on $[Z_2Cu(OH)(NO)(NH_3)(H_2O)](NH_4^+)$.

- **a)** The initial geometries for the reaction pathways.
- **b)** Direct H$_2$NNO (right) and HONO (left) pathways.
- **c)** H$_2$NNO from HONO (right) and NH$_4$NO$_2$ from HONO (left). Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
7.4.5 \([\text{Cu}^{2+}\text{(OH}^-\text{)(NO)(NH}_3\text{)}_3]^+\)

Here, the reduction half cycle pathways over a Cu complex with the three reacting molecules and two additional \(\text{NH}_3\) molecules are investigated.

The energies of the starting geometries for the ZCuOH site are 25.1, 30.6 and 53.4 kJ mol\(^{-1}\) relative to the lowest energy. The most stable geometry shows a five coordinated Si species, an octahedral geometry with NO and an oxygen framework species in the axial bonds and 3 \(\text{NH}_3\) and \(\text{OH}^-\) in the equatorial plane. It is also located toward the 8MR (Fig. 7.20a red). The second lowest energy geometry is positioned more into the chabazite cavity and also shows an octahedral geometry, but at a different orientation compared to the first. NO and an oxygen framework species are in the axial bonds and 3 \(\text{NH}_3\) and \(\text{OH}^-\) in the equatorial plane, with a five coordinated Si (Fig. 7.20a green). The third lowest energy configuration is similar to the second, but with the equatorial plane flat relative to the 6MR with no 5 coordinated Si species (Fig. 8.20a blue). The highest energy complex shows a more seesaw like geometry with NO in the second solvation shell and a five-coordinated Si species (Fig. 7.20a black).

Despite the large range in energy of the starting configurations the transition state energies for the formation of the HONO intermediate are relatively close together, with energies of 101.8, 104.1, 118.4, 120.5 kJ mol\(^{-1}\). The second lowest energy starting configuration provides the lowest overall route of reaction for the formation of HONO (Fig. 7.20b green).

Only one successful route for the formation of \(\text{NH}_3\text{NO}_2\) after HONO was found, which has a transition state energy of 92.8 kJ mol\(^{-1}\) (Fig. 7.20c red). The direct formation of \(\text{H}_2\text{NNO}\) was possible to simulate however no stable routes were found for the formation of \(\text{H}_2\text{NNO}\) via HONO. One route was found for the direct formation of \(\text{H}_2\text{NNO}\) from the highest energy initial complex with a transition state energy of 169.2 kJ mol\(^{-1}\) (Fig. 7.20b black, right).
Figure 7.20 | The reaction profiles for the three different reduction half cycle potential routes on ZCuOH(NO)(NH$_3$)$_3$. a) The initial geometries for the reaction pathways. b) direct H$_2$NNO (right) and HONO (left) pathways. c) H$_2$NNO from HONO (right) and NH$_4$NO$_2$ from HONO (left). Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
As with the $[\text{Cu}^{2+}(\text{OH}^-)(\text{NO})(\text{NH}_3)(\text{H}_2\text{O})_2]^+$ complex it was difficult to successfully simulate the reduction half cycle routes over $Z_2\text{Cu}$ with the reacting species and an additional two $\text{NH}_3$ molecules in the simulation cell. It is possible that crowding in the chabazite cavity leads to more computationally unstable reactions as there are more potential proton acceptors, and therefore an increased likelihood that upon unconstrained optimisation after a proton transfer the transferred proton will move to a stronger base such as $\text{OH}^-$ or $\text{NH}_2$ species.

The two starting geometries on the $Z_2\text{Cu}$ site which can form stable reaction intermediates are separated by 49.9 kJ mol$^{-1}$. The lowest energy complex is positioned toward the 8MR and has an octahedral geometry (Fig. 7.21a black). NO and a framework oxygen are in the axial bonds whereas the three $\text{NH}_3$ molecules and $\text{OH}^-$ are in the equatorial plane with $\text{OH}^-$ coordinated to a Si species. The high energy geometry is octahedral in shape with $\text{NH}_3$ and an oxygen framework species in the long axial bonds and two $\text{NH}_3$ molecules, a framework oxygen and $\text{OH}^-$ in the equatorial plane with NO occupying the second solvation shell (Fig. 7.21a red).

Two reaction pathways for the formation of HONO with transition state energies of 37.2 and 133.1 kJ mol$^{-1}$ are found (Fig. 7.21b, left). The lower energy pathways transition state is lower in energy compared to the higher energy starting configuration so clearly this pathway will be the most favourable of the ones sampled.

$\text{NH}_4\text{NO}_2$ can the form from HONO with a transition state energy of 60.4 kJ mol$^{-1}$ relative to the initial energy and stems from the lowest energy initial complex (Fig. 7.21c).

A reaction pathway for the direct formation of $\text{H}_2\text{NNO}$ is found with a transition state energy of 144 kJ mol$^{-1}$, (Fig. 7.21b right) whereas it was not possible to form $\text{H}_2\text{NNO}$ via HONO on the configurations attempted here.
Figure 7.21 | The reaction profiles for the three different reduction half cycle potential routes on Cu**(OH)(NO)(NH₃)(H₂O)₂. a) The initial geometries for the reaction pathways. b) direct H₂NNO (right) and HONO (left) pathways. c) H₂NNO from HONO (right) and NH₄NO₂ from HONO (left). Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
Thus far, the differences in energetics of the different reduction half cycle have been compared over an exemplar complex, and for different Cu complexes with various ligands in different configurations to understand how the configurational space can impact upon the reaction. In terms of the three different potential routes, it is found that the pathway via HONO and NH₄NO₂ is on average significantly lower in energy than the two different H₂NNO pathways. However, considering that many simulated reactions have activation barriers of 100 kJ mol⁻¹ or lower with a variety of energies it is likely that under SCR reaction conditions and normal operating temperatures of diesel engines (200-700 °C) these pathways will become active alongside the NH₄NO₂ pathway as according to the Arrhenius equation at temperatures approximately 400 °C or above. Furthermore, it is found that the lowest energy route of reaction is dependent upon the geometry of the reacting complex. This means that even if the global minimum energy for the geometry of a certain initial complex is found, it does not necessarily mean it will provide the lowest overall energy pathway. The results in this study commonly show that a higher energy starting geometry will provide a distinct and lower energy activation barrier compared to that which is found from the lowest energy complex found. The reaction routes calculated here are not a comprehensive screening of all possible routes of reaction taking into account all possible starting geometries. It would be computationally impossible to provide a complete energetic analysis of all possible Cu complexes which could undergo the SCR reaction including the different configurations and conformations. Considering it can take up to 50 times more computer power to simulate one reaction pathway than find a local minimum for a starting geometry it would be impossible to give a complete comparison for all the possible reduction half cycle pathways in order to find the lowest energy route. Therefore, the results provided show that even if the global minimum for the starting point of the reaction is found using computationally demanding and complex techniques such as molecular dynamics or simulated annealing it does not guarantee the overall lowest energy route for the reduction half cycle. It is therefore clear that when studying the reaction mechanism for the selective catalytic reduction of NOx a sample of reaction pathways should be studied in order to understand how geometrical variations change how the reaction proceeds.
7.5 Effect of Adding or Changing Ligands
In section 7.4 the effect of changing the geometry of initial complexes in the configurational space has been investigated. Here, the effect of increasing or changing the ligation of the active Cu complex is investigated over the RHC considering the three different reaction pathways over ZCuOH and Z2Cu active sites. Previously the energy of the transition states have been taken relative to the lowest energy initial geometry found, however this does not give the activation barrier but a comparison between the energy of the transition states from the lowest energy initial state. Also, the three different routes; direct formation of H2NNO, H2NNO via HONO and formation of NH4NO2 (equations 7.7-7.20) were compared to one another depending upon the ligation of the complex while taking the different configurations of a particular complex into account. Here, these three reaction pathways are compared to investigate how the activation barrier changes with changing coordination environments. As indicated by literature, as the temperature increases the solvation environment around the Cu active complex is reduced,\textsuperscript{93,175} therefore a low solvated complex can be used to represent a high temperature environment and a highly solvated complex can be used to represent a low temperature environment. As discussed in section 5.2 ammonia out-binds all other species to Cu, but water is the most abundant molecule in the diesel exhaust stream. Therefore, it is expected that over a range of temperatures there will be distribution of solvation environments with different ligands. Hence, we studied, the change in activation barriers with different solvation environments for both Z2Cu and ZCuOH active sites.

Activation barriers for the formation of HONO from the initial starting positions cover a large range of energy, between \(\sim 7-104 \text{ kJ mol}^{-1}\) depending upon the starting geometry and arrangement of ligands around the active Cu centre across the different complexes (Fig. 7.22). This variation in activation barriers clearly highlights the dependence of the SCR reaction on the arrangement of the ligands around the Cu complex. For example, the lowest energy barrier found is just under 7 kJ mol\(^{-1}\) and corresponds to the complex in which NO and OH\(^{-}\) are cis to one another. Due to their close proximity, they can easily interact and form HONO in a low energy process. When adding one water molecule the activation barriers are, on average, lower than when compared to adding one ammonia molecule. However, there is an increase in activation barriers for the formation of HONO with two additional ligands in the simulation as compared to complexes with no, or one additional ligand in proximity of Cu.
This is more evident on the ZCuOH site than the Z\textsubscript{2}Cu site. For example, of the 20 completed simulations for HONO formation on ZCuOH in total, 7 out of 8 highest energy barriers are over complexes which have two additional ligands. The situation is less clear on the Z\textsubscript{2}Cu site, where 2 out of 3 highest energy activation barriers are on sites with two additional molecules, including the highest energy overall barrier. It is therefore possible that upon increasing temperature the solvation environment around Cu will decrease and so will the activation barriers for the formation of HONO. There is only a slight difference on average for activation barriers of HONO with the average values for ZCuOH and Z\textsubscript{2}Cu being 49 and 41 kJ mol\textsuperscript{-1} respectively, and the highest energy barrier on the Z\textsubscript{2}Cu site is 83 kJ mol\textsuperscript{-1} compared to 104 kJ mol\textsuperscript{-1} for the ZCuOH site. The changes in the Cu coordination environment and in particular the steric hinderance induced on the reaction molecules by adding 2 additional spectator molecules is thought to increase the activation barriers.

![Figure 7.22](image_url) | A summary of activation barriers for the formation of HONO on 1Al (left) and 2Al (right) sites.

For the direct formation of H\textsubscript{2}NNO the activation barriers found on ZCuOH range between 72.8 kJ mol\textsuperscript{-1} and 152 kJ mol\textsuperscript{-1} whereas for the Z\textsubscript{2}Cu site they range between 79.5 and 116 kJ mol\textsuperscript{-1} (Fig. 7.23). This process is significantly higher in energy than the formation of HONO in fig. 7.22. The activation barriers for the direct formation of H\textsubscript{2}NNO are lower on the Z\textsubscript{2}Cu site compared to the ZCuOH site with average activation barriers of 97 and 110 kJ mol\textsuperscript{-1} respectively. However, it is calculated that it requires approximately 70 kJ mol\textsuperscript{-1} to first generate the OH\textsuperscript{-}, which acts as the proton receiver. In terms of the effect that having additional water or ammonia there is a slight decrease in activation energies when adding one ammonia molecule, especially when compared to adding one water molecule. This is the
opposite trend to that shown for the HONO reaction where one water molecule lowers the activation energies. Furthermore, three out of the four highest energy barriers found on the ZCuOH site include either one or two additional water molecules, therefore it is possible that when water is directly coordinated to Cu, the activation barriers for the direct formation of H$_2$NNO increase. These trends could be an artifact of the different configurations used, or perhaps a consequence of the different strength of electron donating effects of NH$_3$ and H$_2$O to Cu which effects the ease of the redox reactions. On the Z$_2$Cu site the second highest activation barrier found was when one additional water molecule is included. Of the reaction simulations attempted in the environment with two additional water molecules no stable transition sites were found, implying an unstable or difficult reaction.

**Figure 7.23 | A summary of activation barriers for the direct formation of H$_2$NNO on 1Al (left) and 2Al (right) sites.**

Once HONO has formed, the reaction can take two routes: via NH$_4$NO$_2$ or via H$_2$NNO. The lowest energy route is via NH$_4$NO$_2$ which has a spread of activation barriers of 5.6 to 69.6 kJ mol$^{-1}$ across the two sites and average values of 30 and 33 kJ mol$^{-1}$ for Z$_2$Cu and ZCuOH sites respectively (Fig. 7.24). The wide range of energy the activation barriers can take shows how dependent upon the arrangement of molecules around the Cu active centre the activation barrier is. For the formation of NH$_4$NO$_2$, when HONO and NH$_3$ are in close proximity the reaction barrier is lower than when they are further apart. Overall, there seems to be no obvious pattern that can be observed for how activation barriers change with increasing numbers of ligand, type of ligand or between the two different active sites and it is more configurationally dependent.
Fewer successful simulations for the formation of H$_2$NNO via HONO were found compared to any other route. It was also not possible to find stable reaction routes for complexes with more than one additional ligand, highlighting that this route in simulation conditions representative of a low temperature pathway may not be possible when an active site is crowded, as it would be in low temperature conditions. For both Z$_2$Cu and ZCuOH, the complex with no additional ligands shows the two lowest energy activation barriers indicating that this pathway maybe become more active with increasing temperature and subsequent loss of solvation. Furthermore, the Z$_2$Cu site shows lower energy activation barriers on average as compared to ZCuOH, meaning that once the OH$^-$ ion has formed, which is required for activation of NH$_3$ or HONO, the pathway over Z$_2$Cu is easier. The spread of activation barriers across both sites ranges from 32 to 136 kJ mol$^{-1}$ with average values of 73 and 120 kJ mol$^{-1}$ for the Z$_2$Cu and ZCuOH sites respectively (Fig. 7.25)
7.6 Dissociation of Nitrosamine (H₂NNO)

The reduction half cycle has been proposed in literature and shown computationally in section 7 to terminate with either H₂NNO or NH₄NO₂. However, both of these molecules need to dissociate into H₂O and N₂ only in order to fully close the cycle. H₂NNO has already formed an N-N bond and chemical intuition would imply the thermodynamic stability of the N≡N would drive the dissociation on this species by a succession of two proton transfers to form H₂O and N₂ only. This could feasibly take place through intramolecular transfers or via a proton shuttle mechanism, which is commonly observed in zeolitic systems. NH₄NO₂ however, does not have the N-N bond formed. It has been shown previously in literature that NH₄NO₂ does in fact dissociate via H₂NNO with a low energy process which requires Brønsted acidity. This, therefore, makes H₂NNO the key intermediate in the reduction half-cycle for the SCR reaction, as every possible pathway eventually proceeds via this intermediate. Here the dissociation pathway of nitrosamine is calculated through two different routes: intramolecular and Brønsted acid shuttle. It is feasible that other molecules such as NH₃ could also act as a proton shuttle, but this mechanism has not been considered.

The intramolecular mechanism proceeds via two simple intermolecular protons transfers:

\[ H₂NNO \rightarrow HNNOH \rightarrow N₂ + H₂O \]
In SSZ-13 this process is calculated to have activation barriers of 112 and 121 kJ mol\(^{-1}\) for the first and second step respectively, with the formation of N\(_2\) and H\(_2\)O being very exothermic. Figure 7.26 shows the reaction profile and corresponding stable geometries and their energies. We observe a change of coordination mode from H\(_2\)NNO to HNNOH where originally, H\(_2\)NNO coordinated to Cu from the O atom and upon proton transfer this coordination mode changes to the N atom adjacent to O. These activation barriers are higher than those calculated for the formation of H\(_2\)NNO, and it is generally accepted that H\(_2\)NNO dissociates quickly, therefore it is unlikely that the intramolecular dissociation of H\(_2\)NNO is the dominant mechanism for dissociation of H\(_2\)NNO, but it could become active at high temperatures.

![Image of reaction profile and corresponding stable geometries]

**Figure 7.26** | The intramolecular dissociation pathway for H\(_2\)NNO with the energies of the intermediate and transition states and the geometries of the intermediate states shown as insets. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu

The Brønsted acid shuttle mechanism was found to proceed via a succession of 3 proton transfers (Fig. 7.27):

\[
H_2NNO + Z/H → H_2NNOH + Z → HNNOH + Z/H → H_2O + N_2
\]  

7.13
The starting configuration corresponds to a Brønsted acid site, hydrogen bonded to the O of H$_2$NNO. The first proton transfer is from the Brønsted acid site to O of H$_2$NNO forming H$_2$NNOH. This process has a low barrier of 23.6 kJ mol$^{-1}$ and is an exothermic process. The next proton transfer corresponds to the breaking of the N-H bond and the reforming of a Brønsted acid site, but on a different oxygen framework species, forming HNNOH. This has a barrier of 52.0 kJ mol$^{-1}$ but the transition state energy is only 9.2 kJ mol$^{-1}$ more than the energy of the starting H$_2$NNO-Z/H system, so overall this is a low energy process. The next step in the reaction, corresponds to proton transfer from the newly formed Brønsted acid site to O of HNNOH, to form H$_2$O, N$_2$ and a new Brønsted acid site. When we simulate this reaction the proton transfers to the opposite side of the 8MR to an O no longer coordinated to an Al species. However, this proton transfer was not stable from the geometry produced at the end of the previous step. In order to achieve a stable and successful proton transfer, first a rotation of the H on O of HNNOH needs to occur which points the H species away from the framework. No barrier was calculated for this process. The difference in energy between these two geometries is only 8.0 kJ mol$^{-1}$ and due to the similar configurations, it is likely this rotation of H around O is a low energy process. This rearrangement of H is shown by the solid line in figure 7.27, whereas the other steps are represented with dashed lines to show barriers. The final barrier to form H$_2$O, N$_2$ and a new Brønsted acid site is calculated to be 23.1 kJ mol$^{-1}$. Overall, the Brønsted acid assisted decomposition of H$_2$NNO is found to be a low barrier process of comparable or lower energy process of the formation of HONO and NH$_4$NO$_2$. It should be noted, this dissociation would require the release of H$_2$NNO from Cu and the migration through 8MRs to a chabazite cage absent of Cu with a Brønsted acid site. Our simulation occurs without Cu in the chabazite cavity which provides Lewis acidity rather than the required Brønsted acidity.
7.7 Reduction Half-Cycle Summary

Here, we summarize the main findings from section 7 which correspond to the reduction half-cycle. The reduction half-cycle can proceed over three distinct routes on the mono-Cu active Z\textsubscript{2}Cu and ZCuOH sites, and an OH\textsuperscript{-} ion coordinated to Cu\textsuperscript{2+} is necessary in order to initiate the half-cycle by acting as a strong base. The ZCuOH site possesses an intrinsic OH\textsuperscript{-} ion due to the charge imbalance created by one Al species in the SiO\textsubscript{2} framework in proximity to Cu\textsuperscript{2+}, whereas the Z\textsubscript{2}Cu does not. Therefore, in order for the reaction to proceed on the Z\textsubscript{2}Cu site the OH\textsuperscript{-} ion first needs to be generated, which is calculated to require and activation barrier of ~70 kJ mol\textsuperscript{-1}. On average, activation barriers for Z\textsubscript{2}Cu site are slightly lower than for ZCuOH across the three different routes, but the 70 kJ mol\textsuperscript{-1} needed to first generate the OH\textsuperscript{-} ion significantly outweighs any energy gain by the Z\textsubscript{2}Cu site due to the slightly lower barriers. This therefore indicates that the ZCuOH site will be the preferred site for the reduction half-cycle compared to the Z\textsubscript{2}Cu site.
Of the three potential routes, the NH₄NO₂ pathway is significantly lower in energy compared to the direct H₂NNO, or H₂NNO via HONO pathways. Therefore, the NH₄NO₂ route will be the dominant one, especially in the low temperature regime < 250 °C. However, at elevated temperatures > 400-500 °C the other pathways will become more active and contribute more to the overall SCR activity, especially if the difference in activation energies is 50 kJ mol⁻¹ or less, as described by the Arrhenius equation. This is because at higher temperatures the increased energy within the system will be able to overcome the higher activation barriers required for the H₂NNO pathways and becomes comparable in rate according to the Arrhenius equation. There is a strong dependence of the activation barriers on the initial arrangement of molecules around the active Cu centre. This configurational dependence of activation energies creates a complex and varied environment in which the OH⁻, NO, and NH₃ molecules can react to form H₂NNO or NH₄NO₂, where activation energies can vary by nearly 100 kJ mol⁻¹ for the same process depending on the type and initial arrangement of ligands. It is also observed that the lowest energy initial complex does not necessarily correspond to the lowest energy route for a certain pathway. There are numerous examples of this situation where the lowest energy initial complex found does not correspond to the lowest energy transition state, or lowest activation barrier. This means that finding the global minimum on the potential energy surface for a particular Cu complex in the zeolite cavity is not enough to find the lowest energy reaction pathway. Therefore, to better understand the reaction pathway in a complex system such as Cu-SSZ-13, multiple simulations sampling a range of different starting geometries should be performed. In terms of the type of ligand coordinated to Cu, there is indication that an additional water molecule coordinated to Cu decreases the barrier for the direct formation of HONO but increases it for the direct formation of H₂NNO. Furthermore, two molecules coordinated to Cu in addition to reacting molecules, whether water or ammonia, increases the activation barrier for the formation of HONO, which is particularly noticeable on the 1Al site. However, to be able to conclusively say this, more reactions on different configurations should be sampled. As the formation of NH₄NO₂ via HONO is the dominant pathway, it is possible that the increase in activation energy required due to additional molecules, contributes to the decrease in SCR activity during the “cold start.” This corresponds to when the SCR system is cool before the engine warms up the exhaust system. At lower temperatures there is increased solvation of the Cu active site which is calculated to give larger activation barriers for the low energy NH₄NO₂ pathway. The de-
NOx SCR reaction is a dynamic system with many accessible configurations of Cu complex, each contributing to the overall mechanism. This level of complexity is currently not appreciated in the SCR literature. Once H2NNO or NH4NO2 have formed the reaction intermediates need to dissociate. The literature shows that NH4NO2 easily dissociates into N2 and H2O only, and that the most probable route is via H2NNO by a series of proton transfers initiated by a Brønsted acid site, making this a vital reaction intermediate. We have shown that through a succession of proton transfers assisted by a Brønsted acid site H2NNO dissociates into N2 and H2O with a low barrier.
Chapter 7 has so far analysed the reduction half-cycle reaction mechanism. Here, the less well quantified and more debated oxidation half-cycle reaction mechanism is investigated. The current leading proposal for the oxidation half-cycle mechanism focuses on the low temperature region and proceeds via the formation of transient dimeric Cu complexes \([\text{Cu}^+\text{(NH}_3\text{)}_2\text{O}_2^-\text{Cu}^+\text{(NH}_3\text{)}_2\text{]}\) intermediates obtained from two mobile \([\text{Cu}^+\text{(NH}_3\text{)}_2\text{]}\) complexes.\(^{189,206}\) This mechanism was proposed as a way to explain the quadratic dependence of the SCR rate and the Cu loading at low temperatures and low Cu density. Here, we propose a new mechanism over the mono-Cu active sites which focuses on the importance of NO and \(O_2\) working in conjunction to oxidise \(\text{Cu}^+\), and the formation of nitrate/nitrite intermediate species (\(\text{CuNO}_x\)).\(^{135}\) A peroxynitrite reaction intermediate, which has not been documented in the prior literature is proposed, adding key insight into the atomic level reaction mechanism. The dual site nature of the SCR mechanism will also be considered in this study as there is indication that the 1Al (ZCu) sites show lower activation energies than the 2Al sites (ZCu-Z/NH\(_4\)).\(^{184}\) Considering that FTIR and temperature programmed desorption studies indicate that that \([\text{Cu}^{2+}\text{NO}_x]^+\) only forms on the 1AlCu sites, it is important to understand different oxidation mechanisms at 1Al and 2Al sites.\(^{220,238}\) The calculations performed on the oxidation half-cycle as part of this thesis are presented in conjunction with experimental results obtained by Yiyun Liu and Ryan Wang (UCL chemical engineering) with whom we have collaborated extensively over the past years. We discuss first the experimental results. Despite these being collected by our experimental collaborators, analysis has been performed as a collaborative effort and taking into account both computational and experimental evidence. The structure of this section mirrors that of a joint publication submitted to Angewandte Chemie.

### 8.1 Experimental Analysis of the Oxidation Half-Cycle

The experimental results find the formation of transient \([\text{Cu}^+\text{(NH}_3\text{)}_x\text{O}_{\text{fw}}]\) and \([\text{Cu}^{2+}\text{NO}_x]^+\) intermediate species using time resolved Operando X-ray Absorption EXAFS and XANES and linear combination fitting of reference spectra. A representative Cu-CHA catalyst with 1 wt % Cu and common SAR of 25 (\(\sim\text{Cu/Al} = 0.131\)) is used to study the SCR reaction and NO conversion. According to the phase diagram produced by Paolucci et al. this sample contains
equal proportions of $1\text{AlCu}$ and $2\text{AlCu}$ sites. Under conditions of NO+NH$_3$ representative of reducing conditions, the sample is completely reduced to Cu$^+$ and shows the characteristic XANES feature at the Cu K-edge 8983 eV which corresponds to $[\text{Cu}^+\text{(NH}_3)_2]^+$ (Fig. 8.1a, red). It is then possible to study the oxidation half-cycle by switching the gas feed from NO+NH$_3$ to either NO+O$_2$ or just pure O$_2$. Upon switching to NO+O$_2$ at 200 °C, the feature representing $[\text{Cu}^+\text{(NH}_3)_2]^+$ is no longer visible and a feature at 8996 eV appears. This signifies oxidation to Cu$^{2+}$ and occurs in two stages as in the first stage approximately 65% of the original 8983 eV signal is retained. Linear combination fitting is used to study the Cu speciation during both stages of the oxidation. It is observed that the intermediate state possesses both $[\text{Cu}^+\text{(NH}_3)_2]^+$ (Fig. 8.1c green) and Cu-O$_{\text{fw}}$ features (Fig. 8.1c black), implying a transition from mobile $[\text{Cu}^+\text{(NH}_3)_2]^+$ to framework O bound Cu. At the higher temperature of 400 °C similar behaviour is also seen, but with a shorter intermediate stage. The second oxidation stage corresponds to transient $[\text{Cu}^{2+}\text{NO}_X]^+$ (Fig. 8.1c red), and subsequently partially converts to partially to framework coordinated Cu$^{2+}$ (Fig. 8.1c blue, black).

![Figure 8.1](image_url)

Figure 8.1 | Time-resolved XAS transient experiments. a,b) XANES spectra heatmap and c,d) Cu speciation during the transient experiments of 1 wt% Cu-CHA (SAR25) through Cu oxidation at 200 °C with the mixture of NO+O$_2$ a,c) or O$_2$ alone b, d) after full reduction with NO+NH$_3$. a,b) Top) Averaged XANES spectra at selected time points. a,b) Right) Signal intensity of Cu$^+$ 1s-4p transition peak at 8983 eV. The coexistence of Cu$^+\text{(NH}_3)_2$ and ZCu$^{2+}\text{OH}+Z_2\text{Cu}^{2+}$ in the intermediate stage suggests the formation of Cu$^+\text{(NH}_3)_2\text{O}_{\text{fw}}$. 

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When the gas stream is switched to pure O$_2$ rather than a mix of NO and O$_2$, the oxidation of Cu takes significantly longer, and Cu remains as a framework bound intermediate at both 200 and 400 °C. In addition, very little [Cu$^{2+}$NO$_x$]$^{2+}$ is observed due to lack of NO supply.

The coordination numbers of Cu to N/O can be deduced by fitting of EXAFS at initial, intermediate and final stages of oxidising conditions. The EXAFS analysis shows that at 200 °C the coordination numbers are $2.5 \pm 0.2$, $3.1 \pm 0.3$ and $3.2 \pm 0.4$ respectively, for initial, intermediate and final states, while at 400 °C the corresponding numbers are $2.1 \pm 0.2$, $2.7 \pm 0.3$ and $3.3 \pm 0.5$ respectively initial intermediate and final states. The increase in coordination number for the intermediate states compared to the initial state, can be assigned to the additional Cu-O$_{fw}$ coordination. The intermediate state will subsequently be referred to as [Cu$^+$(NH$_3$)$_x$O$_{fw}$] where $1 < x < 2$ as the number of NH$_3$ molecules directly coordinated to Cu is difficult to tell precisely from this data. The difference in behaviour due to the different gas composition (NO+O$_2$ vs only O$_2$) can be attributed to the fact that although both gas compositions form the long lived [Cu$^+$(NH$_3$)$_x$O$_{fw}$]$^+$ intermediate, the oxidation of [Cu$^+$(NH$_3$)$_x$O$_{fw}$] to [Cu$^{2+}$NO$_x$]$^+$ is only possible with the presence of NO. This difference in oxidation behaviour is also observed in EPR studies.$^{239}$ It is therefore deduced that the activation of [Cu$^+$(NH$_3$)$_x$O$_{fw}$] to break the Cu$^+$$-$$O_{fw}$ bond is the rate-limiting step in the oxidation half cycle.

In order to study the differences in the oxidation half cycle over 1Al and 2Al sites, two ideal representative catalysts are studied experimentally. According to the predicted phase diagram produced by Paolucci et al. a catalyst containing only 1Al sites can be synthesized with parameters of 3 wt % Cu (SAR 25, Cu/Al ~ 0.403) and a catalyst containing only 2Al sites with parameters of 1 wt % Cu (SAR 13, Cu/Al ~ 0.072).$^{93}$ Room temperature EPR studies confirm the two catalyst samples are indeed distinct, as they show a markedly different EPR response (Fig. 8.2). The spectra show overlap of two negative peaks in the high field region at around 315 and 325 mT. The peak at 315 mT belongs to an isotropic EPR signal, suggesting the [Cu$^{2+}$($H_2$O)$_6$]$^{2+}$ complex species with full rotational freedom and hence without bonding to the zeolite framework. The peak at 325 mT is the perpendicular region of an anisotropic EPR signal, assigned to copper water complexes restricted by the zeolite framework through coordination with O$_{fw}$. The comparison between 1AlCu and 2AlCu samples clearly shows that 1AlCu sample has a higher ratio of free Cu species (high isotropic signal), while the 2AlCu
sample has a higher ratio of restricted Cu species (higher anisotropic signal). This result indicates that Cu ions in the 1AlCu sample have weaker interaction with the zeolite framework, while the Cu-framework association is stronger in the 2AlCu sample. This gives a strong indication that in the 1Al sample Cu interacts less with the framework than at the 2Al sample, which is supported by our AIMD calculations discussed in section 6. This is due to the high isotropic signal on 1Al and high anisotropic signal on 2Al showing higher proportion of free Cu species and restricted Cu species on 1Al and 2Al samples respectively.

![EPR spectra](image)

**Figure 8.2** | EPR spectra of the fresh 1AlCu (3 wt % Cu, SAR 25, Cu/Al ~ 0.403) and 2AlCu (1 wt % Cu, SAR 13, Cu/Al ~ 0.072) samples at room temperature.

XANES collected with High-Energy Resolution Fluorescence Detection (HERFD) can reveal additional spectral features compared to standard XANES. HERFD-XANES collected under ambient conditions show signals very similar to that of aqueous $[\text{Cu}^{2+}(\text{H}_2\text{O})_6]^{2+}$ solution. Evidence of ZCuOH and Z$_2$Cu formation can be found in the respective 1Al and 2Al catalyst samples when O$_2$ is applied at 200 and 400 °C, by investigating Cu-O$_{\text{fw}}$ formation. This is because dehydration is induced, which subsequently reduces the intensity at 8996 eV and new features at 8986 / 8983 eV are observed, signifying a bare Cu species is formed.
coordinated to framework oxygen species (Fig. 8.3a). This new 8986 eV feature corresponds to 1s→4pz transition admixing with O-2p states, commonly referred to as 1s 4pz + ligand metal charge transfer shake-down transition.\textsuperscript{240} The 1Al sample shows a broadened 8986 eV feature. This suggests that Cu is coordinated to two distinct O species that have different O 2p energies, which causes the broadening of the shakedown transition. However, the 2Al sample only shows a narrow feature suggesting only one type of O species, which would correspond to the framework oxygen species coordinated to Cu.

Under reducing conditions (NO+NH\textsubscript{3}) the 1Al and 2Al samples show the typical 1s→4p transition at 8983 eV observed for a linear \([\text{Cu}^+ (\text{NH}_3)_2]^+\) complex, the same as the mix site catalyst (Fig. 8.3b).\textsuperscript{138,227,240} The peak maxima of the spectral features changes in energy and intensity as a function of catalyst type, temperature and gas composition. (Fig. 8.3c). Shifts to high energy and low intensity are observed for: decreasing the reducing power of the gas stream from NO + NH\textsubscript{3}, to NH\textsubscript{3}, and to NH\textsubscript{3} + O\textsubscript{2}; increasing the temperature from 200 to 400 °C, and sampling from 1Al catalysts to 2Al catalysts. Furthermore, new features are visible between 8986-8990 eV after increasing the temperature from 200 to 400 °C (Fig. A8.3). This implies a change of geometry from linear to tetrahedral due to the formation of new Cu-O\textsubscript{fw} bonds consistent with formation of the Cu\textsuperscript{+}(NH\textsubscript{3})\textsubscript{x}O\textsubscript{fw} intermediate, which is favoured on the 2Al site (Fig. 8.1c). The Cu\textsuperscript{+}(NH\textsubscript{3})\textsubscript{x}O\textsubscript{fw} intermediate is also observed in the linear combination fitting of HERFD-XANES with mixed \([\text{Cu}^+ (\text{NH}_3)_2]^+\) and Cu-O\textsubscript{fw} component (Fig. 8.3f). The Cu-O\textsubscript{fw} proportion increases for 2Al samples implying stronger framework binding compared to 1Al samples and is consistent with the \([\text{Cu}^+ (\text{NH}_3)_2]^+\) ratio found from the 1s→4p transition peak fitting intensity.\textsuperscript{193,241} Therefore, it is possible to conclude that reduction at 2Al sites produces more Cu\textsuperscript{+}(NH\textsubscript{3})\textsubscript{x}O\textsubscript{fw} species compared to 1Al sites and could affect their oxidation half-cycle behaviour.
Figure 8.3 | Edge region analysis of HERFD-XANES. HERFD-XANES spectra of 1AlCu and 2AlCu samples at 200 °C and 400 °C in a, O₂ and b, NO+NH₃. HERFD-XANES removes the broadening caused by core-hole lifetime and suppress background**, yielding further information on Cu oxidation state and coordination environment. c, Intensity and energy of the Cu⁺ 1s→4p transition for Cu-CHA samples under reductive conditions at 200 °C (open) and 400 °C (full symbols): NO+NH₃ (square), NH₃ (circle), NH₃+O₂ (triangle). d, HERFD-XANES spectra of reference compounds used in the LCF. Spectra of Cu-CHA catalysts in O₂ RT and in NO+NH₃ at 200 °C are used as reference for [Cu²⁺(H₂O)₆]²⁺ and [Cu⁺(NH₃)₂]⁺ in the LCF*. ZCu²⁺OH and Z₂Cu²⁺ are represented by spectra collected with 1AlCu and 2AlCu samples at 400 °C in O₂*. LCF analysis of Cu speciation in the 1AlCu and 2AlCu samples under different gas conditions at e, 200 °C and f, 400 °C, using the same colour code as in d.

Under treatment with NH₃+O₂ the 1Al catalyst shows complete oxidation to ZCuOH whereas the 2Al catalyst shows a mixture of ZCu²⁺OH and Cu⁺(NH₃)xOιw, highlighting a different ease of oxidation of the two sites. Under conditions of NO + NH₃ complete oxidation of Cu⁺ is observed at either 200 °C or 400 °C, but the 1Al and 2Al sites show a different Cu speciation. When NO+O₂ is fed over the reduced catalyst samples the 1Al catalyst exhibits Cu²⁺NOx (x= 2 or 3) which is not present when only NO or O₂ are present in the gas stream or in the 2Al sample (Fig. 8.3e, f, red). This shows that formation of Cu²⁺NOx via oxidation of both Cu and NO, only occurs on the 1Al sites. Cu²⁺NOx is thought to be an essential intermediate in the
oxidation half-cycle. In addition, at the fully oxidised state there is a high ratio of ZCu which implies a stronger CuO\textsubscript{fw} interaction compared to 1Al sites. Therefore it is possible to conclude that Cu\textsuperscript{+}(NH\textsubscript{3})\textsubscript{x}O\textsubscript{fw} in 1AlCu has weaker Cu-O\textsubscript{fw} interaction compared to 2Al, which allows 1Al to be more easily oxidised to form the Cu\textsuperscript{2+}NO\textsubscript{x} intermediate, implying high SCR activity.

During the oxidation half cycle there is a change from Cu-N coordination to mixed Cu-O Cu-N and then to Cu-O coordination, which corresponds to the transition from Cu\textsuperscript{+}(NH\textsubscript{3})\textsubscript{2} to Cu\textsuperscript{+}(NH\textsubscript{3})\textsubscript{x}O\textsubscript{fw} and to Cu\textsuperscript{2+}NO\textsubscript{x}. It is possible to study the change in Cu-N to Cu-O coordination using valence to core (VtC) XES. (Fig. 8.4a) This is because it can probe the transitions from the Cu 3d and 4p states which are mixed with the O/N 2p and 2s orbitals to Cu 1s core levels.\textsuperscript{101,102,134,138} (Fig. 8.4a) Analysis of XES spectra from reference C compounds with well-defined Cu speciation shows that Cu complexes with oxygen coordinations ([Cu\textsuperscript{2+}(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{2+}, Cu(OH)\textsubscript{2}, Cu(NO\textsubscript{3})\textsubscript{2}-3H\textsubscript{2}O) have a double peak Kβ2,5 feature at 8972.4/8976.0 eV, whereas N coordinated [Cu\textsuperscript{2+}(NH\textsubscript{3})\textsubscript{4}]\textsuperscript{2+} has a single peak at 8976.0 eV. Furthermore, a change from H\textsubscript{2}O to OH\textsuperscript{-} and NH\textsubscript{3} ligands can be seen by the shift of Kβ'' peaks from 8951.5 eV in [Cu\textsuperscript{2+}(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{2+} and Cu(NO\textsubscript{3})\textsubscript{2}-3H\textsubscript{2}O to 8955.8 eV in Cu(OH)\textsubscript{2} to 8960.0 eV in [Cu\textsuperscript{2+}(NH\textsubscript{3})\textsubscript{4}]\textsuperscript{2+}. The operando VtC XES performed on 1Al and 2Al samples are similar at 200 °C and show the Kβ2,5 double peak and Kβ'' peak for O-coordination under O\textsubscript{2} / NO + O\textsubscript{2} conditions and under reductive conditions with NH\textsubscript{3} N coordination is observed (Fig. 8.4c green, A8.2). The Kβ2,5 single peak is red shifted from 8976.0 eV in [Cu\textsuperscript{2+}(NH\textsubscript{3})\textsubscript{4}]\textsuperscript{2+} to 8973.6 eV in Cu-SSZ-13 compared to [Cu\textsuperscript{2+}(NH\textsubscript{3})\textsubscript{x}]\textsuperscript{2+} therefore implying reduction to [Cu\textsuperscript{+}(NH\textsubscript{3})\textsubscript{2}]\textsuperscript{+}\textsuperscript{243} which is consistent with XANES results showing a decrease of 1s to 4p transition (Fig. 9.2a,b,c). At 400 °C the Cu coordination in oxidative conditions does not change (3d, green) but under reductive (NH\textsubscript{3}+NO) conditions the double peak feature evolves and the Kβ'' red shifts to 8956.5 eV, indicating that under NO+NH\textsubscript{3} conditions at 400 °C Cu-O coordination is present. This supports the HERFD-XANES results which finds evidence for the [Cu\textsuperscript{+}(NH\textsubscript{3})\textsubscript{x}O\textsubscript{fw}] intermediate (Fig. 8.3b,f). When changing the gas stream from reductive (NH\textsubscript{3}+NO) to oxidative (NH\textsubscript{3}+O\textsubscript{2}) conditions the transformation from Cu\textsuperscript{+}(NH\textsubscript{3})\textsubscript{2} to Cu\textsuperscript{+}(NH\textsubscript{3})\textsubscript{x}O\textsubscript{fw} is observed. In the 1Al sample under oxidative conditions the Kβ2,5 feature matches the fully oxidised state showing oxidation to ZCuOH, whereas the 2Al site keeps the Cu-N signal at 8973.0 eV implying a mixture of Cu-O and Cu-N coordination (Fig. 8.4e, f). Along with the results obtained from the HERFD-XANES it is possible to conclude that 2Al sites contain a mixture of Cu\textsuperscript{+}(NH\textsubscript{3})\textsubscript{x}O\textsubscript{fw} and Z\textsubscript{2}Cu species. In order to achieve complete
oxidation of Cu⁺(NH₃)ₓOₓw to Z₂Cu both NO and O₂ are required for at least one hour. Therefore, the fast Cu-N to Cu-O conversion at 1Al sites and the fact that at 2Al keeps a mixture of Cu-N and Cu-O coordinations are confirmed by VtC-XES.

8.2 Computational Analysis of the Oxidation Half-Cycle

DFT calculations have been performed to examine Cu-Oₓw binding in 1AlCu and 2AlCu samples and the different activation barriers of Cu⁺ oxidation towards Cu²⁺NOₓ. Periodic boundary conditions are used to represent the catalyst and all reaction steps over it; however, initial screening calculations have also been performed using an isolated Cu cluster without the zeolite framework. These screening calculations were used to investigate the relative adsorption energies of ad-molecules to the [Cu⁺(NH₃)₂]⁺ complex, the starting point for the oxidation half-cycle. Despite showing in the reduction half-cycle that different coordination environments can affect the activation barriers, here, only [Cu⁺(NH₃)₂]⁺ is used as the active complex, as there is spectroscopic evidence that this species is the most dominant at the end of the reduction half-cycle at low-mid temperatures. Adsorption energies of NH₃, O₂, NO, H₂O to [Cu⁺(NH₃)₂]⁺ are calculated and shown in table 8.1.
<table>
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<th>Adsorbing species</th>
<th>Energy / kJ mol⁻¹</th>
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</thead>
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<tr>
<td>Additional NH₃</td>
<td>-129</td>
</tr>
<tr>
<td>O₂ side on coordination</td>
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</tr>
<tr>
<td>NO</td>
<td>-96.7</td>
</tr>
<tr>
<td>H₂O</td>
<td>-94.4</td>
</tr>
<tr>
<td>O₂ end on coordination</td>
<td>-71.1</td>
</tr>
</tbody>
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Table 8.1 | Adsorption energies of different ligands to [Cu⁺(NH₃)₂]⁺.

These results show that the side-on coordination mode of O₂ to Cu⁺ binds significantly stronger than the end-on mode, and side-on O₂ adsorption out-binds NO. (Fig. 8.5) The more favourable side-on adsorption mode of O₂ to Cu⁺ allows backdonation into the π* molecular orbital, weakening the O-O bond. In the equilibrium geometry O₂ exhibits an elongated bond length (1.33 Å) compared to the end-on mode (1.22 Å), implying the O-O bond is indeed activated towards dissociation.

![Figure 8.5](image)

Figure 8.5 | (a) Side-on and (b) end-on O₂ coordination to Cu⁺ with the relative difference in energy and bonds lengths

O₂ has been shown to interact with Cu in two different ways; it will either coordinate end-on or side-on, and interaction of Cu⁺, O₂ and NO is required for the oxidation half-cycle to proceed which will increase the coordination number of Cu⁺. Therefore, we now study the [Cu⁺(NH₃)₂]⁺ complex with additional O₂ and NO molecules. As the number of ligands directly coordinated to Cu⁺ is increased from 4 to 5, irrespective of the ligand type or configuration, the side-on coordination mode of O₂ is no longer observed in any calculations. A range of different coordination geometries, ligations and coordinations of Cu⁺ were tried and there...
was no evidence for the side-on mode with 5 ligands or O_{fw} species in the first solvation shell. Figure 8.6 shows example geometries to highlight the difference in bonding configurations between the 4 and 5 ligand scenarios, these calculations were performed in the gas phase and act as an example illustration. However, this change in coordination mode of O_{2} is consistent for both gas phase and periodic boundary condition calculations where the zeolite framework is present, and the O_{fw} sites can act as additional ligands. The end-on coordination mode is accessible for both 4 and 5 coordination numbers.

Several configurations of the [Cu^+\text{(NO)}(O_{2})(\text{NH}_3)_{2}]^+ complex were investigated for both 1Al and 2Al sites in the Cu-SSZ-13 catalyst under periodic boundary conditions. This is the most likely complex the oxidation half cycle proceeds over as O_{2} and NO need to be in proximity to Cu to react. It was found that whenever a Cu-O_{fw} bond was present, the complex was stabilised (by \sim 30 \text{ kJ mol}^{-1} and \sim 60 \text{ kJ mol}^{-1} for the 1Al and 2Al sites respectively) compared to configurations without Cu-O_{fw} bonds. When Cu is free from the framework all configurations found have comparable energies, while the configurational energy range increases for framework-coordinated complexes, indicative of steric and chemical constraints generated by the framework.

It is found computationally that only by increasing the Cu coordination number, through adsorption of NO, O_{2} or additional \text{NH}_3 molecules, can Cu be released from the direct interaction with O_{fw}. When NO and O_{2} molecules are co-adsorbed on [Cu^+\text{(NH}_3)_{2}]^+, the framework-coordinated and free Cu complexes are distinct local minima in the energy
surface. For 1AlCu releasing Cu from O_fw requires 28 kJ mol\(^{-1}\) compared to 67 kJ mol\(^{-1}\) for 2AlCu. This is a significant difference for the low temperature SCR. The stronger interaction of Cu\(^+\) with the framework in 2AlCu has electrostatic origin, since the Al ion replacing Si in the zeolite represents a lattice defect with negative net charge. This result suggests a shift towards framework-coordinated Cu from framework-free Cu, as well as slower Cu-O_fw bond breaking dynamics, in the 2AlCu as compared to the 1AlCu site.

Direct coordination of \([\text{Cu}^+(\text{NO})(\text{O}_2)(\text{NH}_3)_2]^+\) to O_fw has consequences for its interaction with \(O_2\). Framework-coordinated \([\text{Cu}^+(\text{NO})(\text{O}_2)(\text{NH}_3)_2]^+\) invariably yields end-on \(O_2\) adsorption, while in absence of Cu-O_fw bonds, side-on coordination of \(O_2\) is observed for both 1AlCu and 2AlCu sites. As seen earlier in this section side-on \(O_2\) enables backdonation of electrons from Cu to the \(\pi^*\) molecular orbital, activating O-O dissociation. This is validated by the equilibrium O-O bond length of 1.33 Å compared to 1.22 Å for end-on coordination. The release of Cu\(^+\) complexes from the framework to enable the activated side-on coordination of \(O_2\) to Cu\(^+\) is found to be a critical step in the oxidation half cycle.

Oxidation of \([\text{Cu}^+(\text{NH}_3)_2]^+\) for 1AlCu and 2AlCu environments is considered for three different Cu environments with a range of initial coordination environments, and varying the type, number and relative orientation of gas phase ligands (Fig. 8.7).
For both 1Al and 2Al sites three distinct geometries were chosen to be investigated: 1) NO and O₂ co-adsorbed, with Cu coordinated to the framework which causes O₂ to be coordinated end-on (Fig. 8.7, left); 2) NO in the second solvation shell and Cu coordinated to framework where O₂ is adsorbed to Cu end-on (Fig. 8.7, middle); 3) Cu free from the framework, with O₂ and NO co-adsorbed where O₂ can access the side-on coordination mode (Fig. 8.7, right). No evidence for geometries where Cu was coordinated to the framework and O₂ is coordinated to Cu in the side-on was found. Upon inspection of the energy differences between the sites it is clear that there are differences between the two sites. There is an energy difference of 28 and 67 kJ mol⁻¹ between the framework coordinated and framework free configurations where both NO and O₂ are co-adsorbed for the 1Al and 2Al sites respectively (Fig. 8.8). Only when Cu is framework free can O₂ coordinate in the side-on mode. This shows that it is easier for Cu to detach from the framework at the 1Al compared to the 2Al site and therefore under reaction conditions a catalyst prepared to have predominantly 1Al sites will have a greater proportion of framework free Cu exhibiting side-on coordinated O₂ than a catalyst prepared to have 2Al sites.
Figure 8.8 | Equilibrium structures and calculated energy difference between framework coordinated and free Cu⁺ at 1AlCu (top) and 2AlCu (bottom) sites, described under periodic boundary conditions. For 2AlCu site, an NH₄⁺ ion situated in the 8-member ring is used for charge balance and the 2 Al ions are located as 3rd nearest neighbours in the 6-member ring⁶,¹¹.

Only when NO and O₂ are present simultaneously is it possible to observe a stable product for the Cu⁺ oxidation, corresponding to formation of nitrate ions:

\[
[Cu^+(NH_3)_2(NO)(O_2)]^+ \rightarrow [Cu^{2+}(NH_3)_2(NO_3^-)]^+ \quad 9.1
\]

We simulate the reaction using the distinguished reaction coordinate method where intrinsic reaction coordinates are constrained and sequentially reduced, as outlined and used for the reduction half-cycle in chapter 7. A three-step mechanism for the formation of the nitrite ion in the oxidation half-cycle is identified (Fig. 8.9):

1) attack of NO to O₂ to yield a peroxynitrite ion (ONOO⁻) with simultaneous oxidation of Cu⁺ to Cu²⁺;

2) O-O bond dissociation to yield O⁻ and NO₂ both coordinated to Cu²⁺;

3) bond formation between O⁻ and NO₂ to form NO₃⁻.
The intrinsic reaction coordinates used to represent the three steps are: 1) distance between N of NO to O of O₂; 2) O-O distance of O₂; 3) N of NO₂ to O⁻ distance.

Figure 8.9 | Reaction steps involved in the formation of NO₃⁻ on mono-Cu active site. ∆E₁, ∆E₂, and ∆E₃ correspond to the activation energy of the three reaction steps and these energies are given in Table 8.2 for the different configuration tested.

The first step found here must be a two-electron process; one electron oxidises Cu⁺ to Cu²⁺ and another is involved in the oxidation of NO to form the peroxynitrite intermediate species. However, the exact electron movement is undefined. This peroxynitrite intermediate has not been identified in the previous literature. The full reaction profiles and activation barriers for the 6 different configurations of [Cu⁺(O₂)(NO)(NH₃)₂]⁺ tested are shown in Figure A8.3 (1AlCu) and A8.4 (2AlCu).

The lowest energy configuration, for both 1AlCu and 2AlCu sites, corresponds to NO and O₂ co-adsorbed in end-on conformation on framework-coordinated [Cu'⁺(NH₃)₂]⁺, representative of the [Cu⁺(NH₃)₂O₆] species found by operando X-ray spectroscopy (Fig. 8.7, 8.8). This Langmuir-Hinshelwood-like (NO and O₂ co-adsorbed on Cu) species is unable to form a peroxynitrite intermediate: the calculated energy profile shows no minimum on varying the OO-NO separation, and upon geometry optimisation ONOO⁻ always reverts to NO + O₂. A reactive geometry for framework coordinated Cu was found when O₂ is coordinated end-on to Cu and NO approaches the free end of the molecule from the second coordination sphere of Cu. This conformation is likely in the SCR reaction environment given the higher O₂ content compared to NO in the gas stream, and because O₂ out-binds NO in the coordination to Cu. This Eley-Rideal-like (O₂ adsorbed on Cu and NO in the second solvation shell) configuration is 32 and 15 kJ mol⁻¹ higher in energy than co-adsorbed NO and O₂ for 1AlCu and 2AlCu respectively. A [Cu⁺(O₆)-ONO⁻] intermediate is formed with low barrier of 4.9 and 18 kJ mol⁻¹ on 1Al and 2Al sites respectively (ΔE₁ in Fig. 8.9 table 8.2). Subsequent dissociation of the O-
O bond ($\Delta E_2$ in Fig. 8.9 table 8.2) requires in excess of 140 kJ mol$^{-1}$ and can thus be discarded for low temperature reaction mechanisms. If however, [Cu$^+$(NO)(O$_2$)(NH$_3$)$_2$]$^+$ is detached from the framework allowing side-on coordination of O$_2$, NO addition to O$_2$ occurs readily, and O-O dissociation requires a significantly lower activation barrier of 82-83 kJ mol$^{-1}$ for either site. Formation of NO$_3^-$ from NO$_2^-$ and O coordinated to Cu ($\Delta E_3$ in Fig. 8.9 table 8.2) is fast in all cases, due to the very low activation barriers. The calculated reaction barriers indicate that the mechanism concerning the reaction of NO with O$_2$ is similar in 1AlCu and 2AlCu environments and requires release of Cu from framework coordination to progress due to the large 140 kJ mol$^{-1}$ barrier when Cu is bound to the framework compared to a significantly smaller barrier of 80 kJ mol$^{-1}$ when Cu is free from the framework. What differentiates 1AlCu and 2AlCu environments is the strength of the Cu-O$_{fw}$ coordination, that makes formation of framework-free Cu much easier in the 1AlCu sample, in turn activating O$_2$ for bond dissociation, due to the induced side-on O$_2$ coordination to Cu. Table 8.2 summarises the activation barriers for formation of NO$_3^-$ on the mono-Cu active site for the six different Cu configurations highlighted.

<table>
<thead>
<tr>
<th>Site</th>
<th>Coordination Environment</th>
<th>$\Delta E_1$</th>
<th>$\Delta E_2$</th>
<th>$\Delta E_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1AlCu</td>
<td>Cu$^{1+}$-O$_{fw}$, NO in 2$^{nd}$ SS and end-on O$_2$</td>
<td>4.9</td>
<td>143</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Free Cu$^+$, co-adsorbed NO and side-on O$_2$</td>
<td>27</td>
<td>83</td>
<td>3.5</td>
</tr>
<tr>
<td>2AlCu</td>
<td>Cu$^{1+}$-O$_{fw}$, NO in 2$^{nd}$ SS and end-on O$_2$</td>
<td>18</td>
<td>140</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Free Cu$^+$, co-adsorbed NO and side-on O$_2$</td>
<td>60</td>
<td>82</td>
<td>36</td>
</tr>
</tbody>
</table>

*Table 8.2* | The activation barriers for each reaction step of the formation of NO$_3^-$ outlined in figure 8.9 for the different configurations for 1Al and 2Al sites.

A very complex reaction like the SCR over Cu-SSZ-13 is likely to undergo various different reaction pathways depending on environmental variables. The exhaust gas composition, the temperature and the active site structure all affect the ratio between the pathways taken. The Cu dimer complex, which has an amino oxygen bridged structure is a recently proposed active site over which the oxidation half cycle can proceed at low temperatures and can
dissociate the O-O bond. Here, a complementary pathway that occurs on monomeric Cu has been elucidated with the combination of time resolved XAFS, steady state HERFD-XANES and vtc-XES and DFT analysis. It is found that at low temperatures the reduced $[\text{Cu}^+(\text{NH}_3)_2]^+$ species, the main product formed at the end of the reduction half cycle, coordinates to the framework represented as $[\text{Cu}^+(\text{NH}_3)_x\text{O}_{fw}]$. At the 2AlCu site this intermediate species is bound more strongly to the framework compared to the 1AlCu site due to the stronger electrostatic charge generated by the additional Al species in proximity to Cu. Therefore, it is more difficult for Cu to be released from the framework, which assists the dissociation of the O-O bond. When Cu is bound to the framework it allows only the end-on coordination mode of O$_2$ to be accessible rather than the side-on mode, due to increased steric crowding. The side-on coordination mode of O$_2$ to Cu activates the O-O bond for dissociation, which is an essential requisite for the oxidation half-cycle to proceed. This means that non-framework bound Cu is more reactive for O$_2$ dissociation than framework bound Cu, therefore facilitating the formation of nitrite intermediates, where Cu$^+$ and NO are simultaneously oxidised by O$_2$. As a larger proportion of Cu complexes are framework-free on 1Al sites compared to 2Al sites this oxidation is found to happen preferentially on 1Al sites compared to the 2Al counterpart. The oxidation half cycle follows the pathway: $[\text{Cu}^+(\text{NH}_3)_2]^+ \rightarrow [\text{Cu}^+(\text{NH}_3)x\text{O}_{fw}] \rightarrow [\text{Cu}^+(\text{NH}_3)x(\text{NO})(\text{O}_2)]^+ \rightarrow [\text{Cu}^+(\text{NH}_3)x(\text{OONO})] \rightarrow [\text{Cu}^{2+}(\text{NH}_3)x(\text{NO}_3)]^{2+}$. This is not negating the occurrence of the proposed Cu-dimer pathway but provides an alternative and complementary pathway. A new updated full reaction cycle is shown in figure 8.10 which includes the formation of the NO$_3$ ion over mono-Cu. The elementary reaction steps involve first the attack of NO to O$_2$ to form the peroxynitrite intermediate, then the dissociation of the O-O bond creating O- and NO$_2$, finally O- and NO$_2$ form NO$_3$ quickly. An alternative route for the oxidation half-cycle has been provided in this study and is likely to happen complementary to the proposed mechanism over the Cu dimer, with different routes dominating depending upon the Al content, Cu loading, gas stream composition and temperature. It has also been found that side coordinated O$_2$ is a reaction intermediate which assists the splitting of the O-O bond. Understanding the fact that Cu monomers at 1Al sites can favourably release Cu complexes from the framework compared to 2Al sites, inducing the splitting of O$_2$ is a crucial step forward in the rational design of new catalytic reaction which show high selectivity and activity.
In regard to the completion of the SCR reaction cycle, including the dissociation of NO$_3^-$ and reforming of the active sites there is little discussion on these steps within the SCR literature, however it is generally regarded to be non-rate limiting and therefore an easier reaction. In theory, this phase of the reaction could proceed via first an attack of NO from NO$_3^-$ forming NO$_2^-$ still adsorbed onto Cu and the product of NO$_2$. Then, a proton transfer could take place from either H$_2$O or NH$_3$ to another NH$_3$ molecule forming NH$_4$NO$_2$ which is known to dissociate into N$_2$ and H$_2$O only. At the 1Al site proton transfer from H$_2$O to NH$_3$ would regenerate the ZCuOH site, ready to start the reduction half-cycle again. On the 2Al site proton transfer from either H$_2$O or NH$_3$ could take place, where the newly generated NH$_2^-$ molecule could subsequently react with another NO molecule forming H$_2$NNO which then...
dissociates into \( \text{H}_2\text{O} \) and \( \text{N}_2 \). These steps have not been computationally investigated and could be a later area of research that could add important understanding into how the oxidation half cycle is closed and the regeneration of the active sites of mono-Cu SSZ-13.
9. Simulated Vibrational Modes and IR spectra

Vibrational spectroscopy techniques such as IR can provide an additional way to analyse the reaction profile along with other experimental techniques.\textsuperscript{135,157,171,201,227,238,244–247} Characteristic vibrational modes can be used in order to identify molecules involved in the reaction and intermediate species to help understand how a reaction proceeds. Computational techniques are able to simulate the characteristic spectroscopic signals of molecules to allow comparison to experimentally obtained results, which help elucidate complex signals with unknown origins. Methods used to calculate the vibrational frequencies of the material or molecules are based on the harmonic approximation and the calculation of the Hessian matrix, which is usually evaluated analytically. The implementation in the CRYSTAL17 code is based on the analytical evaluation of energy gradients with respect to the nuclear positions. The Hessian matrix is subsequently calculated via the first derivatives by numerical differentiation.\textsuperscript{248} A description of the potential energy surface is required for the simulation and the prediction of IR spectra computationally. This is produced by calculating the normal harmonic frequencies at a minimum energy. The harmonic frequencies are obtained through the second derivatives of the potential energy at an optimised minimum. The IR intensities are approximated from the change of the dipole moment along the respective normal mode vector.

The simulated IR spectra produced computationally can then be compared to experimental results in order to detect key reaction intermediates and make inferences about the reaction mechanism. This, however, is not a simple task in the NH\textsubscript{3} de-NO\textsubscript{x} SCR reaction as strong framework vibrations dominate over a large wavenumber range and therefore can obscure signals from relevant molecules and short-lived intermediates. Also, due to the large number of possible intermediates and the likely diversity of the coordination environment for Cu (see section 5) precise assignment of vibrational peaks is challenging. For example, it is difficult to determine whether an O-H (stretching or bending) vibrational mode is from a hydroxide species or water molecules. Furthermore, it is known that vibrational frequencies can vary depending on the chemical environment of the active molecules, which has been proposed to be due to changes in the dipole moment because of effects from hydrogen bonding networks.\textsuperscript{249}
Here, the IR spectra of relevant molecules and complexes to the SCR reaction in the Cu-SSZ-13 catalyst are calculated, including species proposed to be present under ambient conditions and during the oxidation and reduction half-cycles, under SCR reaction conditions. The main aim of this study is to provide a reference library which can be used to compare experimental results for later consultation.

In order to be able to decouple the signatures of relevant SCR reaction intermediates from more abundant and therefore stronger signatures such as the framework, H$_2$O, NH$_3$ etc it is useful to build up and separate the signatures from one another. Figure 9.1 show the simulated IR spectra for pure silica SSZ-13, Z$_2$Cu sites and ZCuOH sites respectively. Each show strong framework vibrations between 200-1300 cm$^{-1}$. Interestingly the pure Si version shows no vibrations between 870-1080 cm$^{-1}$ whereas frameworks containing Z$_2$Cu and ZCuOH do. These new perturbations of the framework are related to the introduction of Cu and Al into the unit cell. On the Z$_2$Cu site one new intense mode is observed at 927 cm$^{-1}$ corresponding to the vibration of Cu-O bonds in the 6MR. On the ZCuOH site, two new but less intense modes are observed at 993 and 927 cm$^{-1}$ also corresponding Cu-O bond vibration on the 6MR.

Although the vast majority of the framework signatures overlap, the new features observed at 927 and 993 cm$^{-1}$ could be used to show incorporation of Cu in SSZ-13, although it is possible line broadening affects could obscure this signature. Furthermore, a very weak vibration is observed at 3924 cm$^{-1}$ (not shown in figure 10.1) which corresponds to the OH stretch of ZCuOH and is not intense enough to be seen on the figure. This, along with the 993 cm$^{-1}$ feature could potentially be used to identify the ZCuOH site.
Figure 9.1 | The simulated spectra of pure Silica (blue), Z2Cu (orange) and ZCuOH (green) SSZ-13. The images with the matching colours represent the geometry of the simulated vibrational modes. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu

The simulated spectra of an NH₄⁺ Brønsted acid site (where no Cu is present in the simulation) shows an analogous framework pattern to the pure silica zeolite between 200-1300 cm⁻¹ but exhibits NH₄⁺ deformations between 1418-1765 cm⁻¹ with low intensity peaks, and N-H stretching between 2647-3607 with high intensity peaks (Fig. 9.2). It also shows the lack of vibrational modes between 850-1000 cm⁻¹. This is a similar range to that for pure Si, which indicates the new features at 927 and 993 cm⁻¹ are most likely due to the introduction of Cu to the framework rather than Al.
The IR signatures from H$_2$O and NH$_3$ are also simulated with different numbers of these ligands directly coordinated to Cu to understand if and how the coordination environment changes the signatures. A single molecule adsorbed onto Cu$^{2+}$, the square planar, and octahedral geometries are simulated for H$_2$O and NH$_3$. The appendix contains the IR spectra for the single adsorbed molecules and square planar configurations, whereas the main text includes the IR spectra for the octahedral complexes. These simulations are performed on the Z$_2$Cu site for consistency and easier comparison.

A single water molecule adsorbed onto Cu$^{2+}$ shows three weak vibrational modes: H-O-H bending is at 1668 cm$^{-1}$, O-H antisymmetric is observed at 3979 cm$^{-1}$ and the symmetric stretching mode is observed at 3854 cm$^{-1}$ (Fig. A9.1). When the IR spectrum is simulated for the tetraaqua complex in the square planar configuration, it is found that each molecule’s vibrational modes are at different wavenumbers (Fig. A9.2). For example, the O-H stretching modes occur between 2694-3884 cm$^{-1}$ and the H-O-H bending between 1697-1762 cm$^{-1}$. For
the hexaaqua octahedral complex the O-H stretching is observed between 3182-3956 cm\(^{-1}\) and the H-O-H bending modes are between 1594-1728 cm\(^{-1}\) (Fig. 9.3). There is an anomalous O-H stretching mode at 2694 cm\(^{-1}\) which is potentially shifted to significantly lower wavenumbers due to a strong H-bond to the framework. The range of contributions to the different vibrational modes means the experimental spectra produced will appear as bands rather than individual peaks.

![Simulated IR spectra of six H\(_2\)O molecules adsorbed onto Cu\(^{2+}\) in SSZ-13](image)

*Figure 9.3 | the Simulated IR spectra of six H\(_2\)O molecules adsorbed onto Cu\(^{2+}\) in SSZ-13. The inset shows the geometry at the 6 and 8MRs. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu*

A similar situation occurs for NH\(_3\) simulations. For a single adsorbed NH\(_3\) molecule the vibrational modes observed are: asymmetric N-H stretch at 3587 cm\(^{-1}\) and 3514 cm\(^{-1}\), symmetric N-H stretch at 3363 cm\(^{-1}\), H-N-H scissoring at 1722 and 1671 and N-H wagging at 1376 cm\(^{-1}\) (Fig. A9.3). The tetraamine complex exhibits a distorted square planar geometry and has the asymmetric N-H stretching modes between 3512-3573 cm\(^{-1}\), the symmetric N-H stretching modes between 3263-3442 cm\(^{-1}\), H-N-H scissoring between 1676-1756 cm\(^{-1}\) and the N-H wagging modes between 1399-1468 cm\(^{-1}\) (Fig. A9.4). The hexamine complex shows
an octahedral complex with the asymmetric N-H stretch modes between 3522-3588 cm$^{-1}$, the symmetric N-H stretch 2290-3449 cm$^{-1}$, N-H-N scissoring modes between 1687-1753 cm$^{-1}$, and the N-H wagging between 1343-1480 cm$^{-1}$ (Fig. 9.4).

![Hexaamine](image)

**Figure 9.4** | the Simulated IR spectra of six NH$_3$ molecules adsorbed onto Cu$^{2+}$ in SSZ-13. The inset shows the geometry at the 6 and 8MRs. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu

The IR spectrum for a single NO molecule bound to Cu$^{2+}$ is also calculated (Fig. A9.5). A vibrational mode from N-O stretching is observed at 2035 cm$^{-1}$, with the rest of the contribution to the IR modes from framework vibrations. Despite this molecular configuration not resembling a situation found in reality, the vibrational mode of NO it is still representative of what could be observed in IR spectra.

Due to the strong framework vibrations which dominate over a large wavenumber, and the fact the contributions of water and ammonia vibrational modes will likely dominate in the regions their signals are present due to the strong modes and high concentrations of the molecules, it will be difficult to discern shorted lived and transient reaction intermediates from more abundant sources. Furthermore, due to the small number of elements involved,
and their chemical diversity it is difficult to say a certain contribution is caused by a given species. For example, the N-O or N-N stretching frequencies can vary significantly depending on their chemical environment. Simulations on water and ammonia coordinated to Cu$^{2+}$ highlight that the vibrational modes of certain configurations can vary due to different numbers of ligands and the configurations which would be observed in an experimental IR spectrum over a range of wavenumbers. In order to observe the IR signatures from short lived transient intermediates such as H$_2$NNO and HONO it is necessary to separate their signals from the strong and abundant vibrations which can be achieved using modulation excitation techniques. This can allow the separation of reaction intermediates from species not involved during the reaction.

Multiple spectra have been simulated for the HONO complex with a range of different coordination environments to Cu, summarised in table 9.1. Each of these configurations have Cu situated in the 6MR. The OH stretching mode occurs between 3025-3740 cm$^{-1}$, N-O stretching between 1314 and 1466 cm$^{-1}$, and N=O stretch between 1622 and 1787 cm$^{-1}$. Including extra ligands in the simulation cell induces variation in the frequency of the vibrations, however there is no obvious systematic trend to how much the wavenumber of vibrations is raised or lowered by. An H-bond will lower the frequencies of the vibrations, but it is not yet clear how an interaction with the framework, or additional ligands coordinated to Cu affects frequencies.

<table>
<thead>
<tr>
<th>HONO</th>
<th>Lone</th>
<th>+2NH$_3$</th>
<th>+2NH$_3$</th>
<th>+2NH$_3$</th>
<th>+2H$_2$O</th>
<th>+2H$_2$O</th>
<th>+2H$_2$O</th>
<th>+1NH$_3$</th>
<th>+1NH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H</td>
<td>3665</td>
<td>3697</td>
<td>3699</td>
<td>3670</td>
<td>3035</td>
<td>3068</td>
<td>3069</td>
<td>3740</td>
<td>3563</td>
</tr>
<tr>
<td>N=O</td>
<td>1690</td>
<td>1629</td>
<td>1629</td>
<td>1622</td>
<td>1724</td>
<td>1648</td>
<td>1647</td>
<td>1787</td>
<td>1786</td>
</tr>
<tr>
<td>N-O</td>
<td>1345</td>
<td>1317</td>
<td>1314</td>
<td>1333</td>
<td>1459</td>
<td>1466</td>
<td>-</td>
<td>1357</td>
<td>1330</td>
</tr>
</tbody>
</table>

Table 9.1 | wavenumbers of vibrational modes of the HONO molecule in different coordination environments of Cu$^+$. Cu$^+$ is situated in the 6MR for these calculations.

There is an analogous situation with the H$_2$NNO intermediate, where additional ligands coordinated to the Cu complex affects the wavenumber of specific vibrations, but in a non-
systematic way. The wavenumbers of each vibrational mode in different coordination environments are shown in table 9.2. As with the HONO molecule all simulated IR spectra in table 9.2 have Cu situated in the 6MR. N-H stretching modes occur between 3419-3687 cm\(^{-1}\), H-N-H bending modes between 1557 and 1595 cm\(^{-1}\), N=O stretching modes occur between 1522-1670 cm\(^{-1}\), and the N-N stretching modes occur between 1264 and 1300 cm\(^{-1}\).

<table>
<thead>
<tr>
<th></th>
<th>Lone</th>
<th>+2NH(_3)+H(_2)O</th>
<th>+1H(_2)O</th>
<th>+1H(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-H symmetric stretch</td>
<td>3687</td>
<td>3637</td>
<td>3586</td>
<td>3599</td>
</tr>
<tr>
<td>N-H asymmetric stretch</td>
<td>3490</td>
<td>3454</td>
<td>3433</td>
<td>3419</td>
</tr>
<tr>
<td>H-N-H bend</td>
<td>1593</td>
<td>1557</td>
<td>1595</td>
<td>1574</td>
</tr>
<tr>
<td>NO stretch</td>
<td>1576</td>
<td>1552</td>
<td>1670, 1658</td>
<td>1616</td>
</tr>
<tr>
<td>NN stretch</td>
<td>1298</td>
<td>1300</td>
<td>1298</td>
<td>1264</td>
</tr>
</tbody>
</table>

Table 9.2 | Wavenumber of vibrational modes of the H\(_2\)NNO complex in different coordination environments of Cu. Cu is situated in the 6MR for these calculations.

Only one IR spectra simulation has been performed for ammonium nitrite, which corresponds to a lone NH\(_4\)NO\(_2\) species coordinated to Cu\(^+\). N-H stretching modes occur between 3340 and 3540 cm\(^{-1}\) with one very intense N-H stretch at 2222 cm\(^{-1}\) which is the H, H-bonded to O on NO\(_2\) (Fig. 9.5 top). This N-H stretching mode at 2222 cm\(^{-1}\) is not present for just the Brønsted acid bound NH\(_4\)\(^+\) species alone and could be a potential marker to identify the ammonium nitrite intermediate species in the reduction half cycle. NH\(_4\)\(^+\) deformation occurs between 1572 and 1765 cm\(^{-1}\) which is in the same window as Brønsted bound NH\(_4\)\(^+\) so will most likely be obscured by this more abundant species. All the N=O stretching modes of NO\(_2\) are coupled with NH\(_4\)\(^+\) IR modes which occur between 1394 and 1743 cm\(^{-1}\), but with a very weak intensity.

Below ~1300 cm\(^{-1}\) all signals from molecules of interest will likely be completely obscured, and anything above 3000 cm\(^{-1}\) are contributions from X-H harmonic stretching which are difficult to deconvolute from H\(_2\)O, NH\(_3\) etc. Figure 9.5 shows spectra from the three key reaction intermediates HONO, H\(_2\)NNO and NH\(_4\)NO\(_2\) plotted for comparison, ignoring the framework contributions < 1300 cm\(^{-1}\). Most IR signals from the intermediate species involved in the reduction half cycle are present in the same regions, implying it could be difficult to determine intermediates from one another with the additional complexity of separating them.
from more abundant molecules signatures. However, the NH$_4$NO$_2$ signature at 2222 cm$^{-1}$ is an intense IR mode and, in a region, seemingly not occupied by other vibrational modes and therefore could be used to identify this intermediate species in the reduction half cycle.

![The simulated IR spectrum for HONO, H$_2$NNO and NH$_4$NO$_2$ as lone molecules in the chabazite cage with Cu$^+$ in the 6MR.](image)

**Figure 9.5** The simulated IR spectrum for HONO, H$_2$NNO and NH$_4$NO$_2$ as lone molecules in the chabazite cage with Cu$^+$ in the 6MR.

Thus far in this section we have highlighted spectroscopic signals from key reaction intermediates, now we will compare the important signals to results in the literature. The works by Greenaway *et al.* calculate the N=O stretching mode of H$_2$NNO to be at 1431 cm$^{-1}$ which is used to assign a signature from modulation excitation IR spectroscopy at 1436 cm$^{-1}$ to H$_2$NNO. The N=O stretching modes for H$_2$NNO are calculated here to be between 1522 and 1670 cm$^{-1}$, which is a significant difference from the values calculated by Greenaway *et al.* and assigned to H$_2$NNO. This discrepancy could be due to differences in computational parameters or a difference in geometry of the atoms in the simulation cell as the work by Greenaway *et al.* places Cu in the 8MR whereas here Cu is occupying the 6MR. In order to further understand this discrepancy, the IR spectra of H$_2$NNO calculations have been
performed with H₂NNO occupying the 8MR on 1Al and 2Al sites. Interestingly, there are significant differences between the 1Al and 2Al simulations and between the simulations with Cu in the 6MR calculated previously. Table 9.3 shows the wavenumbers of the same vibrational modes for the H₂NNO intermediate that appears for both simulations at the 1Al site, and the 2Al site with the NH₄⁺ counter ion, where Cu is situated in the 8MR. There is a clear discrepancy between them. There appears to be a systematic change of about -50 cm⁻¹ for NH₂ stretching and about +20 cm⁻¹ for NO and NN stretching when NH₄⁺ is included in the simulation cell. Modes appear at 1563, 1558, 1530 and 1419 cm⁻¹ for the 2Al NH₄⁺ simulation which are coupled vibrations of NH₄⁺ N-H and N-N-O stretching, all of which are absent in the 1Al simulation. It is important to note that in these calculations to find the characteristic signatures of H₂NNO, Cu is situated in the 8MR rather than in the 6MR like in table 9.2.

<table>
<thead>
<tr>
<th>H₂NNO</th>
<th>2Al + NH₄⁺</th>
<th>1Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-H symmetric stretch</td>
<td>3633</td>
<td>3688</td>
</tr>
<tr>
<td>N-H asymmetric stretch</td>
<td>3460</td>
<td>3501</td>
</tr>
<tr>
<td>NO stretch</td>
<td>1637, 1562, 1558, 1531, 1419</td>
<td>1600, 1619</td>
</tr>
<tr>
<td>NN stretch</td>
<td>1333</td>
<td>1309</td>
</tr>
</tbody>
</table>

Table 9.3 | The IR modes for H₂NNO at 1Al and 2Al sites when Cu is located in the 8MR.

Greenaway et al. attribute a feature at 1431 cm⁻¹ in their simulation as the NO stretching in H₂NNO, which the authors match to an experimental value of 1436 cm⁻¹. Results here show a signature at 1419 cm⁻¹ assigned to NO stretching strongly coupled to NH₄⁺ deformation on 2Al but not at 1Al (Fig. 9.6). It is likely the 1419 cm⁻¹ found here is the same mode found by Greenaway et al at 1431 cm⁻¹, but differences in computational set up and the complex configurational variety mean they are found at slightly different wavenumbers. It has been seen that different geometries cause the same vibrational modes to be observed at various distinct wavenumbers. Perhaps the key to finding other crucial intermediates such as HONO, NH₄NO₂ and even peroxynitirite (OONO⁻) is to compute the vibrational modes for a range of different configurations and coordination environments to look for further signatures which could be used to identify these molecules. It is also possible that some SCR intermediates are too transient to identify, even with modulation excitation IR techniques.
Figure 9.6 | The simulated IR spectra of H$_2$NNO in the 8MR at the 1Al and 2Al sites. The orange line corresponds to the 2Al site and the blue line to 1Al. The insets show the geometries of the structures. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu

For the oxidation half cycle over mono-Cu active sites it was found that the SCR reaction proceeds via a peroxynitrite species, and that the framework bound [Cu$^+$(NH$_3$)$_2$(NO)(O$_2$)]$^+$ species, more prominent on 2Al sites compared to 1Al sites, hinders the reaction (Section 8). This is because it is found that the non-framework bound species allows O$_2$ to coordinate on the side on mode to Cu which is not accessible for the more crowded framework bound species. Therefore, it follows to now simulate the spectra of framework bound and non-framework bound [Cu$^+$(NH$_3$)$_2$(NO)(O$_2$)]$^+$ in order to see if there are any characteristic differences which could be identified under oxidising conditions over catalyst samples which containing a majority of either 1Al or 2Al sites. In addition, the IR spectra of the peroxynitrite intermediate formed during the oxidation half cycle is simulated to highlight any potential vibrational modes that could be used to identify and confirm the presence of this intermediate species. Figure 9.7 shows a comparison of the IR spectra for the non-reactive framework bound [Cu$^+$(NH$_3$)$_2$(NO)(O$_2$)]$^+$ on the 2Al site and the reactive non-framework
bound $[\text{Cu}^+(\text{NH}_3)_2(\text{NO})(\text{O}_2)]^+$ on the 1Al site. The blue line represents the FW bound 2Al species with end-on coordinated $\text{O}_2$ and the orange line the non-framework bound 1Al species with side-on coordinated $\text{O}_2$. The contributions to the spectra due to $\text{NH}_3$ modes are similar on the two different configurations and that of $\text{NH}_3$ simulations previously discussed here. However, the NO and $\text{O}_2$ stretching modes are separated by a significant amount on the two different sites. The NO stretching mode on the framework coordinated 2Al site with the end-on $\text{O}_2$ species occurs at 1804 cm$^{-1}$ whereas the NO stretching mode on the non-framework coordinated with the side coordinated $\text{O}_2$ is at 2026 cm$^{-1}$, a difference which should be visible in two separate catalyst samples synthesised to contain a majority of either site if signals are strong enough. Furthermore, the $\text{O}_2$ stretching mode for the two different situations is also different. The end-on $\text{O}_2$ coordination mode, which is favoured on the 2Al framework coordinated geometry, has the $\text{O}_2$ stretching mode at 1496 cm$^{-1}$ whereas the side-on $\text{O}_2$ coordination mode which is more prominent in the 1Al non-framework coordinated geometry, the $\text{O}_2$ stretching mode occurs at 1299 cm$^{-1}$. This variation in NO and $\text{O}_2$ modes could potentially be detected by modulation excitation IR spectroscopy experiments under the right conditions.
It was found in section 8 that the 1Al site promotes the formation of the peroxynitrite intermediate on the mono-Cu active site and is thus far an undiscussed SCR intermediate in literature. The peroxynitrite exhibits an N-O stretching mode at 1882 cm\(^{-1}\), which could potentially be used to confirm the existence of this intermediate species in the oxidation half-cycle (Fig 9.8). However, modulation excitation IR techniques would likely need to be used in order to decouple the signature from molecules not participating in the reaction. The simulation does not reveal any other stretching modes for the peroxynitrite species.

Figure 9.7 | The simulated IR spectrum for two types of Cu(NO)(O\(_2\))(NH\(_3\))\(_2\) species with Cu\(^+\) in the 6MR. The blue line shows the framework bound species and the orange the free Cu species. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu

FW bound species compared to non-framework bound species
Figure 9.8 | The simulated IR spectrum for the peroxynitrite intermediate species the chabazite cage with free Cu$^{2+}$.
10. Conclusion

The main goals of this thesis were to further understand the speciation of the active site and to add detail to the reaction mechanism for the NH₃ de-NOₓ SCR reaction over Cu-SSZ-13. We have provided valuable insight into the speciation of the Cu active site by investigating different Cu complexes. The range of reaction temperatures and gas compositions involved in the SCR reaction is large, which means there will be a significant distribution of Cu complexes and speciations which can participate in the reaction all with various ligands, coordination numbers, geometries, configurations, positions and orientation. Furthermore, the synthesis conditions, in particular the Si/Al and Cu/Al ratios determine the form and proportion of the Cu active site. Cu is present in two distinct forms, termed ZCuOH and Z₂Cu, depending on whether it is situated in proximity to 1Al or 2Al. The ZCuOH site has an intrinsic OH⁻ ion present whereas the Z₂Cu sites does not. There are literature reports that a dimeric form of Cu is important to the low temperature mechanism, which forms after one Cu migrates through 8MR ring windows and meets another Cu complex. Literature works appreciate the complexity in the form and speciation of the Cu active site, but they do not consider the added layer of complexity on top of this given by the variation in the configurational space of the Cu complex. We have shown in chapter 5 that there are many accessible configurations for a given complex which can be accessible over a small range of energies, and through AIMD calculations in section 6 we have shown that they are likely to interconvert. Therefore, over typical SCR conditions and on industrial SCR catalysts a distribution of different Cu complexes with distinct coordination environments will be present in the catalyst. When considering the reaction mechanism, it is likely that depending upon the initial state of the active complex the mechanism could take different routes or at least show different activation barriers. Computational techniques can find the global minimum energy structure but at vast expense, while other less expensive techniques can provide an estimate. However, a low energy starting configuration does not guarantee a low energy route and therefore in order to gain a more complete understanding of the reaction multiple routes over different initial complexes should be investigated. In this thesis the main focus of the reaction mechanism is on the Cu monomer rather than the dimer.
The reduction half cycle has previously been simulated in literature and activation barriers for certain steps have been calculated, highlighted in chapters 3.6 and 7. However there are different schools of thought, and these different mechanisms are all computed with a different computational set up, which puts the reactions on different energy scales and therefore means they cannot be compared to each other. We simulate the three leading reaction mechanisms over the two different mono-Cu active sites for 5 different complexes each with various different configurations with consistent computational parameters (section 7). We observe an interesting artifact when investigating the activation of ammonia in Cu-SSZ-13 and comparing the Z\textsubscript{2}Cu and ZCuOH sites. The mechanism proceeds via an heterolytic abstraction of a proton from ammonia to yield the NH\textsuperscript{2−} intermediate; NH\textsubscript{3} can only be activated by OH\textsuperscript{−} (or HONO, formed from OH\textsuperscript{−}), the strongest base present in the reaction environment, and not by other species intrinsically present in the Z\textsubscript{2}Cu site or in the SCR gas mixture. Therefore, for the reaction to proceed on Z\textsubscript{2}Cu an initial generation of OH\textsuperscript{−} is needed. We propose an initial transformation of active site which takes the form of an equilibrium between Z\textsubscript{2}Cu and ZCuOH + ZH as discussed in section 7.2. We find this process to have and activation energy of \(~70\) kJ mol\(^{-1}\) and depending upon the Al distribution the equilibrium can favour ZCuOH compared to Z\textsubscript{2}Cu. This dynamic shift of the active site to the author’s knowledge has not been proposed in literature previously. In terms of activation energies for the three competing pathways, it is found that they all span a surprisingly large energy range (\(~100\) kJ mol\(^{-1}\)) just depending upon the type and initial configuration of ligands around the Cu active site, where the lowest energy initial complex does not always give the lowest energy overall route. Therefore, we have shown that in order to fully sample the reaction energetics a range of initial configurations of the Cu complexes needs to be investigated. On average, the HONO followed by NH\textsubscript{4}NO\textsubscript{2} route requires an activation barrier approximately 50-60 kJ mol\(^{-1}\) lower in energy than either pathway through the formation of H\textsubscript{2}NNO (directly or via HONO). Therefore, according to the Arrhenius equation it is expected that the route via HONO and NH\textsubscript{4}NO\textsubscript{2} will be completely dominant in the low-mid temperature regimes. By 500 °C can be shown that the other pathways become comparable in rates. However, at temperatures above 300 °C literature results show that the activation energy of the SCR reaction changes from approximately 70 kJ mol\(^{-1}\) under temperature conditions to 140 kJ mol\(^{-1}\).\textsuperscript{184} Between 250-300 °C experiments show a low overall rate, the infamous ‘seagull feature’ in the light-off curve. This could signify the beginning of a shift from one reaction pathway to another.
It is generally accepted that as the temperature increases the Cu complex loses solvation and coordinates directly with the framework. We have found that NH$_3$ out-binds all other molecules to Cu$^{2+}$ which agrees to prior literature works. We have also observed that the formation of HONO, the first step in the formation of NH$_4$NO$_2$, is a low energy process when both NO and OH$^-$ are co-adsorbed and adjacent to each other on the Cu complex. It is therefore possible to postulate that as the temperature is increased NO no longer coordinates directly to Cu$^{2+}$ meaning the low energy reaction of NO and OH$^-$ to form HONO is not possible.

At higher temperatures only strongly bound species such as OH$^-$ and NH$_3$ coordinate directly to Cu which is now anchored to the framework. In this configuration where only NH$_3$ and OH$^-$ are co-adsorbed on Cu the higher energy process of a proton transfer from NH$_3$ to OH$^-$ could take place forming H$_2$NNO and NH$_2^-$, then NO attacks NH$_2^-$ from the outer coordination shell of the complex, but still in the chabazite cage, which is a low barrier process. This potential shift in reaction mechanism from the NH$_4$NO$_2$ via HONO to direct formation of H$_2$NNO due to the changing coordination environment could explain the shift in activation energies and the seagull feature. To be able to say this conclusively further simulations and experimental work must be performed. On average, our calculated activation barriers are lower on the Z$_2$Cu site compared to the ZCuOH site; however, OH$^-$ must first be generated on Z$_2$Cu, with an activation energy of 70 kJ mol$^{-1}$. This indicates that it takes less energy to form essential reaction intermediates NH$_4$NO$_2$ and H$_2$NNO on the ZCuOH compared to the Z$_2$Cu site as the lower barrier observed on Z$_2$Cu are not 70 kJ mol$^{-1}$ lower compared to the ZCuOH site. This signifies that 1Al sites may be more active in the SCR cycle than 2Al sites due to the presence of the OH$^-$ ion which acts as a strong base.

In the oxidation half-cycle, calculations predict a reaction route with an 80 kJ mol$^{-1}$ activation barrier, which proceeds via a peroxynitrite intermediate that has not been previously documented in the SCR literature. It is feasible that the short-lived nature of the intermediate means that experimentally or spectroscopically this species is not able to be observed with conventional techniques. Also, NEB DFT techniques could miss this crucial intermediate state as the PES for this reaction is very complex. Our computational techniques although more manual, are likely to find additional levels of detail compared to an automatic NEB transition state search giving a clear advantage when performing complex searches. The current general literature consensus is that for the low temperature regime the NH$_3$-solvated Cu$^+$ complex...
migrates through an 8MR ring and forms a dimeric species with another Cu complex. The mechanism found here proceeds on the Cu monomer so there is no need for Cu to migrate through the zeolite which could mean it is more suited for the high temperature mechanism, where the complex is strongly anchored to the framework. However, it is possible that in the low temperature mechanism both monomer and dimer routes could proceed in competition. We have found that O$_2$ has two distinct coordination modes; end-on and side-on, where the side-on mode activates the O-O bond for dissociation. This side-on coordination mode is only accessible for the [Cu$^+$(NH$_3$)$_2$(NO)(O$_2$)]$^+$ complex when it is released from the framework. We have found barriers of 80 kJ mol$^{-1}$ for the oxidation half-cycle when O$_2$ is activated and Cu free from the framework, and 140 kJ mol$^{-1}$ when O$_2$ is in the un-activated end-on mode, while it is coordinated to the framework. Furthermore, 2Al sites anchor the Cu complex to the framework more than 1Al sites meaning a higher proportion of Cu complexes will be free from the framework exhibiting side-on activated O$_2$ or able to migrate through the 8MRs. This implies greater activity on the 1Al site compared to the 2Al site. Under the low T regime both monomeric and dimeric routes could be competing, but in the high temperature regime the monomeric route is more likely as O$_2$ may dissociate while Cu is attached to the framework, but with an energy barrier of 140 kJ mol$^{-1}$ which also corresponds to the experimentally observed activation barrier of 140 kJ mol$^{-1}$ for the high temperature regime.

Literature studies show that the SCR reduction and oxidation half-cycles occur at very similar rates. The new finding of the peroxynitrite intermediate in the oxidation half-cycle could potentially rationalise the similarity in the rates as the reaction intermediates are of similar structure and could dissociate via the same reaction intermediates.

Overall, additional mechanistic insight into the SCR reaction has been provided. A route for the oxidation half-cycle is proposed which does not require the formation of a dimeric Cu species; the low energy route for the reduction half cycle through NH$_4$NO$_2$ has been calculated. Literature suggests that NH$_4$NO$_2$ dissociates via H$_2$NNO making this a vital reaction intermediate. A low energy dissociation pathway for H$_2$NNO over a Brønsted acid site to complete the reduction half-cycle has been calculated. IR spectra for relevant SCR species have also been simulated including the signatures from the newly proposed peroxynitrite species. DFT simulations suggest that for both the oxidation and reduction half cycle there is a change in reaction mechanism induced by the loss of solvation of Cu causing it to coordinate.
to the framework, which could explain the origin of the seagull feature in the light-off curve. The 1Al site is predicted to be more active for the SCR reaction for both half-cycles.
11. Appendix

An example CRYSTAL17 input file for the formation of HONO on a mono-Cu active site in Cu-SSZ-13:

HONO formation NH3-OH-NO complex, config1

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Appendix Figure 5.1 | The geometries used in to calculate the exchange energy between Z₃Cu and ZCuOH. Each 6MR and 8MR represent separate chabazite cavities in a 2x1x1 supercell. a) [Z₃Cu(H₂O)] and a pure Si chabazite cavity. b) Z₃Cu and water in pure silica. c) ZCuOH and Z/H in separate cavities. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
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**Appendix Table 5.1** | The observed geometry, adsorption energy and bond lengths of single molecules of H₂O, NH₃, N₂, O₂, NO and NO₂ to Z₂Cu, ZCuOH, ZCu and ZCu-Z/NH₄.
**Appendix Figure A5.2** | Water adsorption onto a) Z:Cu b) ZCu-Z/NH4 c) ZCuOH d) ZCu. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu

**Appendix Figure 5.3** | Ammonia adsorption onto a) Z:Cu b) ZCu-Z/NH4 c) ZCuOH d) ZCu. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
Appendix Figure 5.4 | Nitrogen adsorption onto a) Z:Cu b) ZCu-Z/NH₄ c) ZCuOH d) ZCu. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu

Appendix Figure 5.5 | Nitrogen adsorption onto a) Z:Cu b) ZCu-Z/NH₄ c) ZCuOH d) ZCu. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
Appendix Figure 5.6 | Nitrogen oxide adsorption onto a) Z$_2$Cu b) ZCu-Z/NH$_3$ c) ZCuOH d) ZCu. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu

Appendix Figure 5.7 | NO$_3$ adsorption onto a) Z$_2$Cu b) ZCu-Z/NH$_3$ c) ZCuOH d) ZCu. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
Appendix Figure 5.8 | NO\textsubscript{2} adsorption onto a) Z\textsubscript{2}Cu b) ZCu-Z/NH\textsubscript{4} c) ZCuOH d) ZCu. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
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Table 5.2 | The adsorption energies, the difference in energy between different configurations with the same number of ligands and the different coordinations to Cu of H₂O to Z₂Cu, ZCuOH, ZCu-Z/NH₄, and ZCu sites. SSS refers to the number of molecules in the second solvation shell
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**Table 5.3** | The adsorption energies, the difference in energy between different configurations with the same number of ligands and the different coordinations to Cu of NH$_3$ to Z$_2$Cu, ZCuOH, ZCu-Z/NH$_4$ and ZCu sites. SSS refers to the number of molecules in the second solvation shell.
Figure A5.9 | The geometries of the complex used to calculate the adsorption energies of water to ZnCu. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
Appendix Figure 5.10 | The geometries of the complexes used to calculate the adsorption energies of water to ZCuOH. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
Appendix Figure 5.1 | The geometries of the complexes used to calculate the adsorption energies of water to ZCu-Z/NH₂. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
Appendix Figure 5.12 | The geometries of the complexes used to calculate the adsorption energies of water to ZCu. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
Appendix Figure 5.13 | The geometries of the complexes used to calculate the adsorption energies of ammonia to ZnCu. Colour scheme for elements: dark grey = Si; light grey = Al; small white = H; red = O; blue = N; gold = Cu.
Appendix Figure 5.14 | The geometries of the complexes used to calculate the adsorption energies of ammonia to ZCuOH. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
Appendix Figure 5.15 | The geometries of the complexes used to calculate the adsorption energies of ammonia to ZCu-Z/NH$_4$. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
Appendix Figure 5.16 | The geometries of the complexes used to calculate the adsorption energies of ammonia to ZCu. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
Appendix Figure 8.1 | Comparison of the HERFD-XANES Spectra for 1Al and 2Al samples in a) $O_2$ at room temperature b) NO at 200°C and 400°C c) NO+$O_2$ at 200°C and 400°C d) NO+NH$_3$+$O_2$ at 200 and 400°C
Appendix Figure 8.2 | Vtc-XES spectra for 1Al and 2Al samples under 200 °C with a) O-coordination and b) N-coordination. The high energy tail of Kβ_{2,5} peak is likely due to multi-excitations as the energy of the incident X-ray (9400 eV) is high enough to ionize a second electron during core hole creation.

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Appendix Table 8.1 DFT calculated bond lengths.
Appendix Figure 8.3 | Reaction profiles for the formation of NO$_3^-$ at the 1AlCu starting from the configurations shown in Figure 8.7: a) NO and O$_2$ co-adsorbed with framework-Cu coordination. b) NO in the second solvation shell, O$_2$ adsorbed end-on on framework-coordinated Cu. c) NO and O$_2$ co-adsorbed (side-on) with Cu free from the framework. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
Appendix Figure 8.4 Reaction profiles for the formation of NO$_3^-$ at the 2AlCu starting from the configurations shown in Figure 8.7. a) NO and O$_2$ co-adsorbed with framework-Cu coordination. b) NO in the second solvation shell, O$_2$ adsorbed end-on on framework-coordinated Cu. c) NO and O$_2$ co-adsorbed (side-on) with Cu free from the framework. Colour scheme for elements: dark grey=Si; light grey=Al; small white=H; red=O; blue=N; gold=Cu
Appendix Figure 9.1 | the Simulated IR spectra of a single H$_2$O adsorbed onto Cu$^{2+}$ onto SSZ-13. The inset shows a zoomed view of the spectra in order to see the weak vibrational modes and another shows the geometry at the 6 and 8MRs.
Appendix Figure 9.2 | the Simulated IR spectra of four H$_2$O molecules adsorbed onto Cu$^{2+}$ in SSZ-13. The inset shows the geometry at the 6 and 8MRs.
Appendix Figure 9.3 | The simulated IR spectra of a single NH3 adsorbed onto Cu$^{2+}$ onto SSZ-13. The inset shows a zoomed view of the spectra in order to see the weak vibrational modes, and another shows the geometry at the 6 and 8MRs.
Appendix Figure 9.4 | the Simulated IR spectra of a four NH$_3$ molecules adsorbed onto Cu$^{2+}$ onto SSZ-13. The inset shows a zoomed view of the spectra in order to see the weak vibrational modes, and another shows the geometry at the 6 and 8MRs.
Appendix Figure 9.5 | The Simulated IR spectra of an NO molecule adsorbed onto Cu\(^{2+}\) in SSZ-13. The inset shows the geometry at the 6 and 8MRs.
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