A Common Intermediate for $N_2$ Formation in Enzymes and Zeolites: Side-On Cu–Nitrosyl Complexes**

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Understanding the mechanisms of catalytic processes requires the identification of reaction centers and key intermediates, both of which are often achieved by the use of spectroscopic characterization tools. Owing to the heterogeneity of active centers in heterogeneous catalysts, it is frequently difficult to identify the specific sites that are responsible for the overall activity. Furthermore, the simultaneous presence of a large number of surface species on the catalyst surface often poses a great challenge for the unambiguous determination of the relevant species in the reaction mechanism. In contrast, enzymes possess catalytically active centers with precisely defined coordination environments that are only able to accommodate intermediates relevant to the specific catalytic process. Here we show that side-on Cu$-\cdot NO$ complexes, characterized by both high magnetic field solid state (SS) magic angle spinning (MAS) nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy, are the key intermediates in the selective catalytic reduction of NO over Cu-SSZ-13 zeolite catalysts. Analogous intermediates have been observed and characterized in nitrite reductase enzymes, and shown to be the critical intermediates in the formation of $N_2$ for anaerobic ammonium oxidation reactions.[1] The identification of this key reaction intermediate, combined with the results of our prior kinetic studies, allows us to propose a new reaction mechanism for the selective catalytic reduction of NO with $NH_3$ under oxygen-rich environments over Cu-SSZ-13 zeolites, a key reaction in automotive emission control.

Denitrification and anaerobic ammonium oxidation are two processes that account for the release of fixed nitrogen as molecular nitrogen ($N_2$) into our atmosphere. A recent study by Kartal, et al. has shown that hydrazine ($N_2H_4$), a key intermediate in the path to $N_2$ in biological systems, is produced by anaerobic ammonium oxidation, and that NO was a direct precursor to the formation of $N_2H_4$.[1] This study also clearly establishes a crucial role for a side-on copper-nitrosyl species in the enzymatic production cycle of $N_2$. Two types of nitrite reductase enzymes, which contain Cu or Fe porphyrin cofactors as active centers, exist. The Fe-containing enzyme forms N-coordinated Fe$-\cdot NO$ and Fe$-\cdot NO$ intermediates during the catalytic cycle.[2,3] In the nitrite reductase with copper active centers, the binding of NO was controversial until the work of Tocheva, et al. determined an unprecedented side-on Cu nitrosyl configuration, which provided new insights into the catalytic mechanism of this enzyme.[4] A crystallography study on amine oxidase demonstrated the formation of a copper nitrosyl complex in which the Cu$-\cdot N-O$ bond angle was determined to be 117°, a value approaching a side-on configuration. Side-on binding of diatomic molecules (NO and O$_2$) to Fe centers of enzyme catalysts are much better known. For example, in nitroporphyrin 4, a ferric heme–NO complex was observed with Fe–N and Fe–O bond distances of 2.0 Å and 2.6 Å, respectively.[5] In naphthalene dioxygenase, side-on O$_2$ binding was observed, with Fe–O bond distances of 2.2 Å and 2.3 Å.[6] Side-on NO binding to Fe has also been reported in nonbiological systems; for example, nitroprusside with Fe–N and Fe–O bond distances of 1.89 Å and 2.07 Å, respectively.[7]

In a striking similarity to nitrite reductase enzymes, the most efficient heterogeneous catalysts for the selective catalytic reduction (SCR) of NO also contain either Cu or Fe ions as active centers located in ion-exchange positions in metal-ion-exchanged zeolites.[8] Thus, the two key common features of the enzymatic and heterogeneous catalytic systems are the identical nature of their catalytic active centers (the metal ions Cu and Fe), and the very well-defined coordination environment around these active sites (functional groups around the active center in enzymes and the zeolite framework itself).

Metal-ion-exchanged zeolites have been extensively studied for over thirty years for the SCR of NO$_x$, either with $NH_3$ or with hydrocarbons in the presence of excess oxygen.[9] Although, these materials show high efficiency for NO reduction, their practical applications were hindered by the

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The formation of a Cu$^{2+}$–NO$^+$ complex upon exposure of Cu-ion-exchanged SSZ-13 zeolites to NO was confirmed by FTIR studies. The FTIR spectra (for detailed experimental conditions, see the Supporting Information) displayed in Figure 1 show absorption features characteristic of the stretching vibrations of adsorbed NO species: NO adsorbed onto either Cu$^+$ (1812–1806 cm$^{-1}$), or Cu$^{2+}$ (1900–1950 cm$^{-1}$), and an NO$^+$ species coordinated to Cu$^+$. The formation of NO$^+$ on Cu$^{2+}$-SSZ-13 can occur in two different ways: either by the disproportionation of NO$_2$,

$$2\text{NO}_2 \rightarrow \text{NO}^+ + \text{NO}^- \quad (1)$$

or by a redox reaction between Cu$^{2+}$ and NO.

$$\text{Cu}^{2+} + \text{NO} \rightarrow \text{Cu}^+\text{NO}^+ \quad (2)$$

As the FTIR experiments (Figure 1) were conducted in the absence of NO$_2$, the first NO$^+$ formation path can be ruled out. Instead, the amphoteric NO molecule, which possesses an unpaired electron, can reduce a Cu$^{2+}$ ion and form the Cu$^{2+}$–NO$^+$ adduct, thus preserving charge balance in the zeolite framework. The resulting Cu$^+$ ions, in turn, can now interact with unreacted NO molecules to form Cu$^{2+}$–nitrosyls, which is evidenced by the development of an IR band centered at 1810 cm$^{-1}$. Indeed, the FTIR spectra in Figure 1 show a clear correlation between the intensities of the IR features representing NO$^+$ (ca. 2160 cm$^{-1}$), and Cu$^{2+}$–nitrosyls (ca. 1812 cm$^{-1}$). It is also evident from the FTIR data shown that the formation of NO$^+$ is correlated with the Cu content of the SSZ-13 structure; notably, the higher the Cu-ion-exchange level, the higher the amount of NO$^+$ formed. Interestingly, the Cu$^{2+}$ ions, which are present at low Cu loading and known to be located in the windows of the double six-membered prisms of the chabasite structure, bind NO relatively weakly and do not seem to participate in the formation of NO$^+$. This may be a consequence of the high coordination of these Cu$^{2+}$ ions to oxygens in the zeolite framework, which renders them less reactive toward NO. With increasing ion-exchange levels, the number of a second type of Cu$^{2+}$ ions, which are located in the large cavities of the chabasite structure and close to the eight member ring openings, increase, as do the number of NO$^+$ and Cu$^{2+}$–nitrosyl species. These Cu$^{2+}$ ions are readily accessible to NO molecules, and seem to bind them quite strongly. Under catalytic conditions, however, Cu$^{2+}$ ions located in the windows of the six-membered rings become accessible to NO, as they strongly interact with water and NH$_3$ molecules. The chemical properties of these two types of Cu$^{2+}$ ions (for example, reducibility) under these conditions are very similar.

The necessity of the presence of Cu$^{2+}$ ions in specific cationic positions to form NO$^+$ was also confirmed by the results of an FTIR experiment in which a Cu-SSZ-13 sample was reduced with CO at 573 K prior to NO exposure. The FTIR spectrum recorded from the CO-reduced Cu-SSZ-13 sample after NO exposure reveals the presence of NO adsorbed onto both unreduced Cu$^{2+}$ (located primarily in the six-membered rings) and Cu$^+$ sites (Figure S1). The IR feature with the highest intensity is the one representing Cu$^{2+}$–NO (ca. 1808 cm$^{-1}$), followed by the one originating from Cu$^{2+}$-adsorbed NO (ca. 1948 cm$^{-1}$). In contrast, the intensity of the IR band for the NO$^+$ species is very low, as most of the Cu$^{2+}$ sites in the large cavities of the chabasite framework have been reduced to Cu$^+$ prior to NO adsorption. We have also established that an NO$^+$ species can be formed on these zeolites by the disproportionation of NO$_2$. Notably, when a pre-oxidized sample was exposed to NO$_2$, IR features with high intensity developed in both the 1250–1650 cm$^{-1}$ and 2100–2300 cm$^{-1}$ regions; these represent vibrations of ad-
sorbed nitrates and NO$^+$/NO$^3$/NO$_2$ species, respectively (Figure S2). However, in the case where a Cu$^{2+}$/NO$^+$ species was formed by the reaction between Cu$^{2+}$ and NO, no IR features representing nitrates (in the 1250–1650 cm$^{-1}$ region) were observed. Thus, although Equation 1 is possible when Cu-SSZ-13 is exposed to NO$_2$, the lack of nitrates following NO adsorption demonstrates that Equation 2 is responsible for NO$^+$ formation in this latter case.

The interaction of NO with Cu-SSZ-13 was also investigated by $^{15}$N solid state MAS-NMR spectroscopy, with the specific aim to obtain information about the nature and the structure (more specifically, the bonding geometry) of the Cu$^+$/NO$^+$ adduct we observed by FTIR spectroscopy. Figure 2 shows a series of $^{15}$N SS-MAS-NMR spectra recorded from a Cu-SSZ-13 sample after its exposure to $^{15}$NO at room temperature using spinning rates of 5, 10, and 12 kHz. In each spectrum, equally spaced spinning side bands appear on both sides of the isotropic chemical shift centered at $\delta = 399.7$ ppm and assigned to a NO$^+$ species. We need to emphasize here that, owing to paramagnetic line broadening, neither molecularly adsorbed NO nor Cu$^{2+}$/bonded NO$_2$ species are expected to be observed in the $^{15}$N NMR spectra. Therefore, the only reasonable assignment of the isotropic NMR peak is the Cu$^+$-bound NO$^+$. Even more interesting is the information we can extract from the spinning side bands: they clearly suggest a three-dimensional anisotropic environment for the nitrogen atom in the adsorbed NO$^+$ species. In particular, the data presented in Figure 2 clearly indicate that the motion of the NO$^+$ species is frozen in a certain conformation. The coordination environment (the structure of the zeolite framework) of the copper ion is a key factor responsible for the restricted motion of the NO$^+$ ion. In general, it is very difficult to obtain detailed structural information of adsorbed NO species in Cu zeolites by NMR spectroscopy; primarily owing to the fact that fast motion of the adsorbate wipes out structural information. Thus, it is especially interesting that, in small pore zeolites (such as SSZ-13), adsorbed NO in the Cu$^+$/NO$^+$ complex can freeze into a conformation determined by both the location of the Cu$^{2+}$ ions and their coordination environment (zeolite framework).

Fitting the sideband pattern, we determined the anisotropic shielding tensor, where the magnitude of the shielding anisotropy is $\delta = -230.2$ ppm, with an asymmetry parameter of 0.15. The agreement between the experimental and simulated NMR spectra (shown in Figure S3 for 5 kHz spinning rate) is excellent. The principal components of the shielding tensor were determined; the anisotropy is defined as $\Delta = \delta_{11} - \delta_{xx}$, where the elements of the shielding tensor are ordered as $|\delta_{11} - \delta_{xx}| \geq |\delta_{11} - \delta_{yy}| \geq |\delta_{11} - \delta_{zz}|$. The asymmetry parameter ($\eta$) is defined as $(\delta_{xx} - \delta_{yy})/(\delta_{xx} - \delta_{zz})$, and a value of zero indicates axial symmetry (at least a three-fold rotation). As the observed $\eta$ is non-zero, we infer that there is no axial symmetry here, and thus the Cu-N-O atoms are not co-linear.

To interpret the NMR results more completely, a model of the Cu-SSZ-13 was constructed starting from the structure reported by Fickel and Lobo.[19] The model is expanded to several unit cells, initially with all silicon atoms, and then aluminum atoms are substituted, such that the SiO$_2$/Al$_2$O$_3$ ratio is 12:1. The aluminum atoms are placed such that no two are adjacent and at least one is near the known[12,19] copper site in the face of the six-membered rings of the zeolite. The second Cu$^+$ is placed in the center of an eight-membered ring with a NO attached to it. The cluster is then trimmed down to a minimal set of atoms and terminated with hydroxyls. Utilizing a DFT calculation (NWChem)[20] with the Becke three-parameter Lee–Yang–Parr (B3LYP) functional[21] and an Ahlrichs double-$\zeta$ basis set with polarization (pAVDZ)[22] the positions of the protons, Cu$^+$ ions and the NO are then optimized with fixed positions for the Si/Al and oxygen atoms. The optimized geometry, shown in Figure 3, provides a Cu-N-

**Figure 2.** $^{15}$N SS-MAS-NMR spectra of room-temperature $^{15}$NO-exposed Cu-SSZ-13 at different spinning rates. Asterisks indicate spinning side bands.

**Figure 3.** DFT optimized geometry of a Cu–NO adduct in Cu-SSZ-13. ($\alpha = 146.7^\circ$)

O angle ($\alpha$) of 146.7$^\circ$, which is somewhat larger than expected for a perfect side-on adsorption complex. The longer Cu–O than Cu–N bond distance, however, may originate from the interaction of the adsorbed NO$^+$ species with the surrounding ions of the zeolite framework. The structure of the Cu$^+$/NO$^+$ adduct, as determined by analysis of the NMR data, is very similar to the side-on copper–nitrosyl complex observed in Cu–nitrite reductase enzymes in biological systems.[5] The important question about these experimental results is the relevance of the above-discussed Cu$^{2+}$/NO$^+$ species to...
the mechanism of the SCR of NO with NH3 on Cu-SSZ-13 zeolites. To understand the mechanistic importance of this species, we need to recall some of the key findings of prior kinetic measurements on this system: very high N2 selectivity, low NO oxidation activity, and the essential role of water in achieving high SCR activity.\[11,13\] The findings of McEwen, et al., showing that Cu⁺ species are present under standard SCR conditions, as reported in their in operando EXAFS study, are also very important.\[23\] Notably, this work clearly establishes the presence of both Cu⁺ and Cu²⁺ ions during the SCR of NO with NH3 over the Cu-SSZ-13 catalyst. In prior mechanistic studies on other Cu- (and Fe) ion-exchanged zeolites (in particular, on Cu(Fe)-ZSM-5 or Beta) the primary role of the Cu (Fe) centers was assumed to be the oxidation of NO into NO₂. The resulting NO₂ could then disproportionate to form a NO⁺NO⁻ species which, in turn, was shown to be responsible for the formation of NH₂NO₃ and NH₄NO₃. Owing to the limited thermal stabilities of these two compounds, they were proposed to decompose into N₂ + H₂O, and N₂O + H₂O, respectively. NH₂NO₃ was also reported to further react with NO to form NH₄NO₂ and NO₃⁻.\[8,14\] This mechanism could well explain the formation of significant amounts of N₂O over the metal-exchanged ZSM-5 and Beta catalysts, as well as the need for the presence of NO₂ to achieve high reactivity in “Fast” SCR.

Although the change in the oxidation state of the metal cation in ion-exchange positions within the zeolite has been claimed to be mechanistically important, the reactions in which this redox process would take place have not been elaborated on clearly. In biological systems, in contrast, the variation of the oxidation state of Cu has been clearly established in both the denitrification and anaerobic ammonium oxidation processes. Furthermore, the crucial role of the variation of the oxidation state of Cu has been clearly elaborated on clearly. In biological systems, in contrast, the coordination environment around the catalytically active Copper–nitrosyl in nitrite reductase enzyme (discussed above) in the mechanism of molecular-nitrogen oxidation processes. Therefore, the crucial role of the formation of the side-on Cu⁺NO⁻ species in such enzymes and heterogeneously catalyzed reactions. In particular, precise control of the coordination environment around the catalytically active metal centers in enzymes and in the CHA-zeolite-based catalysts studied in this work has enabled the identification of a key reaction intermediate for both systems with a very similar structure.

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Figure 4. Proposed mechanism for the selective catalytic reduction of NO with NH₃ over Cu-SSZ-13.