Mapping Vibrational Spectra to the Structures of Copper Species in Zeolites based on Calculated Stretching Frequencies of Adsorbed Nitrogen and Carbon Monoxides

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Abstract: In this work, adsorption of nitrogen monoxide and carbon monoxide probe molecules on various copper sites in a range of zeolites is studied. Structures of copper sites, binding energies and vibrational frequencies of adsorbed probe molecules are calculated by density functional theory. This allows mapping vibrational spectra regions to specific copper species as a function of the zeolite topology and Si/Al ratio. Carbon monoxide can adsorb on Cu⁺ ions by forming mono- and dicarbonyls, or on copper ions bonded to methoxy species by forming methoxy-monocarbonyls, which exhibit a blue shift in wavenumbers. The stretching frequencies of adsorbed nitrogen monoxide generally increase in the following order: [CuOH]⁺ < [Cu₂O]²⁺/[Cu₂O₂]²⁺ < [Cu²⁺] < [Cuₙ₊₁Oₙ]²⁺/[CuₙOₙ⁺¹]²⁺ (n>3) < [Cu₃O₂]²⁺/[Cu₃O₃]²⁺. The shift values between different species vary between 5 and 20 cm⁻¹, showing the possibility for structure assignment based on infrared frequencies. Zeolite frameworks with smaller pores exhibit a shift of vibrational bands of adsorbed nitrogen monoxide towards lower frequencies, due to a confinement effect of zeolite pore structure. Zeolites with larger pores stabilize copper species of higher nuclearity. Our data indicate that tabulated infrared frequencies of adsorbed carbon and nitrogen monoxides may be used to assign zeolitic copper speciation from experimental data.

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Introduction

Copper-exchanged zeolites continue to be a topic of intensive research due to their unique structural properties, rendering zeolites promising materials for a range of chemicals transformation applications.\textsuperscript{1-3} Porous nature of zeolites facilitates stabilization of copper species, opening the possibility of utilizing them for processes such as selective catalytic reduction (SCR) of NO\textsubscript{x} in exhaust gases,\textsuperscript{4-6} direct decomposition of NO and N\textsubscript{2}O,\textsuperscript{7} and selective conversion of methane to methanol.\textsuperscript{8-13} Determining the structure of copper species present within zeolites is of paramount importance for understanding of the mechanisms of the above reactions, and how these may depend on the type of metal sites present in the material.\textsuperscript{14} However, reliable identification of such structures remains a challenging task.

Fourier-transform infrared (FTIR) spectroscopy of adsorbed probe molecules is a popular characterization technique for studying the configuration of the copper sites in zeolite-based materials. Typically, small molecules that can penetrate the pores of a zeolite and interact with copper oxo sites are used as probes, such as carbon monoxide (CO) and nitrogen monoxide (NO). This approach has been successfully used for studying the speciation of copper in zeolites.\textsuperscript{15-19} Carbon monoxide permits reliable identification of Cu(I) sites, whereas nitrogen monoxide is highly sensitive towards both Cu(I) and Cu(II) sites.\textsuperscript{20-27} The main difference between CO and NO is that the additional electron in NO occupies the $\pi^*$-orbital. Due to this unpaired electron on the antibonding orbital, NO exhibits greater sensitivity to copper (II) cations where it coordinates during the formation of a Cu···NO bond. Upon the formation of such a bond, a partial electron transfer occurs from the antibonding NO 2$\pi^*$ level to the incompletely filled $d$ levels of copper, typically leading to shortening of the NO bond and increasing of the NO stretching frequency compared to the gas phase. The magnitude of these changes depends on the exact configuration of the copper oxo species.\textsuperscript{28,29}

These unique properties of NO also render theoretical investigation of its adsorption challenging. Previous theoretical studies of gas-phase nitrosyls indicated that the nature of the metal–NO interaction could be covalent, dative, and electrostatic, depending on the type, the oxidation state of the metal, and the spin state of the metal–NO complex.\textsuperscript{28,29} The nature of the metal–NO bonding determines the magnitude and the direction of the changes in the N–O bond length and hence the NO stretching frequency. Therefore, the geometrical structure and vibrational properties of NO adsorption complexes in metal-exchanged zeolites are specific for the metal, its oxidation state, and the configuration of the metal oxo species. The latter
constitutes one of the central questions in zeolite chemistry: what is the nuclearity of the species (in our case, number of copper atoms) and the geometrical structure; which zeolite frameworks stabilize which species; and under what conditions these species are formed and observed.

A range of configurations have been suggested over the last decade. Already at the early stages of zeolite catalysis research, several possible copper species were suggested, such as isolated copper ions, oxocations, and oxide particles.30–35 Strong experimental evidence has later been provided for the existence and activity of di-copper sites, comprising two copper atoms connected with either one or two oxo bridges.36–38 Later, combined experimental and theoretical studies suggested the possibility of formation of trimeric sites in MOR39 and MFI10 and have recently also been considered for MAZ.40 In these studies, density functional theory (DFT) calculations indicated that tri-copper sites are more stable than di-copper species under reactive pre-treatment conditions.39,40 Theory has further suggested that Cu$_n$O$_n$ clusters with $n$ up to 9 may be energetically favorable in the framework of chabazite.41 Our own recent theoretical investigation extended this idea to the frameworks of mordenite and MFI, suggesting tetramers and pentamers as thermodynamically more stable species compared to their smaller counterparts.42 At the same time, the role of monomeric species is still debated in the literature, with individual mono-copper hydroxo species suggested as active sites for partial methane oxidation in chabazite,43 mordenite,44 and on alumina45. However, for the conversion of methane to methanol, for which copper exchanged zeolites are the materials of choice, two electrons are required. With copper reduced from Cu(II) to Cu(I), this process therefore requires the participation of two copper atoms to produce one methanol molecule. A number of recent publications implicate involvement of higher nuclearity clusters in the process, and propose that monomeric copper is inactive for partial methane oxidation.46–52 At the same time, we have recently demonstrated the possibility of self-organization of mononuclear hydroxylated cations toward activation of methane, in zeolites mordenite and omega.53,54 As can be seen from the plethora of literature above, zeolite frameworks may be stabilizing a range of different copper species, making clear identification of the exact geometrical configurations of the copper species challenging. As a result, suggestions to transform the discussion of a well-defined copper site towards mixtures of sites or dynamic co-existence of species have emerged.55–59

Notwithstanding these challenges, theoretical chemistry has been successfully applied to unravel the zeolite chemistry via the computational predictions of the vibrational behavior of adsorbed probe molecules. Nachtigall et al. demonstrated the applicability of theoretical
infrared calculations to determine the configurations of the copper sites based on CO adsorption. Hafner et al. have also contributed to a deeper theoretical understanding of CO adsorption in zeolites, for instance in MOR and CHA. The adsorption of NO has also been studied, mostly in the context of the NO decomposition processes, and important insights into metal cation coordination to the framework has been established. Göltl et al. employed ab initio molecular dynamics simulations to study adsorption of NO on SSZ-13 zeolite, demonstrating a possibility of observing complex multi-peak spectra due to the same species.

In the present study, using DFT we model the adsorption of individual and multiple CO and NO molecules to enable assignment of the configurations of copper sites in a range of zeolites (MOR, MFI, CHA, ERI, FER, MAZ, BEA, FAU) with varying Si/Al ratio. By providing a comprehensive computed dataset for various alternative structures and geometries, a goal of establishing a good basis for a more rational assignment of the spectroscopic data is therefore aimed at. We demonstrated that the local environment affects the stretching frequencies of both adsorbed NO and CO. A decrease in copper oxidation state, an increase in copper coordination, and a greater proximity to closely located atoms all tend to shift the CO frequency downward. The coordination number and the nature of the coordination environment have distinctive influences on the NO stretching frequencies in Cu(II), which spans the range from 1850 to 2050 cm$^{-1}$. It has been shown experimentally, that infrared spectroscopy on adsorbed CO is more sensitive than NO in the determination of Cu(I) species, while, in contrast, Cu(II) interacts weakly with CO but is highly sensitive towards NO. Generally, the N–O bond length and frequencies span a much greater range and are thus much more sensitive to the model choice than is the case with carbonyl complexes. This greater sensitivity is consistent with the increased charge transfer and greater covalency in the Cu–NO bond than in the Cu–CO bond. Therefore, we focus on the adsorption of CO on Cu(I) species, i.e. individual Cu$^+$ ions and methoxy species, and on the adsorption of NO on Cu(II) species, i.e. [CuOH]$^+$, various copper oxo dimeric species, and a range of larger systems.

The calculated vibrational frequencies are compared to experimental infrared spectra of CO and NO adsorbed in the corresponding zeolite framework, whenever the experimental data is available. This information is used to map vibrational spectra regions to specific copper species as a function of the zeolite topology and Si/Al ratio. We demonstrate that the stretching frequencies of adsorbed NO probe molecule generally increase in the following order:

\[
n[\text{CuOH}]^+ < n[\text{Cu}_2\text{O}]^{2+/}[\text{Cu}_2\text{O}_2]^{2+} < n[\text{Cu}^{2+}] < n[\text{Cu}_{n+1}\text{O}_n]^{2+/}[\text{Cu}_n\text{O}_n]^{2+} (n>3) < n[\text{Cu}_3\text{O}_2]^{2+/}[\text{Cu}_3\text{O}_3]^{2+}.
\]

The increase in the pore size leads to destabilization of smaller copper
oxide species and stabilization of larger ones, with corresponding shifts in N–O frequency. Carbon monoxide can form mono- and dicarbonyls, with the latter being more stable in larger pores. Zeolite frameworks with larger pores generally exhibit the shift of vibrational bands towards higher frequencies.

Structure wise, we have found that zeolites comprising eight-member ring (8 MR) pores tend to stabilize the monomeric [CuOH]+, dimeric mono- and bis(μ-oxo)dicopper, and trimeric [Cu₃O₂]²⁺/[Cu₃O₃]²⁺ species with the structures similar to the ones observed in the case of mordenite. Monomer species, such as Cu° cations, are preferentially stabilized in the smaller, six-member ring (6 MR) pores, while proximal monomers can either be stabilized in a suitably large single pore, or in two adjacent smaller pores, with the preference of the former, if available. The highest stability is achieved when the pore is similar in size to that of the copper species, with the largest pores providing a unique opportunity to stabilize large copper oxide clusters.

**Computational details**

All ground-state total energy calculations in this work have been performed with the all-electron full-potential DFT code FHI-aims within the periodic boundary conditions model. Electronic exchange and correlation was treated on the hybrid functional level with the PBE0 functional, considered reliable in predicting the spin manifold of transition metals. It should be noted that species care is needed when choosing the level of theory.

All geometry optimizations were done with the “tier2” atom-centered basis set using “tight” settings for numerical integrations. Pre-optimization of all structures in our work was done at the PBE level, followed the final re-optimization and the calculation of all relevant properties discussed in the manuscript at the hybrid PBE0 functional level. Tkatchenko-Scheffler dispersion correction has been used to account for the van der Waals energies arising from the attraction between induced dipoles formed due to charge fluctuations in the interacting species. Including a robust dispersion correction is extremely important for a reliable description of the interaction of adsorbates with the zeolite, and can lead to a significant changes in the calculated values of binding energies.

All geometries reported herein correspond to locally optimized configurations. If several local minima were identified, the one with lowest relative energy has been chosen. The all-electron code used in our work is especially well suited for correct description of the spin
manifold of the transition metals due to the employed numeric atom-centered orbitals. Furthermore, FHI-aims allows an automated optimization of spin-polarized systems through collinear (scalar) spin-DFT formalism. In this case, each geometry optimization is, therefore, effectively coupled with the spin state optimization, and all geometries and energies reported herein correspond to the optimal spin state for each system. Identified optimal spin states are summarized in Supporting Information (Table S3).

It has been demonstrated in the literature, that confinement effects in zeolites can play a crucial role in the energetics of the adsorbate molecules, including providing necessary stabilization for reaction intermediates.\(^{76}\) In order to take these effects into account, all considered structures were identified by performing geometry optimization on fully periodic zeolite models. Due to a very big size of the unit cell (e.g. a periodic model of CuMOR features a unit cell consisting of 147 atoms and measuring 18.0×20.0×7.0 Å\(^3\)) and the fact that all electrons are accounted for explicitly (1504 electrons in total), Brillouin zone integration is performed with a reciprocal space mesh consisting of only the gamma point.

To correct for the inherent errors in the calculated frequencies, as compared to experiment, we applied empirical scaling factors to the calculated harmonic stretching vibrational frequencies of the adsorbed molecules CO and NO. The scaling factor for the calculated CO frequencies was obtained by comparing the calculated stretching frequencies of the free CO and CO\(^+\) molecules with their corresponding experimentally observed gas phase values of 2143 and 2214 cm\(^{-1}\). Similarly, the scaling factor for the calculated NO frequencies was obtained by comparing the calculated stretching frequencies of the free NO and NO\(^+\) molecules with their corresponding experimentally observed gas phase values of 1876 and 2354 cm\(^{-1}\). This scaling procedure is based on the observed trend that the error in the calculated vibrational frequencies of similar internal coordinates is systematic within any particular computational method and can therefore be corrected by a transferable scaling factor determined empirically. Calculated vibrational frequencies are consistently higher than experimental frequencies by about 3% in nitrosyl species and by about 2% in carbonyl species, consistent with previous reports.\(^{28}\) We have, therefore, scaled the calculated NO stretching frequencies by 0.97 and the CO stretching frequencies by 0.98, and compare our scaled frequencies with experimentally determined frequencies.

Previously reported in-depth analysis of the density functional effects on the structures, energetics, and stretching frequencies of the adsorbed molecules on zeolite chabazite by work by Göttl et al.\(^{77-79}\) and Anggara et al.\(^{80}\) indicates that a considerable care should be taken when
describing isolated copper ions. For instance, the interaction of NO involves with copper sites involves electron transfer from the antibonding NO $2\pi^*$ level to the incompletely filled $d$ levels of copper. In copper oxide species, $3d$ orbitals of copper are involved in bonding with oxygen atoms, which makes such species more electronically similar to each other with respect to the interaction with NO. As for Cu$^+$ and Cu$^{2+}$ it is not the case, both the electronic properties of such species, and the influence of the theoretical approach on the description of their $d$-shell, will be more complex. This can lead to significant differences in predicted binding energies and stretching frequencies calculated with different density functionals, sometimes leading to discrepancies in binding energies between GGA and hybrid functional up to 1 eV.

The readers should, therefore, be warned that, although the general trends reported here are expected to be correct, the absolute values of the reported properties might deviate from the ones calculated with different computational setups, especially in the cases of isolated copper ions.

**Results and discussion**

**Copper speciation**

We start our investigation with discussion of the copper site configurations in relation to the zeolite pore size and structure. The following frameworks have been considered, with the size of the channels given in brackets: MOR (8 MR, 12 MR), MFI (10 MR), CHA (8 MR, 6 MR), ERI (8 MR, 6 MR), FER (10 MR, 8 MR, 6 MR), MAZ (12 MR, 8 MR, 6 MR), BEA (12 MR, 6 MR), FAU (12 MR, 6 MR). Each of these zeolite structures provides a unique configuration of pores. These frameworks have been chosen for two reasons: firstly, for the diversity of their geometrical structures, and, secondly, for the application interest these structures hold for SCR of NO$_x$ and methane to methanol conversion.

In each of the above zeolite frameworks, we calculated the most stable configurations of the following copper species structures, chosen to cover the majority of previously suggested structures, as outlined in the Introduction section:

- Cu$^+$ and Cu$^{2+}$ ions;
- [CuOH]$^+$ monomer and a pair of proximal monomers$^{53,54}$ either within the same (sufficiently large) ring of a zeolite, or in two adjacent pores;
dimer structures, including mono(µ-oxo) and bis(µ-oxo) dicopper structures, as well as a hydrated version of the mono(µ-oxo)dicopper, i.e. the dihydroxo Cu–(OH)$_2$–Cu structure, which is formed as a result of the strong interaction of the Cu(II) species with water in zeolites, and which helps to thermodynamically stabilize copper centers.$^{81}$

- larger copper oxo clusters, such as the trimer,$^{10,39}$ tetramer, and pentamer,$^{42}$

- dicopper bridged methoxy species, formed by the reaction of mono(µ-oxo)dicopper with methane.

In each case, we screen the configurational space to find the most energetically favorable geometrical configurations. The following parameters are systematically varied for each zeolite framework and each possible copper site configuration:

- The pore of the zeolite, e.g. 8 MR vs. 12 MR for CuMOR;
- The positions of aluminum atoms in the pore;
- The number of aluminum atoms per pore.

If several local minima were identified, the one with lowest relative energy has been chosen for the subsequent analysis. For each of these cases, we therefore identify the most stable local minimum configuration, a selection of which are presented in Figure 1. For this selection, we present a monomeric [CuOH]$^+$ species, a pair of proximal monomers, mono(µ-oxo)di-copper center, its hydrated Cu–(OH)$_2$–Cu version, and a stoichiometric trimer structure. These were selected as the structures attracting most attention in the literature.$^{36–43, 53–59}$
Figure 1. Zeolite frameworks considered in this work, as well as geometrical configurations of selected copper site structures. Binding energies of the probe molecules adsorbed on different copper sites can be found in Table S2. Please note that the pair of proximal monomers is either stabilized in a sufficiently large single pore (MOR, MFI, BEA, FAU, MAZ), or in two adjacent pores (CHA, ERI, FER).
The main findings on the geometrical structures of copper sites in considered zeolite frameworks can be summarized as follows.

1) All zeolites comprising 8 MR pores tend to stabilize similar oligomeric (containing two to five copper atoms) structures.

In the case of mordenite, two symmetrically located aluminum atoms per 8-ring channel yield the most stable structures of copper species overall. Two aluminum atoms in other positions are on average 0.5 eV less stable (see Table S1 in Supporting Information for the data on relative energetics of Al distribution). Higher loading of Al lead to an increased interaction between the copper oxide species and the framework, causing structural distortion of the copper site. The relative energies of such distorted structures range from +0.7 eV for the dimer up to +1.3 eV in the case of a tetramer.

8 MR can successfully stabilize a range of oligomeric structures, ranging from dimers to pentamers. The first column in Figure 1 depicts some locally optimized structures for CuMOR. In the case of mono(μ-oxo)dicopper species, copper atoms are coordinated with aluminum via two oxygen atoms of the framework. The Cu–O bond length in a Cu–O–Cu bridge amounts to 1.73 Å. In the tricopper center, only one copper atom is coordinated to aluminum, while two others are coordinated to silicon. This is caused by the topology of the eight-membered ring, and assumes a symmetrical distribution of aluminum atoms in the pore. Steric effects require the Cu$_3$O$_3^{2+}$ cluster to be located out of the surface of the 8 MR in order to accommodate its large size. This leads to the increase of bond lengths, resulting in 1.77–1.80 Å Cu–O distances. Tetramer and pentamer structures tend to extend an existing trimer structure out of the plane of the pore to form a larger 3D cluster.

Several zeolite frameworks contain 8 MR pores with configurations similar to mordenite, including CHA, ERI, FER, and MAZ. As a result, one may expect them to form oligomeric copper oxo structures similar to the ones described above for the case of CuMOR. Indeed, in all four cases the identified structures follow the structural trends discussed above. This is generally in line with previously reported theoretical studies on these systems. For the large pore zeolite frameworks, such as MFI, BEA and FAU, symmetrical location of aluminum atoms do not support the formation of stable oligomeric structures, because the pore intersection of the 10 MR and 12 MR (8.5 Å for MFI, for 11.1 Å BEA, for 11.5 Å FAU) is much larger than the size of the corresponding copper structures. As a result, for these three
frameworks, most of copper oxide structures are stabilized on a periphery of the 10 MR or 12 MR rings, typically next to two aluminum atoms separated by two to four silicon atoms.

2) 6 MR pores preferentially stabilize monomeric Cu$^{2+}$ ions and [CuOH]$^+$ species. Monomeric species, comprising both Cu$^{2+}$ ions and [CuOH]$^+$ species, are preferentially formed in smaller 6 MR pores, whenever such pores are available, although it is of course possible to form such species in larger pores, as was previously proposed for CHA. As can be seen from Figure 1, the preference of 6 MR is observed for CHA, ERI, FER, MAZ, and FAU. This agrees with available experimental data, for instance suggesting preferential coordination of the Cu$^{2+}$ ions in a 6-ring of a gme cavity in mazzite. In all the above cases, both Cu$^{2+}$ and [CuOH]$^+$ are preferentially stabilized in 6 MR pores, with copper atom of Cu$^{2+}$ coordinating to four framework oxygen atoms in the plane of the 6-member ring, while the copper atom of [CuOH]$^+$ is coordinating to two (ERI, FER) or three (CHA, MAZ, FAU) framework oxygen atoms. The identified monomer species are more stable in these cases compared to the corresponding monomers in larger pores (up to 0.4 eV on average). The overall preference for the 6 MR pore in the case of [CuOH]$^+$ species can be explained by the hydrogen bond between the hydrogen atom of the hydroxyl group with an oxygen atom of the framework, leading to an additional stabilization of the structure. In the case of CHA, the two possibilities are very close in energy (within 0.1–0.2 eV), and we, therefore, assume the (almost) equal possibility of the formation of the monomeric species in both pores. This is in line with literature data, where the [CuOH]$^+$ species has previously been found to be slightly more stable when located in the 8MR (by 0.5 eV more than that in 6MR), under aqueous conditions.

3) A pair of monomers can either be stabilized in a suitably large single pore, or in two adjacent smaller pores, with the preference of the former, if available.

We have recently demonstrated that samples with high Si/Al ratios preferentially contain isolated monomeric copper species that may become associated. As can be seen from Figure 1, zeolite frameworks with larger pores stabilize such a pair of monomers in the same pore, for instance MFI can stabilize such a system in a 10 MR, whereas BEA and FAU in their 12 MR, similar to mordenite. Such systems can be referred to as containing “proximal” monomeric species. Although retaining their individual nature in a zeolite framework, they can influence each other upon interaction with an adsorbate. Zeolites that do not possess such large pores can only stabilize individual copper monomers in two adjacent pores. This can be seen in Figure 1 by the example of CHA (two 6 MR), ERI (6 MR and 8MR), and FER (6 MR and 8 MR).
most of the structures, two [CuOH]$^+$ monomers tend to be located as far away as possible from each other within the constraints of the available zeolite ring. Thus, in the case of 12 MR (MOR, BEA, FAU), two Al atoms are located five Si away from each other, thus providing an optimum space between the copper monomers. The distance between two copper atoms in such a structure lies within the range of 5.0 to 5.5 Å. In the case of a smaller 10 MR pore (MFI), the corresponding distances decreases to about 3.5 Å, rendering the two monomeric structures effectively associated. In the case of zeolite frameworks able to stabilize two individual [CuOH]$^+$ species in adjacent pores (CHA, ERI, FER, MAZ), the spectrum of configurational possibilities is very rich. Figure 1 depicts the most stable structures, with Cu–Cu distance within the range of 3.5 to 4.5 Å. However, other higher energy structures are also possible for such systems. Most notably, zeolite omega is able to stabilize a pair of closely packed (3.45 Å apart) copper monomers in the 8 MR pore, which can be detected by X-ray diffraction (XRD).

4) Highest stability is achieved when the pore is similar in size to the copper species. Highest stability is achieved when a suitably sized pore is oriented perpendicularly to a larger channel. A good example is the location of dimer and trimer species within the 8 MR of CuMOR (Figure 1, left-most column). Larger structures in smaller pores have a tendency of forming more complex, larger 3D clusters above the eight-member ring pore. While such structures can still exhibit high stability, sterical effects require them to be located slightly above the plane of the 8 MR in order to accommodate their large size. On the other hand, smaller copper oxide species located in larger pores are often distorted, e.g. as seen in the case of BEA and FAU zeolites. There, for example, the Cu–Cu distances increase from 3.0–3.1 Å as, for example, observed in the 8 MR pores of mordenite, to about 3.2 Å. This results in decreased stability by 0.1–0.2 eV per CuO unit. This can be rationalized by the fact that the 8 MR pore provides an optimal symmetrical configuration of two Al atoms in the pore about 7.5 Å apart, which is impossible to achieve in the case of larger pores.

At the same time, large pore zeolites provide unique opportunities to stabilize more complex metal site structures. For the large pore zeolite frameworks, specifically, BEA and FAU, we identified stable configurations of larger oxo copper species, such as for example a $C_{2v}$-symmetrical Cu$_8$O$_{6}$ ($^{4+}$) copper oxo species in FAU, which structure effectively combines four bis(µ-oxo)dicopper motifs in a compact oxide-like cluster. The possibility of stabilization of such species is compatible with the latest experimental evidence that FAU and BEA form copper-oxo clusters upon ion exchange and high-temperature oxidative treatment, in contrast with smaller pore zeolites, such as CuMOR, where mostly copper monomeric species were
found, and CuMFI where the formation of a significant fraction of copper-oxo dimers was demonstrated.\textsuperscript{85} The stabilization of clusters might be associated with the size of the 12 MR pores for BEA and the existence of the supercage in FAU. We did not observe the formation of stable species larger than pentamers in any other zeolite frameworks we considered in this study.

\textbf{CO and NO adsorption on a well-studied CuMOR system}

We start the frequency analysis by making sure that available theoretical methods are capable of reliably modelling infrared spectra of the adsorption of CO and NO on a well-studied system. It has been shown experimentally, that different carbonyl complexes can be formed at Cu(I) sites of zeolites at different pressure and temperature. For instance, relatively stable adducts, such as mono-carbonyl Cu(CO)\textsuperscript{+} and di-carbonyl Cu(CO)\textsubscript{2}\textsuperscript{+} complexes are observed in the 2150–2190 cm\textsuperscript{-1} region in infrared spectra that are recorded at room temperature\textsuperscript{81} (see Figure 2, a). Specifically, in the case of vacuum-activated copper-exchanged mordenite (CuMOR), at low carbon monoxide pressure, the exclusive formation of Cu(I) monocarbonyl is observed (2159 cm\textsuperscript{-1}). The increase of the carbon monoxide pressure leads to the appearance of new bands assigned to the low (2151 cm\textsuperscript{-1}) and high (2179 cm\textsuperscript{-1}) frequency vibrations of Cu\textsuperscript{I}(CO)\textsubscript{2} dicarbonyl species, closely matching the theoretically predicted values of 2150 cm\textsuperscript{-1}, 2160 cm\textsuperscript{-1} and 2175 cm\textsuperscript{-1} (Figure 2, a). In the case of the monocarbonyl complex, the copper atom rises notably out-of-plane of the pore, and the Al–Cu–C angle is 161°. The Cu–C distance is 1.78 Å, while the C–O distance in the CO molecule is increased compared to molecular CO (1.15 Å vs. 1.13 Å). Such configuration yields the vibrational frequency of 2160 cm\textsuperscript{-1}, which is very close to the experimentally observed value of 2159 cm\textsuperscript{-1}. Adsorption of the second CO molecule brings the copper atom closer to the plane of the eight-member ring (8 MR) pore, and orients two CO molecules at 87.8° to each other. Both C–O distances are 1.14 Å. Such structure yields two CO vibrational frequencies of 2150 cm\textsuperscript{-1} (asymmetric) and 2190 cm\textsuperscript{-1} (symmetric), which agrees reasonably well with the experimentally observed values of 2151 cm\textsuperscript{-1} and 2179 cm\textsuperscript{-1} and their assignment.\textsuperscript{23,26}

This high degree of correlation between the experimental and theoretical values demonstrates that the applied methodology is applicable to modelling CO adsorption on zeolites, and is capable of correctly predicting the C–O stretch frequencies in the case of individual and paired CO adsorption on Cu(I) copper sites.
Figure 2. Benchmark systems for calculating infrared frequencies of adsorbed CO and NO. (a) Adsorption of CO on Cu(I) species at copper-exchanged mordenite (CuMOR). Experimental panel depicts adsorption of CO at 100 K onto CuMOR that was vacuum-activated. Three distinctive bands corresponding to the adsorption of one (2159 cm\(^{-1}\)) or two (2151 and 2179 cm\(^{-1}\)) CO molecules are present. (b) Adsorption of NO on Cu(II) species at copper-exchanged mordenite (CuMOR). Experimental panel depicts adsorption of NO at 100 K onto CuMOR that was vacuum-activated. Three distinctive bands corresponding to adsorption of single NO molecule at various possible copper sites are present (1909, 1948, and 1995 cm\(^{-1}\)).

We use the same system also as a benchmark for NO adsorption (Figure 2, b). Experimentally, NO is used to access the changes in copper oxidation state.\(^{81}\) The data obtained after NO adsorption on the CuMOR sample activated in vacuum\(^{81}\) show the presence of bands at 1804, 1731, and 1827 cm\(^{-1}\) that are associated with NO bound to Cu(I) sites, as well as 1909, 1948, and 1995 cm\(^{-1}\) assigned to different Cu(II) species.\(^{27,86}\) Our theoretical calculations identified several possible copper species that might correspond to the observed experimental bands of Cu(II) species. The goal of these calculations is to confirm that the calculated NO–Cu(II) interactions fall in the experimental range of frequencies. Therefore, the following assignment should be taken as a proof of principle, and not as a final unambiguous structure determination. With this in mind, the identified configurations can be divided into three groups: the NO adsorbed on [Cu(OH)]\(^+\), [Cu\(_2\)O]\(^{2+}\), and [Cu\(_3\)O\(_5\)]\(^{2+}\) species. Adsorption of a single NO molecule on [Cu(OH)]\(^+\) species yields two configurations, with NO and OH species either
oriented in opposite directions with respect to the plane of the 8MR pore (1872 cm\textsuperscript{-1}), or aligned in the same direction (1898 cm\textsuperscript{-1}). The N–O bond length in both cases is 1.16 Å, increased from 1.15 Å in the free molecule. In the case of adsorption of the NO molecule at a dimeric species, also two non-equivalent possibilities were identified. The first one corresponds to the nitrogen atom coordinating to the neighboring framework oxygen atom (1948 cm\textsuperscript{-1}), with the NO adsorbed located closer to the plane of the pore, and the second one corresponds to the on-top coordination of NO to one of the copper atoms (1937 cm\textsuperscript{-1}). In both cases, the N–O bond length is decreased to 1.12 and 1.13 Å, respectively. In both cases, the Cu–N–O angle is far away from being linear, with the values ranging between 138° and 146°. Finally, the highest vibrational frequency peak (1995 cm\textsuperscript{-1}) may be assigned to the adsorption of NO on a larger, trimeric structure.

Overall, the two cases above demonstrate that the used computational model is applicable to be combined with available experimental infrared measurements both to assess the reliability of our models and to help interpret experimental observations.
Adsorbed NO and CO vibrational frequencies analysis for other zeolite systems

Having established the geometrical configurations of copper species, as well as having validated our computational setup, we are now able to analyze the adsorption of NO and CO molecules on these, and their corresponding vibrational frequencies. Table 1 and Figure 3 present the main finding on the vibrational frequencies of the probe molecules adsorbed on a range of zeolite frameworks (relative stabilities are given in Table S2 in Supporting Information) that can be summarized as follows:

1) CO stretching frequencies shift to higher wavenumbers in the case of adsorption on copper (I) atoms bound to methoxy species compared to adsorption on isolated Cu$^+$ ions.

For the adsorption of CO on individual Cu$^+$ ions, the CO stretching frequencies lie within 2135–2165 cm$^{-1}$, with binding energies range of 1.00–1.15 eV. In the case of multiple CO molecules adsorption, the frequencies correspond to the lower end of this range. This is due to the increased coordination of copper, which generally increases the electron donor capability, and leads to lower binding energies (by 0.15 eV) compared to the single molecule adsorption, and the corresponding decrease in the C–O stretching frequency. In contrast, carbon monoxide adsorbed on a copper (I) atoms bound to methoxy species exhibits the frequencies in the range of 2150–2185 cm$^{-1}$, i.e. the frequencies for these Cu(I) species are slightly shifted towards higher wavenumbers. The binding energy also rises by 0.05–0.15 eV, and lies within 1.20–1.30 eV range. This can be explained by the additional bridging oxygen in the methoxy species facilitates partial charge transfer onto itself (electron withdrawing via σ bonds). This makes the copper atom a better electron acceptor, and as a result the C–O bond shortens and the C–O stretching frequency increases.

2) Frequency of NO adsorbed over Cu$^{2+}$ ions does not depend on the zeolite framework.

As discussed above, Cu$^{2+}$ ions are preferentially coordinating close to the middle of the 6-ring plane, for most of zeolite frameworks. NO adsorbed on such Cu$^{2+}$ ions exhibits stretching frequencies within the range of 1935–1950 cm$^{-1}$ for all considered zeolite frameworks. The binding energies lie within 1.3–1.5 eV. This can be explained by the fact that the local coordination of the Cu$^{2+}$ ion is very much the same for all considered models.

3) Individual [CuOH]$^{+}$ and proximal [CuOH]$^{+}$ monomers show very similar behavior with respect to NO adsorption.

Both individual [CuOH]$^{+}$ monomer species, and proximal monomer pairs exhibit similar bonding behavior and vibrational frequencies of adsorbed NO. In both cases, the NO stretching
frequencies lie within the range of 1875–1900 cm$^{-1}$, with binding energies of 1.25–1.35 eV. This is explained by the nature of such monomer pairs. While the proximity of the monomers in the pair is exploited through their association in a concerted electron transfer with, for example, a methane molecule used as a mediator, those monomers do retain their individual character in the absence of reactants. As a result, similar binding energies and absorption frequencies are observed.

4) Dimer [Cu–O–Cu]$^{2+}$ and [Cu–O$_2$–Cu]$^{2+}$ species exhibit higher NO stretching frequencies compared to monomers. Interaction of NO with Cu(II) species generally stems from a partial charge transfer from the NO 2$\pi^*$ level to the incompletely filled Cu $d$ level, resulting in a shorter NO bond and higher NO stretching frequency than those of gas phase NO.$^{28,29}$ As available $d$ level in a dimer has higher capacity than the one in monomer, and thus allows accommodating the excess charge more efficiently (the system gets disturbed less), it facilitates stronger bonding, and, as such, higher stretching frequencies. The observed NO stretching frequencies in the case of dimeric copper oxo species lie within the range of 1935–1960 cm$^{-1}$, with binding energies of 1.50–1.60 eV. Experimentally, the bands with low vibration frequencies (~1900 cm$^{-1}$) are believed to be due to the copper monomeric species, while the bands at high frequencies starting from ~1940 cm$^{-1}$ belong to oligomeric species interacting with NO.$^{52,87–89}$ Our theoretical data above in general matches these experimental observations.
Table 1. Summary of the calculated C–O and N–O stretching frequencies (cm⁻¹) for the probe molecules adsorbed on copper sites of Cu-exchanged zeolites. CO is assumed to interact with Cu(I) species, while NO is assumed to interact with Cu(II) species. Average values are given when multiple structures were calculated. Gas phase values: v(NO)= 1876 cm⁻¹, v(CO)= 2143 cm⁻¹.

<table>
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<th>FER</th>
<th>MAZ</th>
<th>BEA</th>
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<td>2155</td>
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<tr>
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<td>1940</td>
<td>1935</td>
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<td>1890</td>
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<td>1945</td>
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<td>1950</td>
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<td>1945</td>
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<tr>
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<td>1950</td>
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<tr>
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<td>1930</td>
<td>1935</td>
<td>1945</td>
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<tr>
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Figure 3. Graphical summary of the calculated N–O stretching frequencies (cm$^{-1}$) for a single NO molecule adsorbed on copper sites of Cu-exchanged zeolites.
5) NO on trimeric species exhibits higher stretching frequencies than dimers and larger copper species. Trimeric copper oxo species accommodate NO adsorption more efficiently than their smaller counterparts. This stabilization is clearly observed when the size is increased from monomers to dimers to trimers (binding energies increase from 1.20 eV to 1.50 eV to 1.60 eV, see Table S2), while the effect is saturated for larger species. While in the case of trimers, all three copper atoms are equally available and exhibit similar electronic properties, this is not necessarily the case for large structures. We, therefore, can consider the trimer species sufficiently large in order to sustain the electronic effects of adsorption. This is reflected in the stretching frequencies of adsorbed NO. In the case of trimeric species, the observed NO stretching frequencies lie in the range of 1965–1990 cm\(^{-1}\), with the binding energies of 1.40–1.60 eV. Larger clusters exhibit frequencies of ~1945–1975 cm\(^{-1}\), with binding energies of 1.25–1.55 eV.

6) Stretching frequency of adsorbed NO depends on the zeolite framework and is inversely proportional to the efficiency of adsorbate stabilization. Figure 4 compares a typical medium pore CuMOR with a large pore CuFAU zeolite frameworks. The results for the remaining considered frameworks are presented in Supporting Information (Figures S1 to S6). The following three trends are apparent. Firstly, the monomer species do not change their vibrational frequency from 8 MR to 6 MR, as can be seen from the frequencies clustering around 1900 cm\(^{-1}\) in both CuMOR and CuFAU. As discussed above, this can be rationalized in terms of the structural environment of a monomer species, which does not depend on the size of the hosting pore. As such, monomer species may be considered the most unambiguously assigned based on the vibrational features.

Secondly, the position of the vibrational bands of the dimer species is shifted towards higher frequencies in the case of CuFAU (1940–1945 cm\(^{-1}\)) compared to CuMOR (1930–1940 cm\(^{-1}\)). This can be explained in terms of the lower stability of dimer species in a larger pore, discussed above. As a result, the electronic system of such species is disturbed to a larger extent upon adsorption of NO molecule. This leads to a stronger interaction with the adsorbate, and, subsequently, a higher N–O stretching frequency.

Finally, larger copper oxo species exhibit the opposite trend compared to the dimers: their stability increases, and the vibrational stretching frequency of adsorbed N–O decreases. Again, this behavior makes sense, if one considers the sterical constraints experienced by the larger structures in small zeolite pores. In a 12 MR these constrains are alleviated, thus the
structures are efficiently stabilized, and do not exhibit strong electronic distortion upon interaction with adsorbate molecules.

The overall ordering of the NO stretching frequencies for the copper oxo species of different size remains stable across the range of zeolite frameworks. Generally, the NO stretching frequencies follow the following order: monomers < dimers < large clusters < trimers.

Results for the other zeolite frameworks generally fall into the trends outlined above and are presented in the Supporting Information. We are therefore confident that these results allow analyzing possible assignment of spectral features to specific geometrical structures within a specific zeolite framework. Considering that a plurality of structures exists, combining experimental and theoretical vibrational spectroscopy is rendered a promising tool for this rich chemistry.
Figure 4. Graphical summary of the calculated N–O stretching frequencies (cm$^{-1}$) for a single NO molecule adsorbed on copper sites of CuMOR and CuFAU.
Conclusions

In this work, we have presented a set of vibrational frequency calculations for adsorbed carbon and nitrogen monoxides as probe molecules bound to zeolite supported copper species. We have shown that the results of these calculations can be combined with available experimental infrared measurements both to assess the reliability of our models and to help interpret experimental observations. In general, our models yield C–O and N–O stretching frequencies in ranges that are consistent with experimental infrared spectroscopy measurements.

The stretching frequency shifts experienced by the probe molecules upon adsorption exhibit a clear dependence on the nature of copper-exchanged zeolite, particularly on how efficiently a particular copper species is stabilized in a given zeolite framework. The main results of the present study can be summarized as follows:

- Monomeric copper species are preferentially stabilized in the smaller, 6 MR pores, while proximal monomer pairs can either be stabilized in a suitably large single pore, or in two adjacent smaller pores, with the preference of the former, if available. Highest stability is achieved when the pore is similar in size to the copper species, with the largest pores of FAU and BEA zeolites providing an opportunity to stabilize large copper oxide clusters.

- The N–O stretching frequency in nitrogen monoxide upon adsorption on individual Cu$^{2+}$ ions does not depend much on the zeolite framework. [CuOH]$^+$ and proximal monomers show very similar behavior with respect to NO adsorption. NO adsorption complexes/adducts with dimer species, NO@[Cu–O–Cu]$^{2+}$ and NO@[Cu–O$_2$–Cu]$^{2+}$, exhibit higher NO stretching frequencies compared to monomers. Finally, trimers and larger clusters are even more efficient in stabilizing adsorbate molecules, and yield higher binding energies and vibrational frequencies than any smaller species.

- Zeolite frameworks with larger pores shift vibrational bands towards higher frequencies.

The above data indicate the possibility of stabilizing a range of copper sites in various zeolites frameworks, depending on copper loading, aluminum distribution, and availability of suitably sized pores. Infrared spectra of adsorbed carbon and nitrogen monoxides provides a tool to suggest possible assignment of copper speciation based on the shifts of the adsorbed molecule stretching frequencies, which is specific to the copper species geometry and zeolite framework.
Acknowledgements

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Supporting Information

Graphical summary of the calculated N–O stretching frequencies on copper sites of CuMFI, CuCHA, CuERI, CuFER, CuMAZ, and CuBEA zeolites (Figures S1 to S6). Relative stability of the Cu(II) oligomer species as a function of Al atom distribution for the 8 MR pore of zeolite mordenite (Table S1). Binding energies of the probe molecules adsorbed on copper sites of Cu-exchanged zeolites (Table S2). Optimal spin states of the identified copper species in Cu-exchanged zeolites (table S3). Comparison of bonding energies and NO stretching frequencies calculated at PBE and PBE0 density functional level for selected copper oxide sites in zeolite mordenite (Table S4). Choosing optimal structures among several identified isomers (Section S1). Geometrical configurations of all considered structures are available as a downloadable “Supporting Information 2” archive.

Note

The authors declare no competing financial interest.
References


