Theoretical analysis of oxygen-bridged Cu pairs in Cu-exchanged zeolites

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O- and O_2-bridged Cu pairs in zeolitic environments are examined using density functional theory with cluster models. Both types of oxocation ($[CuOCu]^{2+}$ and $[CuO_2Cu]^{2+}$) are found to be highly stable for conditions likely to exist in Cu-ZSM-5. A variety of geometric isomers with different electronic states and preferred Cu–Cu distances are described. Possible implications for "autoreduction", NO decomposition, and other reactions involving Cu pairs in ZSM-5 are explored.

Keywords: copper zeolite catalysts, oxygen-bridged Cu pairs, Cu oxocations, density functional theory, Cu-ZSM-5

1. Introduction

Cu-ZSM-5 has been widely studied as a catalyst for NO decomposition and reduction [1]. The existence and behavior in this material of Cu ion pairs bridged by oxygen – sometimes referred to as Cu dimers or oxocations – have been extensively debated. These species may be responsible for the short Cu–Cu separations (2.91–3.13 Å) observed in extended X-ray absorption fine structure (EXAFS) measurements [2,3] on highly exchanged Cu-ZSM-5. Other experimental evidence for Cu oxocations includes the sigmoidal relation between NO turnover frequency and Cu exchange level in NO decomposition [4–7], and infrared (IR) [8–10] and temperature-programmed reduction (TPR) [8,11] data.

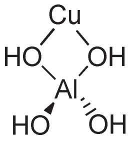
Arguments against the existence of Cu pairs in Cu-ZSM-5 have also been proposed. For example, an alternative interpretation of the sigmoidal relation between NO turnover frequency and Cu exchange level is that there are two or more mono-Cu sites, with the catalytically most active sites being less favorable for cation exchange [4]. Additionally, an EPR signal attributed to $[Cu^{2+}O^{2-}Cu^{2+}]^{2+}$ oxocations is observed in Cu-Y [12] but not in Cu-ZSM-5 [13]. The EPR silence in the latter case has been attributed to antiferromagnetic coupling of the copper spins via superexchange [9], but a magnetic susceptibility study [14] found no antiferromagnetism in dehydrated Cu-ZSM-5. Finally, some have suggested [14] that due to Loewenstein's rule, two tetrahedral (T) Al sites in close enough proximity to charge balance a $[Cu–O–Cu]^{2+}$ species would be unlikely in a highly siliceous zeolite. Loewenstein's rule does not exclude Al T-sites as next nearest neighbors, however, and inspection of the ZSM-5 structure suggests that an oxygen-bridged Cu pair would likely be supported by an Al–(O–Si)$_n$–O–Al linkage.

To date, the only theoretical studies of Cu pairs in ZSM-5 have been based either on empirical atomistic simulations or very low-level quantum calculations [15–18]. Over the last few years, our groups have elucidated many aspects of the binding and catalytic reactions of NO_x and related species on *single* Cu sites in zeolites using an accurate, first-principles DFT cluster approach [19–24]. Here we present a systematic extension of that work to O- and O_2-bridged Cu pairs. The latter species have not previously been considered in the context of Cu zeolite catalysis, but are known to be important in certain biological enzymes with similar Cu environments [25,26]. We first examine the key structural and electronic properties of both types of oxocation in zeolitic environments. We then demonstrate that both species are remarkably stable over a range of Cu–Cu distances typical of those expected in ZSM-5. Finally, we comment on the implications of these results for a number of processes potentially involving oxocations in Cu-ZSM-5, including "autoreduction", the equilibrium between reduced and oxidized Cu sites, and NO decomposition.

2. Computational details

Density functional theory (DFT) calculations were performed with the Amsterdam Density Functional (ADF) [27,28] code version 2.3. Geometries and vibrational frequencies were determined within the local spin density approximation (LSDA) [29], and the final energies improved with Becke exchange [30] and Perdew correlation (BP86) [31] gradient corrections. A valence double-ζ plus polarization Slater-type basis was used for all main group elements, and Cu was further described by a double-ζ s and p and triple-ζ d basis. Numerical parameters were chosen to ensure convergence of energies and geometries to within 0.1 kcal mol^{-1} and 0.001 Å, respectively.

There is growing evidence [19–24,32–34] that the local chemistry at extra-framework Cu sites in zeolitic environments is well described by small cluster models. A particularly useful model for isolated Cu sites represents the zeolite framework (denoted Z) by a single Al(OH)$_4^-$ “T-site” [23,24,34,35]; the Cu is assumed to be two-fold coordinated and the negative framework charge makes the Cu oxidation state in ZCu nominally 1+.



In the present work we extend this model to Cu pairs by allowing each Cu to be two-coordinated to a separate Al(OH)$_4^-$, making the CuOCu or CuO$_2$Cu charge nominally 2+. While this model does not represent ZSM-5 specifically, it does allow us to explore generic aspects of Cu pairs in zeolites in a computationally convenient manner.

In reality, the zeolite will restrict the possible coordination environment of the Cu pairs. These constraints may in fact be what differentiates the catalytic activity of ZSM-5 from other zeolites. The most important constraint will be on the Cu–Cu separation. To study this effect, we vary the separation and optimize all remaining coordinates. The zeolite lattice imposes additional orientational constraints on the Cu coordination environment, but test calculations [36] show this effect to be less significant. In what follows, we use our T-site model to explore both the limiting case of fully relaxed species and the effects of constrained Cu–Cu distances.

3. Results

Before presenting our results for Cu pairs, we briefly summarize previously reported [24] predictions for the series ZCu, ZCuO, and ZCuO$_2$ (figure 1). ZCu and ZCuO represent the two extremes of Cu oxidation, with the former closed shell and Cu(I) (d^{10}), and the latter an open-shell triplet, with unpaired electrons shared between the formally Cu(II) (d^9) and O$^{\cdot -}$ centers. The two ZCuO$_2$ isomers occupy an intermediate position of Cu oxidation, best described as a hybrid between ZCu(I)–O$_2$ and ZCu(II)–O$_2^-$. As this bonding description suggests, both isomers maintain the short O–O separations and triplet ground states characteristic of molecular oxygen, with the side-bound, square planar ZCu(η^2-O$_2$) 5 kcal mol^{-1} lower in energy than the end-bound, bent ZCu(η^1-O$_2$). These single Cu species clearly play a major role in determining the redox properties of Cu-exchanged zeolites and, when in close proximity (as expected under conditions of high Cu loadings and low Si/Al ratios), may combine to form O- or O$_2$-bridged Cu pairs.

We first consider the single O-bridged ZCuOCuZ in the absence of constraints. A bound structure is obtained with the Cu centers separated by 3.45 Å and the bridging oxy-

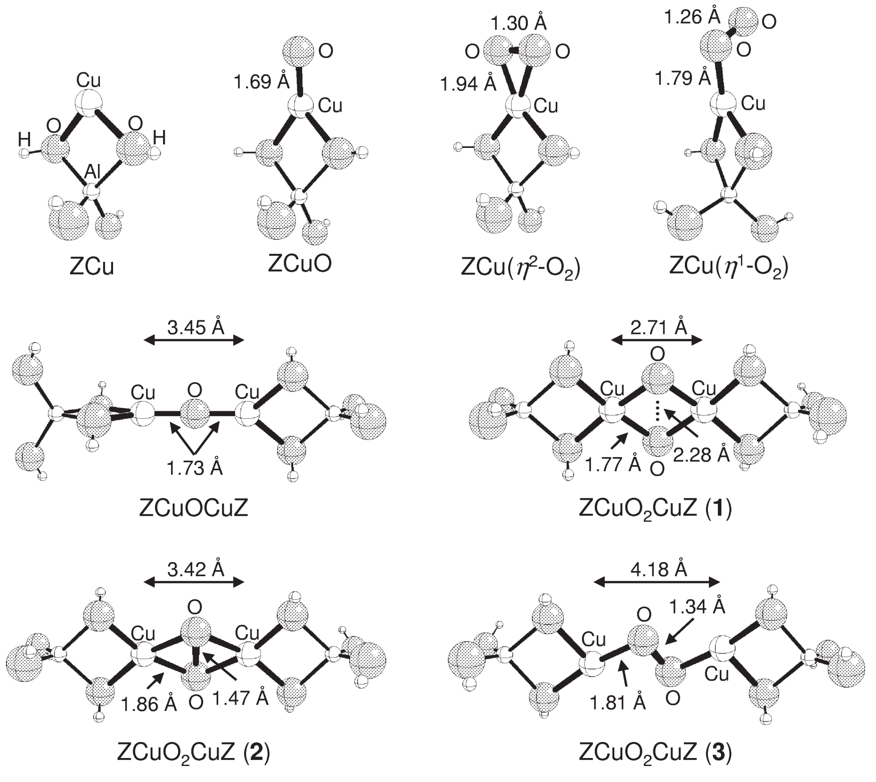


Figure 1. Optimized structures of mono- and di-Cu species within the T-site model.

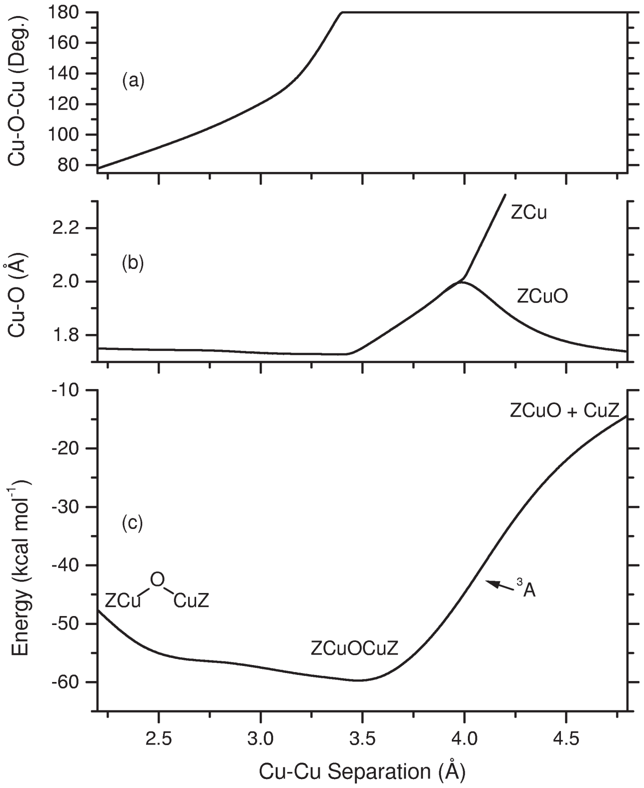


Figure 2. Cu–O–Cu angle (a), Cu to bridging O distance (b), and energy (c) vs. Cu–Cu separation for ZCuOCuZ. The zero of energy is the ZCuO + ZCu dissociation limit.

gen on a line halfway in between (figure 1). The formation of ZCuOCuZ from one oxidized site, ZCuO, and one reduced site, ZCu, is highly favorable thermodynamically (reaction (1) and figure 2):

$$\mathrm{ZCuO} + \mathrm{ZCu} \rightarrow \mathrm{ZCuOCuZ} \quad -60\ \mathrm{kcal\,mol^{-1}} \qquad (1)$$

The energy of the oxocation is nearly insensitive to the orientation of the T-site ligands. For example, rotation by 90° of one T-site ligand about the Cu–O–Cu axis decreases the binding energy by only 4 $\mathrm{kcal\,mol^{-1}}$. In the fully relaxed geometry, ZCuOCuZ has a triplet ground state with both charge and spin significantly delocalized:

$$\mathrm{Cu(I)\text{–}O^{\bullet -}\text{–}Cu(II)} \leftrightarrow \mathrm{Cu(II)\text{–}O^{2-}\text{–}Cu(II)}$$
$$\leftrightarrow \mathrm{Cu(II)\text{–}O^{\bullet -}\text{–}Cu(I)}$$

Figure 2 shows the effects of constraining the Cu–Cu distance in ZCuOCuZ. Compression below the preferred Cu–Cu separation of 3.45 Å causes the Cu–O–Cu angle to deviate from linearity. This bending allows the Cu–O bond length to remain fixed at around 1.74 Å and allows the energy surface to remain relatively flat to Cu–Cu separations as small as 2.5 Å. As the Cu–Cu separation is increased beyond 3.45 Å, the bridging O remains centered until about 4.0 Å, and then shifts asymmetrically toward one Cu at longer Cu–Cu separations. The electronic structure varies continuously from being primarily $\mathrm{Cu(II)\text{–}O^{2-}\text{–}Cu(II)}$ at the shortest Cu–Cu distances to essentially $\mathrm{Cu(II)\text{–}O^{\bullet -}\text{–}Cu(I)}$ in the asymmetric region beyond 4.0 Å. The triplet state remains lowest in energy over the entire range of figure 2.

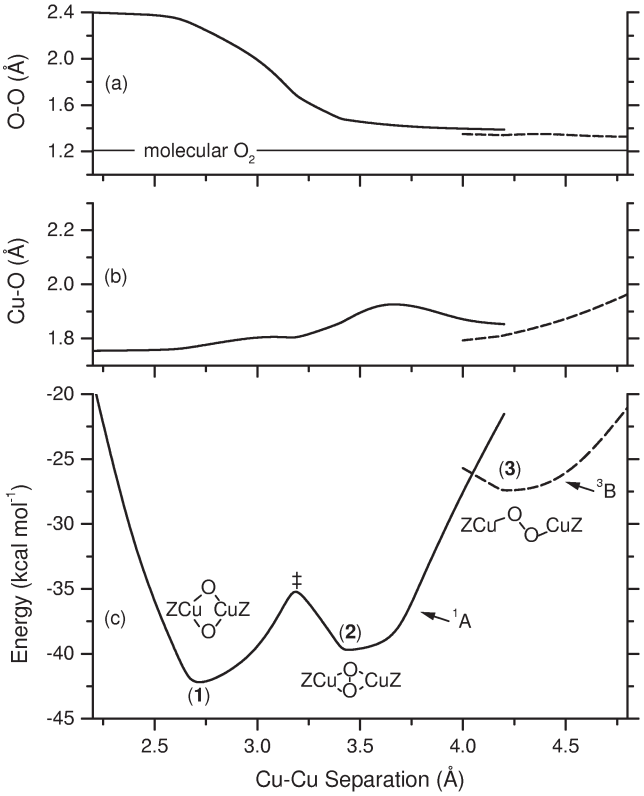
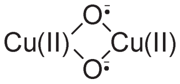


Figure 3. Bridging O–O distance (a), Cu to bridging O distance (b), and energies (c) for singlet (solid) and triplet (dashed) states vs. the Cu–Cu separation for $\mathrm{ZCuO_2CuZ}$. The zero of energy is the $\mathrm{ZCuO_2}$ + ZCu dissociation limit.

A similar analysis of $\mathrm{ZCuO_2CuZ}$ reveals three low-energy geometric isomers with unique molecular and electronic characters (figures 1 and 3). The most stable (**1**) has the shortest Cu–Cu separation (2.71 Å), a singlet ground state, and a planar $\mathrm{Cu_2O_2^{2+}}$ core with square planar coordination about both Cu ions. The bridging O atoms are widely separated (2.28 Å) and are bonded only to the neighboring Cu ions. The Cu centers are highly oxidized, suggesting the following valence bond description:



with the "unpaired" electrons singlet coupled.

As with ZCuOCuZ, formation of **1** from mono-Cu species is highly favored thermodynamically:

$$\mathrm{ZCu} + \mathrm{ZCuO_2} \rightarrow \mathrm{ZCuO_2CuZ} \quad -42\ \mathrm{kcal\,mol^{-1}} \qquad (2)$$

$$2\mathrm{ZCuO} \rightarrow \mathrm{ZCuO_2CuZ} \quad -63\ \mathrm{kcal\,mol^{-1}} \qquad (3)$$

Rotation of the T-sites decreases the binding energy by up to 14 $\mathrm{kcal\,mol^{-1}}$, reflecting the strong preference of Cu for square planar coordination.

Decreasing the Cu–Cu separation below 2.71 Å results in a monotonic rise in singlet energy and a puckering of the $\mathrm{Cu_2O_2^{2+}}$ moiety such that the Cu–O and O–O separations are maintained near 1.75 and 2.40 Å, respectively (figure 3). In contrast, as the Cu–Cu separation is increased beyond 2.71 Å the $Cu_2O_2^{2+}$ core remains rhombohedral, with the Cu–O and O–O separations gradually increasing and markedly decreasing, respectively. A transition state at a Cu–Cu distance of 3.16 Å leads to a second $ZCuO_2CuZ$ isomer (**2**, Cu–Cu = 3.42 Å) only 3 kcal mol^{-1} higher in energy than **1** and reminiscent in structure to ZCu(η^2-O_2). The O–O separation and vibrational frequency in **2** (1.47 Å and 840 cm^{-1}) are consistent with those expected for a peroxide (O_2^{2-}) complex [37], although the electronic structure results indicate a considerable amount of charge sharing between the two Cu and O_2 and a decrease in Cu oxidation state compared to **1**:

$$\begin{aligned}&\mathrm{Cu(I)}\text{–}\mathrm{O}_2^-\text{–}\mathrm{Cu(II)} \leftrightarrow \mathrm{Cu(II)}\text{–}\mathrm{O}_2^{2-}\text{–}\mathrm{Cu(II)}\\ &\quad\leftrightarrow \mathrm{Cu(II)}\text{–}\mathrm{O}_2^-\text{–}\mathrm{Cu(I)}\end{aligned}$$

The small intrinsic barrier between **1** and **2** (8 kcal mol^{-1} with respect to **1**) suggests a facile pathway for the formation or cleavage of an O–O bond.

At still greater Cu–Cu separations the singlet energy rises rapidly and the O atoms reorient such that one remains bound to each Cu and the O–O bond is retained. Above 4.0 Å, a triplet state drops below the singlet in energy and introduces a third $ZCuO_2CuZ$ isomer (**3**) 15 kcal mol^{-1} higher in energy than **1**. The Cu–O–O–Cu connectivity in **3** is similar to that found in ZCu(η^1-O_2), and the O–O separation and vibrational frequency (1.34 Å and 1049 cm^{-1}) are as expected for a superoxide (O_2^-) complex [37]. Indeed, the Cu centers are the least oxidized in isomer **3**, and the electronic structure in this case can be represented as

$$\mathrm{Cu(I)}\text{–}\mathrm{O}_2^-\text{–}\mathrm{Cu(II)} \leftrightarrow \mathrm{Cu(I)}\text{–}\mathrm{O}_2\text{–}\mathrm{Cu(I)} \leftrightarrow \mathrm{Cu(II)}\text{–}\mathrm{O}_2^-\text{–}\mathrm{Cu(I)}$$

Further increase in Cu–Cu separation leads to the dissociation of $ZCuO_2CuZ$ into mono-Cu fragments.

4. Discussion

Figure 4 combines the thermodynamic results of this work with those obtained previously for ZCu, ZCuO, and $ZCuO_2$ [24]. Relative to those mono-Cu fragments, formation of the oxocations ZCuOCuZ and $ZCuO_2CuZ$ is favored by 42 kcal mol^{-1} or more in the T-site model. Further, as shown in figures 2 and 3, this stability persists over a fairly broad range of Cu–Cu separations, and is only weakly dependent on the T-site orientation. The available ion coordination sites within the zeolite will strongly influence the accessible Cu–Cu separations. These separations will be highly zeolite-dependent: in ZSM-5, for instance, visual inspection suggests Cu–Cu separations up to 2.5 Å in a single 5- or 6-membered ring, and up to 4.5 Å across a channel. While it would be premature to make specific assignments, the lowest energy regions for both ZCuOCuZ and $ZCuO_2CuZ$ do include the Cu–Cu distances (near 3 Å) observed in EXAFS experiments [2,3] on Cu-ZSM-5. The present work thus strongly supports the existence of oxocations in Cu-exchanged zeolites and suggests that O_2-bridged Cu pairs are as likely to be important as O-bridged Cu pairs. It is clear that the formation and stability of Cu oxocations will be influenced by the proximity of Al T-sites, by the framework flexibility, and by Cu ion mobility. Further, the catalytic activities of the oxocations, and their sensitivities to the zeolite environment, remain to be examined.

We now consider the implications of the above results for a number of proposed reactions involving oxocations in Cu-ZSM-5. One of the most debated is "autoreduction" of Cu^{2+}, which has been inferred from the disappearance of the Cu^{2+} EPR signal upon calcination [13,38] (see, however, [39]). Oxocation formation has been postulated to explain this observation [4,8,40]:

$$2[\mathrm{ZCuOH}] \rightarrow \mathrm{H_2O} + \mathrm{Z}\left[\mathrm{Cu}^{2+}\text{–}\mathrm{O}^{2-}\text{–}\mathrm{Cu}^{2+}\right]\mathrm{Z} \qquad (4)$$

The EPR silence of the resulting oxocation was attributed to antiferromagnetic coupling of Cu-localized spins through the oxygen via a superexchange mechanism. The present results indicate that ZCuOCuZ actually has a more delocalized spin density and a triplet ground state. Although in principle such species may be EPR active, we note that other triplet species, such as ZCuO and $ZCuO_2$, have also not been observed in EPR studies of Cu-ZSM-5 [13]. We predict reaction (4) to be exothermic by 8 kcal mol^{-1}, lend-

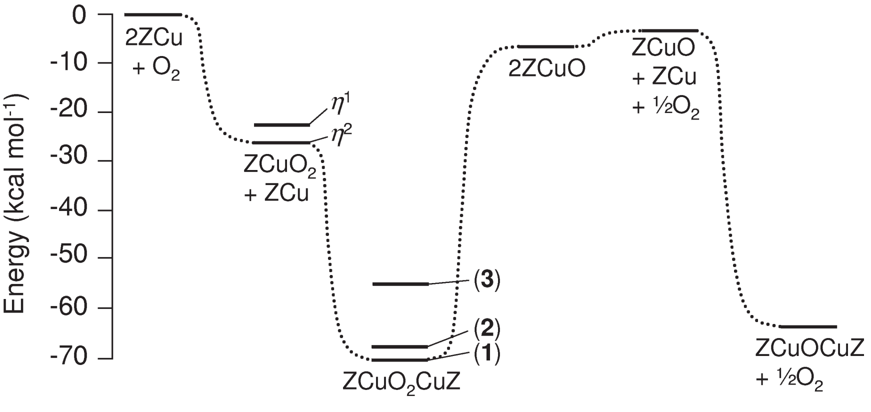


Figure 4. Relative energies of systems with 2ZCu and 2O within the T-site model.

ing support for its role in autoreduction. In contrast, we find autoreduction to mono-Cu products [13] to be highly endothermic:

$$2[\mathrm{ZCuOH}] \rightarrow \mathrm{H_2O} + \mathrm{ZCu} + \mathrm{ZCuO} \quad +51\ \mathrm{kcal\,mol^{-1}} \quad (5)$$

in agreement with [41].

Peaks in the temperature-programmed reduction of Cu-ZSM-5 by H_2 (293 K) and CO (343 K) have been interpreted in terms of reduction of ZCuOCuZ [8]:

$$\mathrm{ZCuOCuZ} + \mathrm{H_2} \rightarrow \mathrm{ZCuOH_2} + \mathrm{ZCu} \quad -13\ \mathrm{kcal\,mol^{-1}} \quad (6)$$

and

$$\mathrm{ZCuOCuZ} + \mathrm{CO} \rightarrow \mathrm{ZCuCO_2} + \mathrm{ZCu} \quad -22\ \mathrm{kcal\,mol^{-1}} \quad (7)$$

where the expected adsorption of H_2O [24] or CO_2 [42] to one of the reduced Cu sites is explicitly included. Interestingly, the reactions of $ZCuO_2CuZ$ with H_2 and CO are predicted to be even more highly exothermic, and may also contribute to the experimentally observed reductions:

$$\mathrm{ZCuO_2CuZ} + \mathrm{H_2} \rightarrow \mathrm{ZCuOCuZ} + \mathrm{H_2O} \quad -49\ \mathrm{kcal\,mol^{-1}} \quad (8)$$

and

$$\mathrm{ZCuO_2CuZ} + \mathrm{CO} \rightarrow \mathrm{ZCuOCuZ} + \mathrm{CO_2} \quad -67\ \mathrm{kcal\,mol^{-1}} \quad (9)$$

NO has also been proposed as an oxocation reductant [10], which we find to be more favorable for $ZCuO_2CuZ$:

$$\mathrm{ZCuOCuZ} + \mathrm{NO} \rightarrow \mathrm{ZCu} + \mathrm{ZCuNO_2} \quad +10\ \mathrm{kcal\,mol^{-1}} \quad (10)$$

and

$$\mathrm{ZCuO_2CuZ} + \mathrm{NO} \rightarrow \mathrm{ZCuOCuZ} + \mathrm{NO_2} \quad -18\ \mathrm{kcal\,mol^{-1}} \quad (11)$$

Of even greater interest is the possible role of oxocations in NO decomposition and selective catalytic reduction reactions. We have previously detailed a mechanism for NO decomposition which involves the coupling of two NO on a single ZCu site to produce ZCuO and N_2O, and subsequent recombination of the latter to form ZCu, N_2, and O_2, via $ZCuO_2$ [23,24]. It was suggested that maintenance of an equilibrium between reduced (ZCu) and oxidized (ZCuO) sites would be key to catalytic activity, and that the presence of O_2 could perturb that equilibrium:

$$2\mathrm{ZCu} + \mathrm{O_2} \rightleftharpoons 2\mathrm{ZCuO} \quad (12)$$

For distant Cu centers, reaction (12) can be catalyzed by, e.g., NO [24]:

$$\mathrm{ZCu} + \mathrm{O_2} \rightleftharpoons \mathrm{ZCuO_2} \quad (13)$$

$$\mathrm{ZCuO_2} + \mathrm{NO} \rightleftharpoons \mathrm{ZCuO} + \mathrm{NO_2} \quad (14)$$

$$\mathrm{ZCu} + \mathrm{NO_2} \rightleftharpoons \mathrm{ZCuO} + \mathrm{NO} \quad (15)$$

For proximal Cu ions, the oxocation results provide an alternative pathway (figure 4) combining reactions (2) and (3):

$$\mathrm{ZCuO_2} + \mathrm{ZCu} \rightleftharpoons \mathrm{ZCuO_2CuZ} \rightleftharpoons 2\mathrm{ZCuO}$$

This cycle is similar to the reversible binding and activation of O_2 proposed in di-Cu enzymes [25,26]. While the microscopic details of the bond forming and breaking reactions remain to be fully explored, our structural and thermodynamic results support the thermal accessibility of such pathways and a role for oxocations in mediating equilibrium (12).

One can also imagine a more direct role for Cu oxocations in NO chemistry on Cu zeolites. For instance, Iwamoto and co-workers proposed a scheme for NO decomposition on two adjacent Cu centers [43], and Lei et al. [9] proposed that the coupling of two NO occurs on two ZCu sites rather than one:

$$2\mathrm{ZCu} + 2\mathrm{NO} \rightarrow \mathrm{ZCuOCuZ} + \mathrm{N_2O} \quad -102\ \mathrm{kcal\,mol^{-1}} \quad (16)$$

Reaction (16) is more thermodynamically favorable than the analogous reaction on a single ZCu site to produce ZCuO, which has an exothermicity of 42 $\mathrm{kcal\,mol^{-1}}$ [23]. The additional driving force obviously derives from the binding energy of the oxocation, but whether this driving force can be harnessed in a kinetically feasible mechanism remains to be investigated.

Another interesting possibility is oxocation involvement in the conversion of N_2O to N_2:

$$2\mathrm{ZCu} + \mathrm{N_2O} \rightarrow \mathrm{ZCuOCuZ} + \mathrm{N_2} \quad -69\ \mathrm{kcal\,mol^{-1}} \quad (17)$$

or

$$\mathrm{ZCuOCuZ} + \mathrm{N_2O} \rightarrow \mathrm{ZCuO_2CuZ} + \mathrm{N_2} \quad -14\ \mathrm{kcal\,mol^{-1}} \quad (18)$$

Clearly, both reactions (17) and (18) are thermodynamically favorable. N_2O decomposition reactions involving single ZCu or ZCuO sites have relatively high barriers ($>36\ \mathrm{kcal\,mol^{-1}}$) [24] and either of the above reactions might provide a more kinetically feasible pathway for N_2 formation.

5. Conclusions

The present quantum chemical results for Cu pairs in zeolitic environments strongly support the existence of *both* O- and O_2-bridged oxocations in Cu-ZSM-5. A number of stable isomers with preferred Cu–Cu separations within the range that is likely to be important in zeolites were identified. The structures and energetics of these species are consistent with their involvement in both autoreduction and chemical reduction by H_2, CO, or NO, as well as their direct participation in NO decomposition. Further theoretical and experimental work is clearly needed to fully characterize the behavior of oxocations in Cu-ZSM-5 and to clarify their role in the catalytic decomposition and selective catalytic reduction of NO.

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