On the nature of spin- and orbital-resolved Cu^+ –NO charge transfer in the gas phase and at Cu(I) sites in zeolites

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Abstract

Electronic factors essential for NO activation by Cu(I) sites in zeolites are investigated within spin-resolved analysis of electron transfer channels (natural orbitals for chemical valence). NOCV analysis is performed for three DFT-optimized models of Cu(I)–NO site in ZSM-5: $[\text{CuNO}]^+$, (T1)CuNO, and (M7)CuNO. NO as a non-innocent, open-shell ligand reveals significant differences between independent deformation density components for α and β spins. Four distinct components are identified: (i) unpaired electron donation from NO $\pi_{||}^*$ antibonding orbital to $\text{Cu}_{s,d}$; (ii) backdonation from copper d_{yz} to $\pi_{\perp}^*$ antibonding orbital; (iii) donation from occupied $\pi_{||}$ and Cu d_{xz} to bonding region, and (iv) donation from nitrogen lone-pair to $\text{Cu}_{s,d}$. Channel (i), corresponding to one-electron bond, shows-up solely for spin majority and is effective only in the interaction of NO with naked Cu^+ . Channel (ii) dominates for models b and c: it strongly activates NO bond by populating antibonding π^* orbital and weakens the N–O bond in contrast to channel (i), depopulating the antibonding orbital and strengthening N–O bond. This picture perfectly agrees with IR experiment: interaction with naked Cu^+ imposes small blue-shift of NO

stretching frequency while it becomes strongly red-shifted for Cu(I) site in ZSM-5 due to enhanced backdonation.

Keywords NO activation · Cu(I) sites · Charge transfer · Donation and backdonation · Natural orbitals for chemical valence

Introduction

Cationic sites in mesoporous structures, in particular Cu(I) sites in zeolites, have long-attracted attention and stimulated vigorous research due to their high-catalytic activity and selectivity. On the other hand, nitric oxide (NO) is the target of paramount importance in environmental catalysis. After Iwamoto's discovery of an unusually high activity of Cu(I) zeolites in NO decomposition and its revival [1–3] there has been an ongoing experimental [4–12] and theoretical research [13–23] to understand the details of the mechanism of this process. Despite this tremendous effort, there are still a number of unsettled questions, including fundamental query about the nature of the bonding between various forms of copper and NO molecule. Following this line this study deals with the bonding of nitric oxide by Cu/MFI zeolite, showing high-catalytic activity in direct NO_x decomposition [4–7], as opposed to naked Cu^+ ions in gas phase that do not catalyze this reaction [22].

After many discussions, the consensus seems to be reached in the literature that charge-transfer processes constitute crucial factor for the activation of a molecule bound to a transition-metal cationic site in a zeolite. Already classical view on binding and activation of ligands with multiple bonds in complexes with transition-metal cations ascribed them to two main electronic contributions:

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donation and backdonation processes [24, 25]. On the other hand, it was suggested, after analyzing atomic population changes upon ligand adsorption on a bare cation versus the cation embedded in a model environment that the unusual catalytic activity of transition-metal exchanged zeolites should be due to the activation of the transition-metal ion by the zeolite framework which functions as a specific ligand. Theoretical studies devoted to the interaction of small ligands with multiple bonds bound by zeolitic sites clearly indicated that the charge flow upon adsorption involves several transfer channels, strongly dependent on a zeolite framework type and a cation position [23, 26–30]. Populations within orbital resolution and devised selection schemes, frequently supported by topological analyses of electron density, were able to discriminate distinct electron transfers for a model metal–ligand bond [23, 26, 27]. Nevertheless, modern tools serving this purpose are still desirable to get better insight into individual charge-transfer processes between fragments constituting the complex system, within general partition schemes into preselected fragments with arbitrary symmetry. With this end, new electron-density analysis method based on natural orbitals for chemical valence (ETS-NOCV) was formulated [31–34]. Pairs of natural valence orbitals (linked by the absolute value of appropriate eigenvalues), where the one depicts spatial region with electron-density depletion and the other spatial region with electron inflow, define independent density transfer channels. This procedure allows decomposing total deformation density of the system (e.g., metal–ligand complex) into individual charge flow processes between predefined fragments. This method may also serve to follow changes in electron transfer processes imposed by metal environment. ETS-NOCV methodology has already been applied by us with flexible strategy of dividing multicomponent zeolitic active site into fragments and shown to perform well for copper (I) sites interacting with closed-shell ligands like ethene, ethyne, benzene, or formaldehyde [28–30, 35].

NO moiety is a special case of a non-innocent ligand: it is an open-shell, redox-active molecule with intricate as well chemical as electronic properties. Therefore it presents a challenge for the theory being, as already stated, desirable target of research due to its importance for environmental and bio-medical sciences. Recently, dramatic changes in Cu–ligand interaction upon insertion into a zeolite were clearly demonstrated for nitric oxides interaction with the Cu/MFI system [22, 23, 36–38]. Thus, prompted by the previous successful applications of NOCV methodology, we devote the following study to the analysis of the interaction of this demanding molecule with copper cation from the point of view of electron transfer processes, with special attention paid to the role of a zeolite as a generalized ligand. To this end, appropriate models will be

subjected to DFT modeling and their electronic properties will be discussed with the focus on the analysis of orbital interaction as described in the language of NOCV orbitals.

Computational details

Models

In this study, we consider three models of Cu(I) site in ZSM-5 interacting with NO molecule: (a) $[\text{CuNO}]^+$, (b) (T1)CuNO, and (c) (M7)CuNO. For reference purposes the model (a) composed solely of a bare Cu^+ cation (free cation) and NO molecule is considered. In model (b) Cu^+ cation is coordinated to an $[\text{Al}(\text{OH})_4]^-$ anion (T1) which is the simplest mimic for the nearest surrounding of the cation in a zeolite framework. The model (c) is composed of the fragment of ZSM-5 framework (M7 cluster cut-off the wall in the main channel) hosting Cu(I) cation and NO molecule. M7 cluster is a fragment of ZSM-5 framework containing six-membered ring, composed of 7 T (Si or Al) atoms. To saturate peripheral bonds in model (c), silicon atoms from the next coordination sphere are replaced by hydrogen atoms. Each of the models (b) and (c) has one Al atom thus they are electroneutral while model (a) is positively charged (+1). Figure 1 shows optimized geometries of the models together with their schematic orientation in a coordinate system. Models (a) and (b) have a plane of symmetry (C_s group) while model (c) has symmetry C_1 .

With this selection of geometric models we are addressing two issues: (i) what is the impact of embedding in a zeolite framework on electronic properties of the cation and its electronic interaction with the bound nitric oxide molecule and (ii) what is the minimal size of the model capable of accounting for most important features of embedding, responsible for modification of electron transfers and thus tuning catalytic properties of Cu(I) sites in zeolites.

Calculations

Geometry optimization of models (a) and (b) has been performed employing Turbomole package [39]. Density-functional theory (DFT) was used with hybrid potential B3LYP [40–42] and triple-zeta basis set (def2-TZVP) [43]. The calculations for model (c) were carried out by combined quantum mechanics/molecular mechanics method (QM/MM), analogously as in Ref. [18]. In this scheme the selected part of the system, containing adsorbed molecule, cationic centre and its nearest neighborhood, is treated with quantum chemical accuracy (QM) while the rest of the framework is treated with less computationally demanding molecular mechanics (MM) with periodic

Fig. 1 Optimized geometries of the three models of Cu(I) site in ZSM-5 interacting with NO molecule: **a** $[\text{CuNO}]^+$, **b** $(\text{T1})\text{CuNO}$, and **c** $(\text{M7})\text{CuNO}$; *insets* depict schematic orientation of local coordinate system

boundary conditions. Turbomole package was applied at QM level and Gulp code [44] in MM part, both linked via QMPOT interface [45]. In classical part of calculations core-shell model potential [46] was used with the parameterization from papers by Sauer and Sierka [47] for Si, Al, O, and H atoms and Nachtigallova et al. [48] for Cu(I) ion. Short-range interactions between the NO molecule and framework O atoms are described by Lennard-Jones potential with parameters from Universal Force Field [49]. The Cu–NO interaction is described only at the QM level.

Total spin densities on the atoms have been calculated by Turbomole while single point calculations were performed with ADF [50] software at PBE level [51] for models (a, b) and QM cluster after QM/MM optimization for model (c) to obtain Nalewajski–Mrozek bond orders [52] and Hirshfeld populations [53]. The charge flow between predefined fragments of the systems of interest has been studied based on recently proposed natural orbitals for chemical valence method (NOCV) [31–34]. In this paper natural orbitals for chemical valence were computed with our home-made program Natorbs [54] since the Copper(I) nitrosyls considered in this study are all open-shell systems where original NOCV analysis as implemented in ADF code could not be done routinely. The NOCV's were calculated for each spin channel (α and β) independently, based on unrestricted, canonical Kohn–Sham orbitals. This protocol for the NOCV analysis was applied for all three models: $[\text{Cu–NO}]^+$ (a), $(\text{T1})\text{Cu–NO}$ (b), and $(\text{M7})\text{Cu–NO}$ (c).

The key issue in NOCV analysis is the separation of the complex into *fragments*, which define a suitable *promolecule*. Clearly, the choice of the fragments is arbitrary as it corresponds to a question which of the bonding interactions present in a complex is to be analyzed. Here, focusing on

the nature of the Cu–NO bonding, the complexes (a)–(c) were separated into an NO fragment and a fragment containing Cu and (if present) a zeolite group: Cu^+ , $(\text{T1})\text{Cu}$, or $(\text{M7})\text{Cu}$. While for typical cases the choice of fragments is just specification of their atomic coordinates (since the electronic density and the density matrix of the fragments are then uniquely defined), this is not the case here for the NO fragments. A complication arises from the electronically degenerate ground state of NO ($^2\Pi$). More specifically, for the $(\pi^*)^1$ ground-state configuration, the shape of the singly occupied π^* orbital may be chosen in an infinite number of ways—as π_x^* , π_y^* , or (in general) as an arbitrary combination of the both. Although all these choices are energetically equivalent, they produce *spatially distinct* electronic densities, and thus they are *not* equivalent from the point of view of the NOCV analysis. Some clue for the optimal choice of the NO π^* occupancy may be obtained from the spin densities of CuNO complexes, for which the degeneracy of the NO π^* orbitals is lifted. In these complexes the unpaired electron (coming from NO) resides in a π^* -based molecular orbital lying in the Cu–N–O plane (denoted $\pi_{\parallel}^*$), while the complementary ($\pi_{\perp}^*$) orbital is unoccupied. Therefore, in order to keep the electronic structure of the NO fragment as close as possible to the electronic situation in the CuNO complexes, we choose the $(\pi_{\parallel}^*)^1$ configuration for the NO fragment. In the other words, the electronic density on the NO fragment is chosen as already prepared for the formation of the bond with Cu. This choice should minimize a reorganization of charge density during the formation of the complex, avoiding in particular a meaningless reorganization of electronic charge solely within the NO π^* orbitals—a contribution to the deformation density which would appear otherwise.

Table 1 Population analysis results (e^-) and optimized geometric parameters (deg., Å) for the three considered models of Cu(I) interacting with NO

		Cu ⁺ –NO (a)	T1–Cu–NO (b)	M7–Cu–NO (c)
Hirschfield charges (spin densities)	Z	–	–0.33 (0.02)	–0.38 (0.0)
	Cu	+0.70 (0.01)	+0.40 (0.06)	+0.44 (0.07)
	NO	+0.30 (0.99)	–0.07 (0.92)	–0.05 (0.93)
	N	+0.14 (0.63)	–0.04 (0.62)	–0.02 (0.57)
	O	+0.16 (0.36)	–0.03 (0.30)	–0.03 (0.36)
Angle (Cu–N–O)		133.2	151.6	145.9
Distances (bond orders)	Cu–N	1.893 (0.41)	1.759 (0.53)	1.779 (0.51)
	N–O	1.144 (2.40)	1.176 (2.28)	1.178 (2.29)

Results and discussion

Results of population analysis and most important geometric parameters are summarized in Table 1. Brief inspection of the Table shows that geometric parameters of all models closely follow trends reported previously for similar systems. The Cu–N–O angle is far from linearity. As already discussed by other authors, [22, 55] angle deviation from linearity prompts the transfer of electron density from the singly occupied NO π^* orbital into the copper 4s orbital and the formation of one-electron bond, which might be also rationalized by a positive charge on the ligand but *not* by unitary spin density. The increase of the bond angle (by about 20°) when the interaction of Cu with oxygens belonging to AlO₄ tetrahedron is involved, seems to be in line with a significant drop of NO charge up to small negative value (decrease of unpaired electron donation) ascribed by other authors to the weakening of one-electron bond, surprisingly, *not* accompanied by the up-shift of NO spin population. This seemingly unexpected behavior of spin density confirms suggestions formulated for other transition metal–NO systems [56] that the spin on NO moiety does not directly correlate with apparent oxidation state while total charge is rather an effect of the balance between opposing electron transfer processes that is spin-resolved donation and backdonation channels.

However, actual Cu–N bond shortening and increase of its bond order after interaction with AlO₄ tetrahedron (Table 1), suggests that this drop of one-electron bonding should be balanced by triggering or enhancing the other contribution to the bonding interaction (e.g., π^* backdonation). On the other hand, the strength of the NO bond is significantly decreased by embedding the cation in a zeolite to form Cu(I) site, what is clearly evidenced by the bond elongation and the decrease of its bond order. The other important clue stemming from the data comprised in Table 1 is that a single AlO₄ tetrahedron seems sufficient to cover main features of the realistic model of zeolitic environment: neither populations nor geometric parameters change significantly when going to a bigger model of ZSM-5 framework.

In the following, we are presenting an evidence that a quantitative, spin-resolved separation of donation and backdonation well settles the discussion and partially resolves queries concerning the bonding between Cu(I) and NO from electronic interaction orbital perspective, especially in the context of the impact of embedding. In brief, the bonding between Cu(I) and NO has been conceptually ascribed to the two cooperating mechanisms which have been described previously and discussed in terms of canonical orbital picture of the Cu(I)–NO interaction and its structural implications [22, 23, 55]. The first mechanism is donation from a singly occupied NO $\pi_{||}^*$ orbital into an unoccupied Cu 4s orbital. In accord to spatial orientation of our models (see Fig. 1), the subscript “ $||$ ” identifies the orbitals lying in the xz plane, while the subscript “ $\perp$ ” is used for orbitals lying out of this plane. The donation is accompanied by rehybridisation on Cu through mixing of empty 4s with doubly occupied $3d_{z^2,xz}$. The second mechanism is backdonation from the doubly filled Cu $3d_{yz}$ orbital into the empty NO $\pi_{\perp}^*$. Donation and backdonation mechanisms have a clear connection with the structures. The donation effectively depopulates the antibonding NO orbital, thus it strengthens the N–O bond; in contrast, the backdonation effectively populates the antibonding NO orbital, thus it weakens the N–O bond. Structurally, the second effect should prevail for embedded cation as the N–O bond is longer for the models of NO coordinated to Cu(I) site than for free NO. The donation is also responsible for a characteristic bent binding mode of NO in the Cu(I) complexes. For symmetry reasons, the mixing of the singly occupied NO π^* (as well the doubly occupied NO π) with the empty Cu 4s is effective only in a non-linear arrangement of Cu–N–O; in a hypothetical linear arrangement there would be no acceptor orbitals for electrons in the NO π^* and π orbitals [22]. Thomas et al. [55] also described the interaction between Cu⁺ and NO in terms of a one-electron bond, where the singly occupied bonding orbital exhibits π symmetry (the nodal plane corresponding with the plane of the molecule), though with contributions from copper 3d, 4s and from the NO π^* orbital.

As already alluded in connection to our data gathered in Table 1, even more complex scheme of orbital interactions involved in the bonding should be expected here. Figure 2 shows the dominant electron-density transfer channels (with the eigenvalues over 0.1) between copper cation and NO ligand bound to it for CuNO^+ model. They are represented as 3-D contour plots of independent NOCV components of the differential density, together with their eigenvalues. The

Fig. 2 Contour plots of dominant electron density transfer channels between copper cation and NO ligand bound to Cu^+ (model a); blue (black)—electron inflow; red (gray)—electron outflow; contour value 0.003) (Color figure online)

shape and spatial distribution of regions showing density depletion (red) and density inflow (blue) illustrate donation or backdonation character of a particular channel, eigenvalues correspond to amount of electrons transferred within a particular channel. Figure 2 depicts relevant entries showing various spatial characteristics; as already foreseen, spin-resolution reveals significant differences between independent deformation density components within alpha and beta spin manifolds. Predominant contribution for majority spins (nearly half electron transferred) depicts density outflow from the singly occupied NO antibonding orbital $\pi_{||}^*$ (red) to the empty s orbital on copper (blue). In line with general predictions, there is no corresponding contribution within beta spin manifold where it is replaced with the channel depicting donation from doubly occupied NO orbital $\pi_{||}$ (with some admixture of $\pi_{||}^*$, allowed in reduced symmetry), accompanied by copper d_{xz} , to the bonding region between Cu and NO. Only the second channel for both spins corresponds to backdonation from Cu d_{yz} to $\pi_{\perp}^*$ antibonding NO orbital. The third important contribution in beta spin manifold may be called a “classical” σ donation from a lone-pair on nitrogen. Since the donation of unpaired α electron overwhelms electron transfer within this spin manifold, here the contributions corresponding to donation from doubly occupied $\pi_{||\text{NO}}$ and “classical” σ donation channel are pushed down, below the threshold of 0.1 electrons (therefore not shown in Fig. 2).

Figure 3 shows the dominant electron-density transfer channels (with the eigenvalues over 0.1) between copper cation and NO ligand bound to it for $\text{Cu(T1)}\text{--NO}$ (model b). The striking difference is a significant amplification of a backdonation channel. Backdonation from copper d_{yz} to $\pi_{\perp}^*$ antibonding NO orbital becomes upped to the first position and with the eigenvalue of 0.39 (α) or 0.33 (β) dominates entire electron transfer. Simultaneously, the channel corresponding to the donation of the unpaired electron becomes pushed down below the threshold—a fact which could not be easily elucidated from simple population and orbital analyses. Both effects help to better rationalize strong activation ability of copper sites in zeolites: not only $\pi_{\perp}^*$ becomes populated (enhanced backdonation) but also depopulation of $\pi_{||}^*$ antibonding orbital becomes suppressed. The other components of charge density flow are only weakly influenced upon embedding (see Table 2).

Figure 4 depicts the dominant electron-density transfer channels for $\text{Cu(M7)}\text{--NO}$ (model c). Inspection of this figure together with Table 2 shows clearly that main components of electron transfers between the fragments in a more realistic model of zeolitic framework do not change in comparison to a single aluminum tetrahedron (model b): neither spatial distribution of transfer channels (telling minute donation and backdonation character) nor the

Fig. 3 Contour plots of dominant electron density transfer channels between copper cation and NO ligand bound to (T1)Cu (model b); blue (black)—electron inflow; red (gray)—electron outflow; contour value 0.003) (Color figure online)

eigenvalues (corresponding to amount of transferred electrons) are influenced by increasing the size of the zeolite model. Subtle differences between framework topology for various zeolites or cation siting cannot be described with the use of a one-tetrahedral model; nevertheless, the essential features of the impact of embedding on the bonding between a specified cation and a small ligand are sufficiently reproduced with the use of such simple model. Presumably, this is because even the small model correctly describes the coordination of Cu^+ to the two oxygen atoms

Table 2 Description of independent electron transfer channels with corresponding spin-resolved eigenvalues (in arbitrary units) for models (a), (b), and (c)

Electron transfer character		Eigenvalue v_i		
		Cu^+-NO	$\text{T1}-\text{Cu}-\text{NO}$	$\text{M7}-\text{Cu}-\text{NO}$
(i) Donation of unpaired electron	α	0.46	<0.1	<0.1
	β	—	—	—
(ii) Backdonation	α	0.23	0.39	0.38
	β	0.21	0.33	0.32
(iii) Donation from doubly occupied $\pi_{ }$	α	<0.1	<0.1	<0.1
	β	0.22	0.22	0.23
(iv) σ Donation	α	<0.1	0.22	0.22
	β	0.14	0.17	0.16

from the aluminum tetrahedron and thus mimics the coordination to specified bridging oxygens in a framework.

IR spectra constitute very well-known signature and descriptor of the character of the bond and its activation. Infrared stretching frequencies have been both measured [57, 58] and calculated [23] for NO interacting with naked cation (in argon or neon matrices) as well as Cu(I) site in ZSM-5 zeolite. Table 3 presents a summary of previously published data. The agreement of the impact of zeolitic environment on the activation ability of copper cation (elucidated from the analysis of the character of electronic processes underlying the bonding) with direct IR evidence of NO bond activation is excellent for as well experimental as calculation results. Indeed, while the interaction of the naked copper cation imposes blue-shift of about 30 cm^{-1} in NO stretching frequency (due to strong donation of unpaired electron from antibonding $\pi_{||}^*$ orbital), the frequency becomes strongly red-shifted (by about 100 cm^{-1}) for Cu(I) site in ZSM-5 (in effect of enhanced backdonation to the antibonding $\pi_{||}^*$ antibonding NO orbital). Comparative inspection of results shown in Tables 1, 2, and 3 brings about very clear understanding of the role of the electron transfer in the process of NO activation. Definitely, the process of backdonation plays the dominant role: it strongly activates the NO bond by populating its antibonding orbital and it is very sensitive to the coordination of Cu^+ . While naked Cu^+ itself shows some ability to do backdonation due to fully occupied d-shell, for naked cation the effect becomes cancelled by the formation of one-electron bond in the bent bonding mode, causing depopulation of the antibonding orbital. Only after interaction with a donating ligand (be it a single aluminum-oxygen tetrahedron or more sophisticated model of the Cu(I) site)) donation of the unpaired electron becomes suppressed while backdonation becomes strongly enhanced which causes tremendous weakening of the N–O bond.

Fig. 4 Contour plots of dominant electron-density transfer channels between copper cation and NO ligand bound to (M7)Cu (model c); blue (black)—electron inflow; red (gray)—electron outflow; contour value 0.003 (Color figure online)

Table 3 Measured and calculated stretching frequencies (cm^{-1}) for free NO molecule, NO interacting with naked Cu^+ and Cu(I) site in ZSM-5

	NO	Cu^+ -NO	Cu(I) ZSM-5-NO
Experiment ^a	1,876	1,908	1,812
Calculations ^b	1,970	1,988	1,865

^a After Refs. [57] and [58]

^b After Ref. [23] (not scaled)

Conclusions

As we have shown in this contribution and postulated previously for other molecules [28–30], in order to fully

understand the nature of electron transfer between the active site and a ligand total differential density must be resolved into independent electron transfer channels since various symmetries and transfer directions may coexist, either corroborating or opposing activation. All the more for the NO ligand, which due to its specific open-shell electronic structure is a special case, and thus requires NOCV analysis with spin-resolution and careful selection of initial fragment density, prerequisite for defining proper deformation density.

New insights into the nature of the bonding between various forms of copper and nitric oxide molecule fully pay for additional effort. We hope that by applying quantitative, spin-resolved separation of donation and backdonation we have partially resolved queries concerning the bonding between Cu(I) and NO from electronic interaction orbital perspective, especially in the context of the impact of embedding. Four distinct components of electron flow between NO and Cu^+ were identified:

- unpaired electron donation from $\pi_{||}^*$ antibonding orbital on NO to $\text{Cu}_{s,d}$,
- backdonation from copper $d_{\perp}$ to $\pi_{\perp}^*$ antibonding NO orbital,
- donation from occupied $\pi_{||}$ and Cu $d_{||}$ to the bonding region,
- donation from nitrogen lone-pair to $\text{Cu}_{s,d}$.

The electron transfer channel (i) obviously shows-up as important solely in the spin majority manifold and corresponds to the concept of one-electron bond; it is effective only in the interaction of NO with naked Cu^+ cation (where it is the most important one) and upon interaction with both framework models becomes replaced by the donation from nitrogen lone-pair. Channel (ii) depicts distinct backdonation component of the bonding between copper and NO (for α and β spins) and is very sensitive to the environment: only upon interaction with electron-donating ligand (e.g., framework oxygens in a zeolite) it becomes upgraded to the first position and plays major role. Remaining channels (iii) and (iv) are generally of minor importance and only weakly sensitive to the embedding. The channels (i) and (ii) are of paramount relevance to the issue of NO-bond activation by copper sites. The process of backdonation plays here dominant positive role: it strongly activates the NO bond by populating its antibonding orbital. On the other hand, channel (i) depopulates antibonding π^* orbital which strengthens the NO bond. Therefore global view on effective charge flow provided by total charge differences does not suffice to clarify the activation mechanism: the final efficiency relies on a delicate balance between individual electron transfer channels, with diverse dependence on the cation embedding to form Cu(I) site.

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