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LETTERS

First-Principles Analysis of Elementary Steps in the Catalytic Decomposition of NO by Cu-Exchanged Zeolites

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First-principles quantum calculations are potentially of great value for assessing the plausibility of proposed catalytic reaction mechanisms. The present analysis of reaction pathways and energetics for key elementary steps in the catalytic decomposition of NO to $N_2 + O_2$ by Cu-exchanged zeolites yields novel insights into this widely studied reaction. We find evidence for a pathway involving two successive O-atom transfers to an isolated, zeolite-bound Cu^+ center, initiated by formation of a short-lived and difficult to detect isonitrosyl intermediate, and yielding sequentially N_2O and Cu-bound O followed by N_2 and Cu-bound O_2. The calculations allow us to identify a complete catalytic cycle with reasonable energetics.

Introduction

Catalytic reactions often proceed by a complex series of elementary steps that are difficult to discern experimentally. The application of modern surface science techniques has greatly advanced our understanding of catalytic mechanisms,[1] but even these techniques provide only incomplete information that may be misleading. For example, surface spectroscopic data tend to be dominated by long-lived species that may only be spectators for the reaction of interest but that are easily misidentified as key intermediates.

A powerful alternative to a purely experimental approach to catalysis is the complementary use of first-principles quantum mechanical calculations.[2] Steady advances in computing power, fundamental theory, and computational algorithms have continuously expanded the range of successful applications of these methods. Quantum calculations are already used almost routinely to determine equilibrium geometries, binding energies, and other adsorbate properties for many catalytic systems.[2] An even more promising aspect of this approach is its ability to probe entire reaction pathways and thereby assess directly the kinetic plausibility of proposed catalytic mechanisms. A limited number of such studies have already been reported for various homogeneous reactions[3] and for simple heterogeneous reactions on metal surfaces[4] and at zeolite acid sites.[5] Here we present a first-principles analysis of the elementary steps in a complete heterogeneous catalytic cycle for the decomposition of NO (reaction 1) by Cu-ion-exchanged zeolites. Our results suggest

$$2\,NO \rightarrow N_2 + O_2 \qquad (1)$$

a likely pathway for this widely studied reaction[6] that differs

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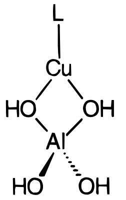
TABLE 1: Selected LSDA Geometry Parameters (Distances in angstroms), Mulliken Charge and Spin Densities, and Becke−Perdew Post-scf Binding Energies (kcal mol^{-1})[a]

	state	BE	Mulliken charges (spin densities)			selected geometry parameters		
N_2	$^1\Sigma_g^+$	−378.3				N−N: 1.098		
O_2	$^3\Sigma_u^-$	−220.8				O−O: 1.218		
NO	$^2\Pi$	−277.0	N: 0.26 (0.69)	O: −0.26 (0.31)		N−O: 1.154		
N_2O	$^1\Sigma$	−482.5	N_1: 0.16	N_2: 0.62	O: −0.46	N−N: 1.130	N−O: 1.181	
[ONNO]‡	$^3A''$	−516.3	O_1: −0.40 (0.31)	N_1: 0.64 (0.28)		O_1-N_1: 1.183	N_1-N_2: 1.163	N_2-O_2: 1.695
			N_2: −0.01 (−0.03)	O_2: −0.24 (1.43)		$O_1-N_1-N_2$: 165.1°	$N_1-N_2-O_2$: 109.2°	
[NNOO]‡	$^3A''$	−501.8	N_1: −0.07 (0.48)	N_2: 0.50 (0.10)		N_1-N_2: 1.145	N_2-O_1: 1.292	O_1-O_2: 1.593
			O_1: −0.27 (0.14)	O_2: −0.16 (1.28)		$N_1-N_2-O_1$: 145.7°	$N_2-O_1-O_2$: 116.0°	
ZCu	$^1A'$	−1157.9	Cu: 0.50			Cu−O(H): 1.938		O−Cu−O: 85.9°
ZCuO	$^3A''$	−1271.8	Cu: 0.93 (0.50)	O: −0.53 (1.28)		Cu−O: 1.700		
$ZCuO_2$	$^3A''$	−1401.6	Cu: 0.79 (0.33)	O_1: −0.22 (0.70)	O_2: −0.10 (0.89)	$Cu-O_1$: 1.792	O_1-O_2: 1.264	$Cu-O_1-O_2$: 119.0°
ZCuNO	$^2A'$	−1473.5	Cu: 0.71 (0.06)	N: 0.08 (0.57)	O: −0.31 (0.37)	Cu−N: 1.741	N−O: 1.174	Cu−N−O: 144.9°
ZCuON	$^2A'$	−1455.0	Cu: 0.68 (−0.03)	O: −0.38 (0.23)	N: 0.19 (0.82)	Cu−O: 1.821	O−N: 1.185	Cu−O−N: 136.0°
ZCuONNO	$^3A''$	−1744.0	Cu: 0.71 (0.21)	O_1: −0.42 (0.37)	N_1: 0.18 (0.52)	$Cu-O_1$: 1.819	O_1-N_1: 1.207	N_1-N_2: 1.742
				N_2: 0.31 (0.45)	O_2: −0.28 (0.40)	N_2-O_2: 1.161		
						$Cu-O_1-N_1$: 128.5°	$O_1-N_1-N_2$: 108.8°	$N_1-N_2-O_2$: 112.3°
[ZCuONNO]‡	$^3A''$	−1736.7	Cu: 0.87 (0.44)	O_1: −0.59 (0.73)	N_1: 0.02 (−0.03)	$Cu-O_1$: 1.756	O_1-N_1: 1.642	N_1-N_2: 1.173
				N_2: 0.53 (0.31)	O_2: −0.42 (0.34)	N_2-O_2: 1.196		
						$Cu-O_1-N_1$: 103.6°	$O_1-N_1-N_2$: 110.5°	$N_1-N_2-O_2$: 154.0°
[ZCuOONN]‡	$^3A''$	−1718.3	Cu: 0.96 (0.43)	O_1: −0.50 (0.55)	O_2: −0.29 (0.14)	$Cu-O_1$: 1.758	O_1-O_2: 1.553	O_2-N_1: 1.343
				N_1: 0.37 (0.10)	N_2: −0.08 (0.18)	N_1-N_2: 1.154		
						$Cu-O_1-O_2$: 108.0°	$O_1-O_2-N_1$: 111.9°	$O_2-N_1-N_2$: 133.8°

[a] *Z* is the $Al(OH)_4$ single T-site model, with Cu coordinated to two O atoms and C_s symmetry imposed. Binding energies are referenced to hypothetical spin-restricted atoms.

from all previous mechanistic speculations[6−9] and that involves a number of unusual and unanticipated intermediates. These new insights into the decomposition chemistry of NO may have broad implications, given the known environmental[6] and biological[10] significance of this molecule.

Below ∼1000 K, reaction 1 is thermodynamically favorable, although it does not proceed at an appreciable rate in the absence of a catalyst. Of the known catalysts for this reaction, Cu-ion-exchanged zeolites, and in particular Cu-ZSM-5, exhibit the highest sustained activities.[6] Despite a wealth of experimental data[6−9] and a growing number of theoretical studies[9c,11,12] of possible intermediate species, the detailed mechanism by which reaction 1 is catalyzed by Cu zeolites has yet to be convincingly demonstrated. The catalytically active sites are believed to be chemically isolated Cu cations, atomically dispersed throughout the zeolite nanopores and stabilized by interactions with locally anionic, Al tetrahedral- (or T-) sites of the aluminosilicate framework.[13] Depending on the conditions of preparation and pretreatment, a variety of Cu ions can be present, charge compensated by either one or two framework Al and possibly extraframework species.[14] We have found previously that an isolated Cu ion near two Al T-sites (a nominally Cu^{2+} ion) is unlikely to be active catalytically,[15] and we focus here on the case of a single, zeolite-bound Cu ion charge-compensated by one Al T-site (a nominally Cu^+ ion). Such a site is generically denoted ZCuL, Z representing the formally anionic zeolite fragment and L any ligated extralattice species. Previous work has demonstrated that Cu^+ chemistry is relatively insensitive to the choice for model Z.[11] All calculations reported here are for the "single T-site model" (**1**),



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in which the Cu ion is two-coordinated to a single $Al(OH)_4^-$ fragment. The simplicity of this model makes it particularly attractive computationally, and calculations on larger clusters are consistent with this two-coordinate binding mode near an Al T-site.[12b,d] We employ density functional theory (DFT), which has proven to be an efficient and reliable method for treating transition-metal complexes.[16] While we cannot expect **1** to quantitatively represent any particular Cu zeolite, we do expect the qualitative chemical insights derived from it to be reliable for high-silica catalysts like Cu-ZSM-5.

Computational Details

Geometries and vibrational spectra were obtained within the local spin density approximation (LSDA)[17] and the final energies improved by perturbative application of Becke exchange[18] and Perdew correlation[19] gradient corrections.[20] Energies and energy gradients were calculated with the Amsterdam Density Functional code[21] which was interfaced to the efficient natural internal coordinate and geometry optimization algorithms implemented in the GAMESS code.[22] A valence double-ζ plus polarization Slater-type basis was used for all atoms save Cu, for which a double-ζ s and p and triple-ζ d basis was employed. A numerical integration parameter of at least 5.0 was used in all calculations,[21b] and geometries were converged to maximum and root-mean-square gradients of less than 0.001 and 0.00033 hartree/bohr, respectively. A summary of key results is provided in Table 1. As a simple example of the reliability of the computational approach, reaction 1 is calculated to be exothermic by 45 kcal mol^{-1} at 0 K, compared to an experimental value of 43 kcal mol^{-1}. We cannot expect this same level of accuracy for the entire NO decomposition reaction profile, and in fact the accuracy of DFT for inorganic reaction profiles is an area of active research (see, *e.g.*, ref 23). For the present study we are concerned only with the qualitative characterization of the NO decomposition potential energy surface, for which the present approach is adequate.

Results and Discussion

The interaction of two free NO provides important clues for possible Cu-zeolite-catalyzed NO decomposition mechanisms. The *concerted* reaction of two NO to produce N_2 and O_2 (*i.e.*,

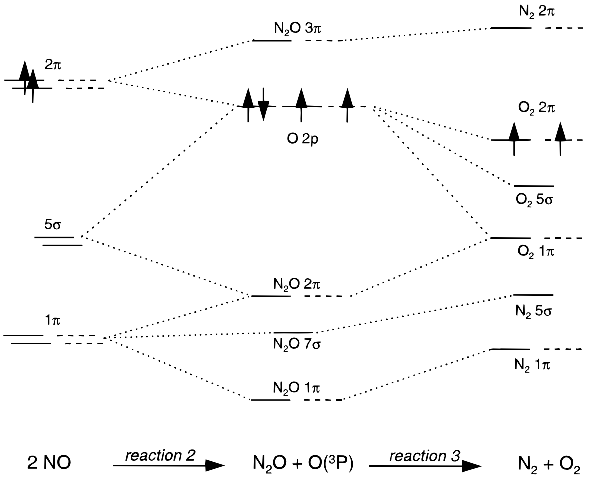

Figure 1. Schematic orbital correlation diagram for reactions 2 and 3 on a planar reaction coordinate, derived from LSDA calculations. Arrows denote filling of highest occupied molecular orbitals, and solid and dashed lines denote symmetric (a′) and antisymmetric (a″) orbitals. The diagram demonstrates the smooth evolution of occupied and virtual orbitals characteristic of an electronically allowed reaction pathway. Inclusion of ZCu does not qualitatively alter the orbital description but does substantially modify the reaction energetics.

through a cyclic transition state) is forbidden by orbital symmetry and thus intrinsically unfavorable, both in the absence and presence of a Cu catalyst.[15] The first step in the high-temperature decomposition of free NO is instead formation of N_2O and O (reaction 2).[24]

$$\mathrm{ON + NO \rightarrow [ONNO]^{\ddagger} \rightarrow O(^3P) + N_2O} \qquad (2)$$

Calculations indicate that reaction 2 occurs along a coordinate in which the two NO approach through their N ends, and on the $^3A''$ potential surface yields ground state products (Table 1 and Figure 1). The calculated barrier to reaction 2 (38 kcal mol^{-1}) is due almost entirely to its net endothermicity (36 kcal mol^{-1}). At high temperatures reaction 2 initiates a series of Zeldovich atom substitution reactions,[24] but in the present context it is more useful to consider a simpler process in which N_2O and O(^{3}P) recombine through their O centers on the same $^3A''$ energy surface to produce ground state products (reaction 3, Figure 1).

$$\mathrm{N_2O + O(^3P) \rightarrow [NNOO]^{\ddagger} \rightarrow N_2 + O_2} \qquad (3)$$

This second step is both highly exothermic (81 kcal mol^{-1}) and has a modest barrier (16 kcal mol^{-1}). Reactions 2 and 3 suggest a possible Cu zeolite NO decomposition mechanism in which the active sites accept and stabilize O(^{3}P) in an initial N_2O-forming step and then back-donate the atom to produce final products. The calculations below demonstrate the plausibility of this mechanism and identify a microscopic route by which such successive atom transfers can occur.

An isolated ZCu site is a likely candidate to serve as an O(^{3}P) atom reservoir. ZCuO has been postulated to be formed during the NO decomposition process but has not been definitively identified experimentally.[9] ZCuO has a $^3A''$ ground state in the single T-site model—corresponding to ZCu-bound O(^{3}P)—with a singlet−triplet splitting of 8 kcal mol^{-1}. The extralattice O atom partially oxidizes the Cu center, yielding an electronic structure intermediate between $Z^-{-}Cu^+{-}O$ and $Z^-{-}Cu^{2+}{-}O^-$, with unpaired electron density distributed over both the Cu and O centers. While the latter resonance structure more closely represents the charge distribution (Table 1), the former makes explicit the binding of oxygen as O(^{3}P) to ZCu. The absence of a ZCuO signal in EPR experiments has led some to suggest that, if it exists, ZCuO must be diamagnetic. More likely, the random orientation of many triplet ZCuO within the zeolite and the resulting anisotropic intra- and intermolecular dipole−dipole interactions obscure any EPR signal.[25] The binding energy of O(^{3}P) to ZCu is 78 kcal mol^{-1} in the single T-site model; coupled with reaction 2, ZCuO formation provides a net driving force for that reaction of 42 kcal mol^{-1}.

It remains to be demonstrated precisely how two NO might simultaneously transfer an O(^{3}P) atom to a ZCu site and form N_2O. A ZCu center is known from both experiment[7d,26] and theory[9c,11,15] to form stable N-down mono- (ZCuNO) and dinitrosyl (ZCu(NO)$_2$) adducts, and both of these have been proposed as precursors to ZCuO and N_2O.[6,9,26] We have been unable to identify a molecular pathway leading either directly from ZCu(NO)$_2$ or indirectly from ZCuNO plus a second gas-phase NO to ZCuO and N_2O products, which suggests that both of these adducts are in fact spectators and not intermediates in this reaction. O-down adducts of NO with ZCu, which calculations indicate are only somewhat less stable than the observed N-down complexes, are possible alternative reaction intermediates. For example, the isonitrosyl ZCuON is bound by 20 kcal mol^{-1} in the single T-site model, only 19 kcal mol^{-1} less than that of the N-down analog. Addition of a second, triplet-coupled O-down NO to the isonitrosyl yields the hyponitrite complex ZCuO$_2$N$_2$,[15] which is only 18 kcal mol^{-1} less stable than ZCu(NO)$_2$ in the single T-site model and which has an electronic configuration ($^3A''$ ground state) and geometric structure (short N−N bond, partially cleaved N−O bonds) that are particularly suggestive of the first step in an NO decomposition process.

While it is possible that the hyponitrite is itself an intermediate in the catalytic decomposition of NO, more likely the same favorable electronic and geometric effects are achieved without the second NO ever interacting directly with the Cu. Specifically, we consider an Eley−Rideal type process in which one NO adsorbs in an activated O-down conformation (reaction 4)

$$\mathrm{ZCu + NO \leftrightarrow ZCuON} \qquad (4)$$

and subsequently reacts with a second gas-phase NO along the triplet energy surface to form N_2O, leaving behind a Cu-bound O(^{3}P) atom (reaction 5).

$$\mathrm{ZCuON + NO \rightarrow [ZCuONNO]^{\ddagger} \rightarrow ZCuO + N_2O} \qquad (5)$$

Using transition state searching and intrinsic reaction coordinate (IRC) following techniques,[27] we are able to map out a molecularly detailed pathway for this process (Figure 2). Following the barrierless adsorption of the first NO in an O-down conformation, a second gas-phase NO approaches with its N end directed toward the first N. Calculations indicate the existence of a relatively weakly bound adduct (ZCuONNO), but this species would likely have a fleeting existence, as the energy barrier to form ZCuO and N_2O from the adduct is only 7 kcal mol^{-1}, less than the adsorption energy of the second NO. The transition state for this reaction ([ZCuONNO]‡, Figure 2 and Table 1) has an imaginary frequency of 537i cm^{-1} along the reaction coordinate and a structure consistent with the simultaneous cleavage and formation of O−N and N−N bonds, respectively. Other planar conformations of the transition state, including that derived from the hyponitrite above, were found to have essentially the same structure and energy. These results provide strong evidence that the occasional O-down adsorption of NO produces a highly reactive intermediate that may be too

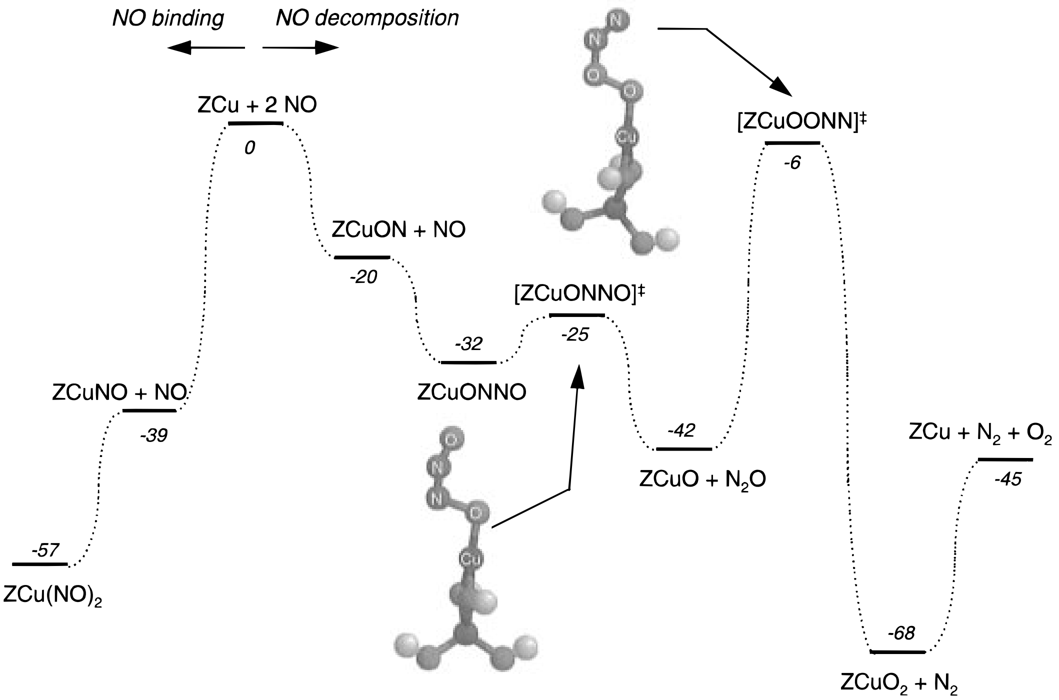

Figure 2. Potential energy surface, based on the single T-site model, for the sequence of reaction steps leading to NO decomposition. Numbers in italics are calculated relative energies (in kcal mol^{-1}) obtained from the single T-site model.

short lived to be easily detected but that provides a template for O-atom transfer to Cu and N$-$N bond formation in the form of N_2O. N_2O is indeed often observed during NO decomposition by Cu zeolites and other catalysts,[28] but the present explanation for its production is novel and more plausible than any previous proposals.

From the analogy with gas-phase NO chemistry drawn above, a possible next step in a catalytic NO decomposition cycle is recombination of N_2O and O(^{3}P) to produce N_2 and O_2. Presumably the O_2 thus generated would remain coordinated to the Cu center; thus, we consider $ZCuO_2$, another intermediate that has been postulated but not observed directly in Cu-zeolite chemistry.[9] Calculations predict $ZCuO_2$ to have an end-on, bent "superoxo" structure, with an O$-$O bond length increased by 0.05 Å and an O$-$O stretch frequency red-shifted by about 250 cm^{-1} with respect to free O_2. These features are typical of superoxo complexes of other transition-metal ions. While rare, mononuclear superoxo complexes of Cu have been observed in environments protected by bulky polydentate ligands;[29] the zeolite lattice is also likely to provide sufficient protection for individual Cu ions to coordinate O_2. In contrast to earlier studies,[9c] we find no evidence for a bidentate ("peroxo") binding mode. The electronic structure of $ZCuO_2$ can be described as a roughly equal mix between $Z^-{-}Cu^+{-}O_2$ and $Z^-{-}Cu^{2+}{-}O_2^-$; *i.e.*, the Cu is in an intermediate state of oxidation between ZCu and ZCuO. As the qualitative description suggests, $ZCuO_2$ has a $^3A''$ ground state, with the spin density distributed between the Cu and the two O centers.

We consider then a second Eley$-$Rideal process in which a gas-phase N_2O reacts with ZCuO (reaction 6).

$$ZCuO + N_2O \rightarrow [ZCuOONN]^{\ddagger} \rightarrow ZCuO_2 + N_2 \qquad (6)$$

Again, a molecularly detailed pathway can be traced out on the $^3A''$ surface for this reaction, involving the interaction of the two species through their O centers and direct formation of the transition state $[ZCuOONN]^{\ddagger}$ (Figure 2). The reaction has an early transition state, with the $N_2$$-$O bond lengthened by just 0.10 Å and the O$-$O bond only partially formed and with an imaginary frequency of 690*i* cm^{-1} along the reaction coordinate. The transition state is 36 kcal mol^{-1} higher than the separated reactants in the single T-site model: a barrier larger than that for reaction 5 but still 6 kcal mol^{-1} lower than separated ZCu + 2NO. Clearly, ZCuO is the crucial intermediate in establishing the balance between reactions 5 and 6: environments (or Z models) that stabilize ZCuO will promote the N_2O-forming step but inhibit subsequent N_2 formation, while environments that destabilize ZCuO will have the opposite effect. The ability to balance these two effects may well be an important criterion for a successful catalyst system.

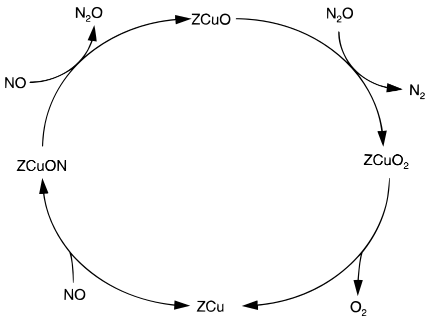

Figure 3. Catalytic cycle for NO decomposition based on reported calculations.

The decomposition cycle is completed by desorption of triplet O_2 to regenerate the reduced Cu site (reaction 7).

$$ZCuO_2 \leftrightarrow ZCu + O_2 \qquad (7)$$

The O_2 desorption energy of 23 kcal mol^{-1} in the single T-site model is comparable to that of O-down NO. Thus, reactions 4$-$7 constitute an electronically, thermodynamically, and kinetically plausible pathway for the conversion of NO to N_2 and O_2 on a single Cu site, shown schematically in Figure 3. A distinguishing feature of this mechanism is the successive transfer of two O atoms to the mononuclear active site, the first transfer oxidizing the active site and the second partially re-reducing it. The ability to act as a template for O_2 production without irreversible formation of more highly oxidized species may in part account for the high activity of Cu zeolites for NO decomposition and suggests a criterion by which to evaluate other exchanged metal ions for this activity. Aspects of this generic mechanism may also play a role in nonzeolitic NO chemistry, *e.g.*, in the gas-phase disproportionation of NO to N_2O and NO_2 at high pressures,[30] where an additional NO molecule may play the O-atom accepting role outlined here for Cu, and in other inorganic[31,32] and enzymatic[10b] NO decomposition reactions, where N_2O is a known intermediate.

A variety of more complicated NO decomposition mechanisms for Cu-exchanged zeolites have been proposed, postulating for instance the intermediacy of Cu ion dimers[8] or the spontaneous decomposition of ill-defined $Cu-N_2O_3$ aggregates.[7d] One clearly cannot dismiss these mechanisms on the basis of the results reported here. Rather, we have demonstrated that these more complicated mechanisms are not necessary to explain the fundamental observation of stoichiometric NO decomposition over Cu-zeolite catalysts. The fairly simple mechanism described here satisfies that requirement and is consistent with other aspects of the observed chemistry, such as inhibition by O_2[7b] and the production of N_2O[28] at low temperatures. It is likely that the species central to the mechanism described here—reduced ZCu and oxidized ZCuO and $ZCuO_2$—will be fundamental to any mechanism of NO decomposition over Cu-exchanged zeolites. The formation and interconversion of these three, for instance through NO_2 and NO_3 intermediates, and their role in other possible NO decomposition mechanisms remain to be examined. Clearly, first-principles calculations will be increasingly important in analyzing such processes, both to complement experiment and ultimately to guide the rational design of catalysts.

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