Theoretical Study of the Structure of $ZCu(NO_2)(NO)$. A Proposed Intermediate in the NO_x Decomposition by Cu−ZSM-5

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The geometries and harmonic vibrational frequencies for eight $ZCu(NO_2)(NO)$ and two $ZCu(N_2O_3)$ structures have been determined using the B3LYP density functional approach. For $ZCu(NO_2)(NO)$ both the singlet and triplet states have been considered. The most stable structure (**T1**) is a triplet state in which Cu presents square-pyramidal five-coordination with NO in the apical position. The lowest singlet structure (**S1**) shows square-planar four-coordination and lies only 0.7 kcal mol^{-1} above **T1**. In **T1** the $ZCu(NO_2)$−NO interaction is mainly electrostatic, whereas in **S1** the bonding is covalent. In $ZCu(N_2O_3)$ species, the N_2O_3 ligand interacts with ZCu through one oxygen, the bonding being mainly electrostatic. These $ZCu(N_2O_3)$ structures are less stable (∼11 kcal mol^{-1}) than the lowest singlet $ZCu(NO_2)(NO)$ one. All structures are stable with respect to the ground-state ZCuO + 2NO asymptote, the corresponding $\Delta G°$ at 298 K for **S1** being −30.5 kcal mol^{-1}.

I. Introduction

Nitrogen oxides are unwanted pollutants produced in a high-temperature combustion processes. Although NO is thermodynamically unstable to decomposition to N_2 and O_2, it is kinetically very stable in the absence of suitable catalysts. The most active catalysts are metal ion-exchanged zeolites. In particular, Cu−ZSM-5 has been shown to exhibit a high activity both for the direct decomposition and for the selective catalytic reduction of NO.[1−6] Because of that, many experimental studies using ESR, XAFS, and IR spectroscopies have been performed to understand the coordination and redox properties of Cu cations in Cu−ZSM-5[7−14] as well as to elucidate the mechanism by which NO is decomposed.[8,12,15−19] Despite these efforts, many aspects, especially those concerning the elementary steps of the reaction and the nature of the species involved in the mechanism, are still unclear.

Several mechanisms have been proposed for the NO decomposition by Cu−ZSM-5. One of the proposed mechanisms assumes the existence of $Cu^{2+}(NO)_2$ dinitrosyl species of Cu^{2+}, which can act as intermediate in the one-step formation of N_2 and O_2.[20] Alternatively, several mechanisms involving more than one step have been suggested. One common step in most of them is the $ZCu(NO)_2$ decomposition to form N_2O and ZCuO.[21−23] Then, N_2O decomposes into N_2 and O, which reacts with ZCuO to form $ZCuO_2$.[23] Desorption of O_2 would regenerate the active sites. Other studies suggest, however, that the transient ZCuO would lead, in the presence of nitric oxide, to the real catalytic intermediate $ZCu(NO_2)(NO)$ from which N_2 and O_2 would be formed.[18,22,24] Finally, copper ion pairs or $Cu^{2+}-O^{2-}-Cu^{2+}$ species have also been suggested to be the active sites.[7,16,25−27]

Several theoretical studies have been performed to obtain electronic and structural properties of some of the species that might be involved in the mechanism of NO decomposition.[28−37] Schneider et al. performed density functional calculations on Cu−dinitrosyl species.[33] This study showed that the single-step, symmetric, concerted decomposition reaction of NO in the vicinity of Cu ion sites in zeolites is forbidden by orbital symmetry and it is expected to have an activation barrier similar to that of the gas-phase reaction. The same authors propose a multistep mechanism involving two successive O atom transfer reactions: one in which ZCu reacts with two NO molecules to produce ZCuO and N_2O through a [ZCuONNO] transition state structure, and a second one in which ZCuO reacts with N_2O to produce $ZCuO_2$ and N_2.[34] Trout et al., using local spin density functional (LSDFT) calculations, also proposed a pathway going through ZCuO and $ZCuO_2$ species.[36]

At this point it is worth mentioning that despite the experimental evidence of the existence of species such as $ZCu(NO_2)(NO)$ or $ZCu(N_2O_3)$,[12,18,19,22−25] to our knowledge none of the theoretical studies appeared up to now reports an analysis of the bonding and molecular structure of such systems. In this paper, we present the molecular geometry and vibrational frequencies of several isomers of these species. For $ZCu(NO_2)(NO)$, we have considered both the singlet and triplet electronic states. The results obtained show that $ZCu(NO_2)(NO)$ is a stable species with respect to both ZCu + NO_2 + NO and ZCuO + 2NO asymptotes.

II. Details of Calculations

The zeolite is modeled by the same tritetrahedral cluster $[H_3SiOAl(OH)_2OSiH_3]$ used in our previous study of the coordination of NO_2 to Cu^+ in zeolites.[37] This model was proven to be successful since an almost identical structure of $ZCu(NO_2)$ was obtained when the model was embedded in the periodic structure of zeolite ZSM-5.

Molecular geometries and harmonic vibrational frequencies are computed using the nonlocal hybrid three-parameter B3LYP density functional approach.[38,39] This hybrid scheme has been shown to provide accurate results for many transition metal containing systems. In particular, B3LYP calculations on the $Cu(NO_2)_2$ system, which has a similar bonding to $ZCu-(NO_2)$, were found to be in quite good agreement with CCSD(T) calculations using larger basis sets.[40] Moreover, calculations on the Cu^{2+}−NO system have shown that the energy difference between the singlet and triplet states at the CCSD(T) level is similar to that obtained with the B3LYP functional, the

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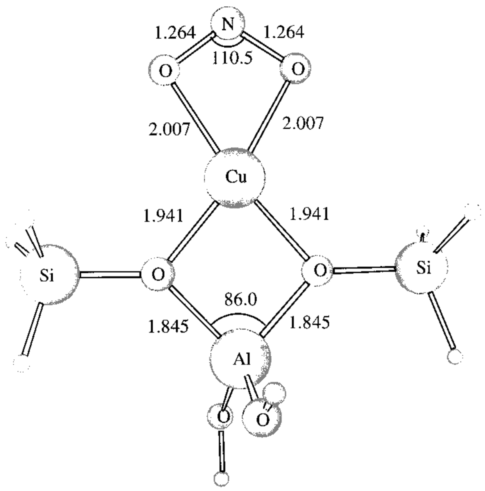
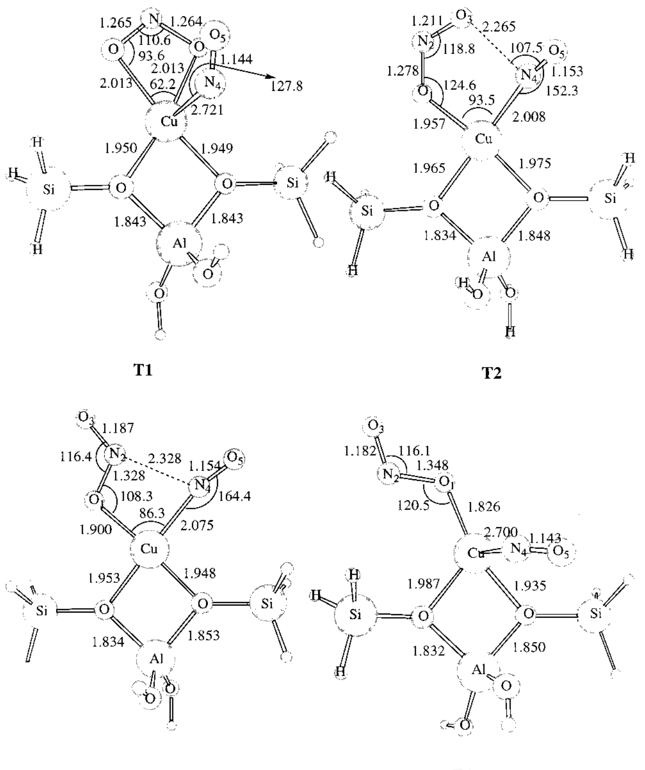


Figure 1. Optimized geometry of ZCu(NO_2). Distances are in angstroms, and angles in degrees.



T1 **T2** **T3** **T4**

Figure 2. Optimized geometries of the triplet state structures of ZCu(NO_2)(NO). Distances are in angstroms, and angles in degrees.

variations being less than 10%. Thus, we expect that the B3LYP approach would provide reasonably accurate results for both the singlet and triplet states of ZCu(NO_2)(NO).

Geometry optimizations and frequency calculations have been performed with the same basis sets used in our previous study for ZCu(NO_2).[37] These basis sets are those optimized by Ahlrichs and co-workers.[41] For Cu the final basis set is (14s10p5d)/[8s6p3d] derived from the double-ζ one supplemented with a p function of exponent 0.155 065. For the N and O atoms of nitrogen oxides interacting with the zeolite, we have used the triple-ζ plus polarization (10s6p1d)/[6s3p1d] basis sets. For the zeolite model, the O basis set is the same triple-ζ basis, whereas for the remaining atoms, we have used a double-ζ plus polarization basis set; for Si and Al the basis is (11s7p1d)/[6s4p1d], and for H is (4s1p)/[2s1p]. All calculations have been performed with the GAUSSIAN-94 package.[42]

III. Results and Discussion

Our previous study on ZCu and ZCu(NO_2) showed that Cu^+ is coordinated to two oxygen atoms of the zeolite and that the preferred coordination mode of NO_2 to ZCu is the η^2-O,O one.[37] This leads to a square-planar coordination around copper (Figure 1). The electronic ground state for this system was found to be $^2A''$, the open-shell orbital lying on the CuO_4 coordination plane. A similar bonding was found for the $Cu(NO_2)_2$ system for which the most stable structure has D_{2h} symmetry with a coplanar η^2-O,O coordination for the two NO_2 ligands.[40]

The formation of ZCu(NO_2)(NO) can be viewed as the interaction of NO with ZCu(NO_2). Since both ZCu(NO_2) and NO have a doublet ground state, the resulting ZCu(NO_2)(NO) system can either be in a singlet or in a triplet state, and so, we have considered both electronic states. The addition of a NO molecule to ZCu(NO_2) can lead to a five-coordinated system, if the η^2-O,O coordination of NO_2 is retained in the final complex, or to four-coordinated systems, if NO_2 changes its coordination mode from η^2-O,O to η^1-O. For these structures, all possible relative orientations of NO_2 and NO have been considered as starting points in the optimization processes. Finally, different coordination modes of N_2O_3 to ZCu have also been studied in the singlet state.

Among all the structures explored, only four triplet structures (**T1**−**T4**) and six singlet structures (**S1**−**S6**) have been found to be minima on the respective potential energy surfaces. Figures 2 and 3 show the optimized geometries of these structures. Within each spin multiplicity the numbering follows the increasing order of energy. Relative energies with respect to the most stable structure (**T1**) are given in Table 1. This structure is 57.7 kcal mol^{-1} more stable than the ZCuO ($^3A''$) + 2NO ($^2\Pi$) ground-state asymptote. Net atomic charges and spin densities obtained from natural population analysis[43] are shown in Table 2.

Let us first consider the triplet structures. The lowest **T1** structure is a square pyramid with NO in the apical position. The bonding in this system can be viewed as the interaction of the ground-state structure of ZCu(NO_2) with NO. That is, as in ZCu(NO_2), NO_2 acts as a bidentate ligand, interacting through the two oxygen atoms, the ZCu−NO_2 bonding having a significant ionic contribution. NO binds to ZCu(NO_2) through the nitrogen atom. The bonding energy between ZCu(NO_2) and NO is only 2.4 kcal/mol, so that the interaction is very weak. This is not surprising considering the large Cu−NO distance. The geometry parameters, the net atomic charges and spin densities of the ZCu(NO_2) fragment in the complex are very similar to those obtained for free ZCu(NO_2).[37] Moreover, the NO geometry in the complex is very close to that of isolated NO.[44] The open shell orbitals correspond to the π^* orbital of NO which is perpendicular to the Cu coordination plane and to the open shell orbital of ZCu(NO_2). Thus, the 2.4 kcal mol^{-1} bonding energy mainly arises from an electrostatic interaction between the NO ligand and the positive charge of Cu.

The **T2** and **T3** structures present a square-planar coordination. In these structures, NO_2 loses the bidentate coordination to permit the NO in plane coordination. As for **T1**, the NO and ZCuNO$_2$ spin populations are not far from the ones corresponding to the isolated fragments. Population analysis also shows that NO has a slight negative charge, which produces a small increase of the N−O bond length with respect to that in free NO.[44] Thus, in these cases, the nature of the bonding is also mainly electrostatic. However, it can be observed in Figure 2

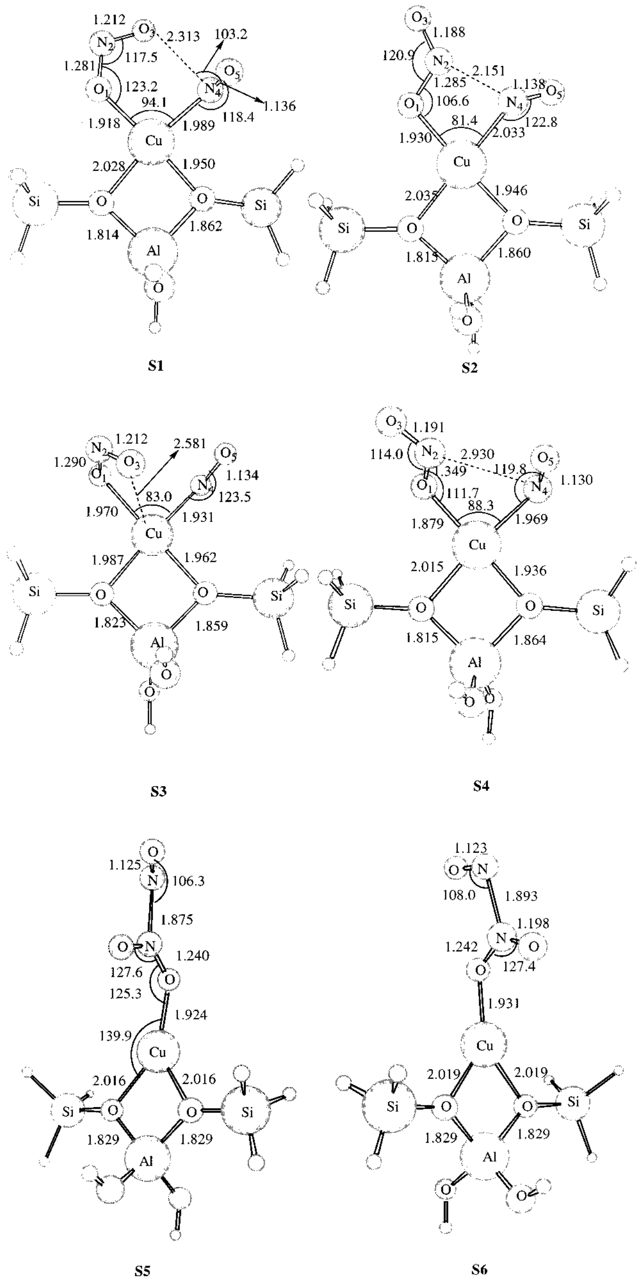


Figure 3. Optimized geometries of the singlet state structures of ZCu(NO_2)(NO) and ZCu(N_2O_3). Distances are in angstroms, and angles in degrees.

TABLE 1: Relative Energies of Different Structures of ZCu(NO_2)(NO) and ZCu(N_2O_3)

structure[a]	ΔE^b	structure[a]	ΔE^b
T1	0.0	**S2**	2.8
T2	5.6	**S3**	3.4
T3	10.3	**S4**	8.6
T4	12.0	**S5**	11.0
S1	0.7	**S6**	12.1

[a] See Figures 2 and 3. [b] In kcal mol^{-1}.

TABLE 2: Natural Population Analysis for ZCu(NO_2)(NO) and ZCu(N_2O_3)

	charge					spin			
structure[a]	Z	Cu	NO_2	NO	N_2O_3	Z	Cu	NO_2	NO
T1	−0.74	1.34	−0.62	0.02		0.17	0.66	0.19	0.97
T2	−0.74	1.32	−0.47	−0.10		0.17	0.57	0.26	1.00
T3	−0.71	1.40	−0.56	−0.13		0.15	0.64	0.16	1.05
T4	−0.78	1.32	−0.56	0.02		0.14	0.58	0.31	0.97
S1	−0.76	1.17	−0.50	0.09					
S2	−0.79	1.17	−0.41	0.04					
S3	−0.75	1.17	−0.55	0.12					
S4	−0.74	1.21	−0.63	0.16					
S5	−0.88	0.98			−0.10				
S6	−0.89	0.98			−0.09				

[a] See Figures 2 and 3.

that the Cu−N_4 distance in **T2** and **T3** is much smaller than in **T1**. This is due to the fact that metal−NO repulsion is larger in **T1** than in **T2** or **T3**, since the metal d-orbitals pointing to NO in **T1** are doubly occupied, whereas in **T2** and **T3** the metal d-orbital directed toward NO is singly occupied. Though the electrostatic interaction between ZCu(NO_2) and NO in **T2** and **T3** is larger than in **T1**, the latter is the most stable structure we have obtained. One of the reasons might be that **T1** maintains the great stabilization of the ZCu−(NO_2) bidentate structure, the larger ZCu(NO_2)−NO interaction in **T2** or **T3** not being strong enough to compensate the stability loss due to the NO_2 coordination change. The difference between **T2** and **T3** arises basically from the ligand−ligand interaction.

Finally, **T4** has a structure similar to that of **T1**, but they differ from each other in the NO_2 coordination mode. The energy difference between **T1** and **T4** (12.0 kcal mol^{-1}) is almost the same as the one determined between the η^2-O,O bidentate and η^1-O monodentate structures of ZCu(NO_2) (12.4 kcal mol^{-1}).[37]

Let us now analyze the ZCu(NO_2)(NO) singlet structures. The most stable structure **S1** shows a square-planar coordination. NO_2 acts as a monodentate ligand interacting through one of the oxygen atoms, and NO binds through the nitrogen atom. As for the triplet structures, the ZCu−NO_2 bonding shows a significant ionic contribution. However, ZCu(NO_2) and NO form a covalent bond. In the $^2\Pi$ ground state of free NO the unpaired electron lies on the antibonding π^* orbitals, which are polarized toward the nitrogen atom. To allow the formation of a covalent bond between the unpaired electron of NO and the open shell orbital of ZCu(NO_2), NO interacts forming a Cu−NO angle of 118.4°. Figure 4 shows the bonding molecular orbital that arises from this interaction. As a result, there is some electron donation from NO to ZCu(NO_2) (see Table 2), which produces a decrease of the NO bond length compared to that of free NO.[44] A similar decrease is found for Cu^+NO.[45] The other NO π^* orbital remains unoccupied and it is directed to the O_3 atom leading to a stabilizing interaction between ligands.

The second most stable singlet **S2** lies 2.1 kcal/mol above **S1** and the bonding between NO and ZCu(NO_2) is similar to that discussed for **S1**. However, the orbital presented in Figure 4 shows that there is also a significant bonding interaction between both nitrogen atoms.

Structures **S3** and **S4** show a similar ZCu(NO_2)−NO bonding. The difference with respect to the previous **S1** and **S2** structures is the relative orientation of the NO_2 and NO ligands, which does not allow a stabilizing interaction between them. This interaction between ligands might be one of the reasons of the larger stability of **S1** and **S2**. In **S3**, NO_2 is nearly perpendicular to the Cu coordination plane. The Cu−O_3 distance seems to indicate that there is a weak interaction between these two atoms. This might explain the relative stabilities of **S3** and **S4**.

The last two singlet structures **S5** and **S6** correspond to a η^1-O coordination of N_2O_3 to ZCu. The binding energies are 24.9 kcal mol^{-1} for **S5** and 23.8 kcal mol^{-1} for **S6**. **S5** and **S6** are two different conformers arising from the rotation around the N−N bond. These structures are clearly different from the previous ones. The ZCu−N_2O_3 interaction is mainly electrostatic

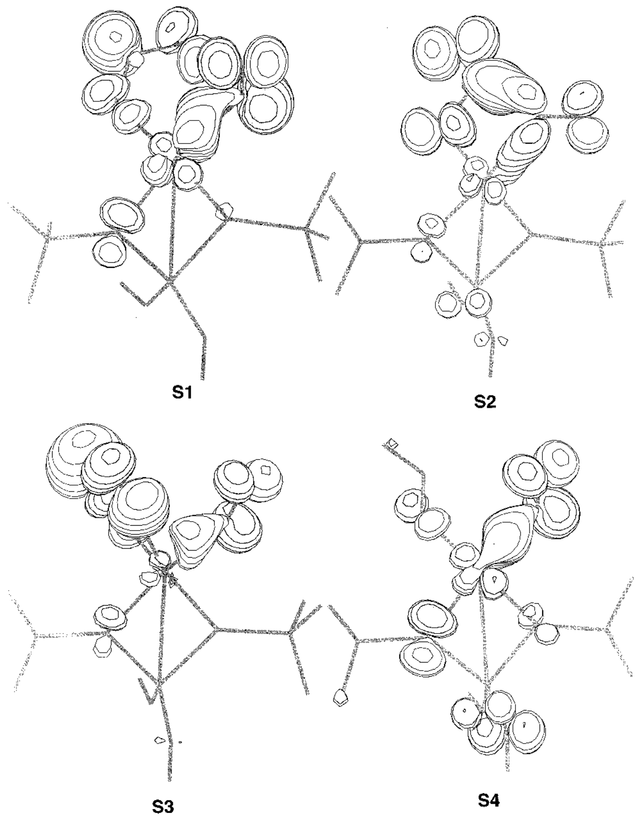


Figure 4. Molecular orbitals corresponding to the bonding interaction between $ZCu(NO_2)$ and NO in **S1**−**S4** structures.

with a little charge transfer from Cu to N_2O_3. For this reason, the geometry of the N_2O_3 ligand is very close to that of free N_2O_3.[46]

It has to be mentioned that we could not find any $ZCu-N_2O_3$ with an in-plane η^2-O,O coordination of N_2O_3 to ZCu, in contrast to $ZCu(NO_2)$ for which the η^2-O,O bidentate structure is the most stable one. All attempts to optimize such a structure lead to the monodentate structures (**S5**−**S6**). This could be explained by considering that although the bidentate in plane coordination leads to a maximal stabilizing electrostatic interaction, it also presents maximal metal−ligand repulsion. Since $N_2O_3^-$ is not stable, the Cu to ligand charge transfer is not favorable. Thus, N_2O_3 adopts an out of plane η^1-O coordination mode to minimize repulsion.

Frequency calculations have been performed for all the studied structures. Table 3 presents the values corresponding to the N−O stretching modes of NO_2 and NO ligands. For comparison we have included those of isolated NO_2, NO_2^-, NO, and N_2O_3. In general, the stretching values associated with the NO_2 fragment are different from those we obtained for free NO_2 and NO_2^- due to the loss of symmetry. However, their values agree with a certain NO_2^- character. This is especially clear in **T1**, which has a η^2-O,O coordination mode and its frequencies are closer to those of NO_2^- than to those of NO_2. The ν_2 stretching frequency of NO_2, when acting as a monodentate ligand, ranges from 1466 to 1653 cm^{-1}. Experimental values assigned to NO_2 coordinated to Cu−ZSM5 are 1400−1500[22] and 1619−1630 cm^{-1}.[19]

The computed NO stretching mode lies in the 1870−1990 cm^{-1} range, in good agreement with the experimental values observed for $ZCu^{2+}NO$ species (1880−1985 cm^{-1}).[19,22,23] In **T1** and **T4**, where NO is weakly interacting with Cu, the determined values are very similar to that of free NO (1971 cm^{-1}). Furthermore, **T2** and **T3** present a less energetic NO mode, which is in good agreement with the elongation of the NO bond.

TABLE 3: N−O Stretching Frequencies (IR intensities) in $ZCu(NO_2)(NO)^a$ and $ZCu(N_2O_3)$ Complexes

structure[b]	NO_2 ν_1	NO_2 ν_2	NO ν_3
T1	1203(325)[d]	1334(20)[c]	1986(61)
T2	1106(308)	1474(402)	1897(307)
T3	1012(201)	1653(430)	1897(276)
T4	829(190)	1644(876)	1989(69)
S1	1121(171)	1466(210)	1884(854)
S2	1110(116)	1646(500)	1871(851)
S3	1056(167)	1493(284)	1913(925)
S4	880(540)	1628(305)	1935(845)
S5	1273(27)	1609(299)	1955(1754)
S6	1255(12)	1613(393)	1963(1479)
N_2O_3	1369(301)	1693(414)	1937(453)
NO_2	1386(0)[c]	1679(433)[d]	
NO_2^-	1268(507)[d]	1346(23)[c]	
NO			1971(42)

[a] In cm^{-1} (in km mol^{-1}). [b] See Figures 2 and 3. [c] NO_2 symmetric stretching. [d] NO_2 asymmetric stretching.

On the other hand, the NO stretching for the singlet state structures is, in general, less energetic than the one corresponding to isolated NO. This seems to be in contradiction with the shortening of the N_4-O_5 distance. However, this effect is also found in isolated N_2O_3 where the N_4-O_5 distance is shorter than the bond length in NO and the vibrational mode is less energetic.[47,48] Despite that, within the singlet **S1**−**S4** structures there is a correlation between the N−O distance and the stretching frequency value. That is, the larger the distance, the smaller the stretching frequency. Finally, stretching frequencies of **S5** and **S6** are very similar to those of free N_2O_3. The computed values are in agreement with the assignments of Aylor et al. (1298, 1578, and 1876 cm^{-1}).[23]

As mentioned in the Introduction, $ZCu(NO_2)(NO)$ is thought to be an important intermediate in the NO decomposition process.[22] Even though the triplet **T1** is the most stable structure, we expect the singlet states to be the ones involved in this proposed mechanism, since they correlate with the ground-state products ZCuO ($^3A''$) + N_2 ($^1\Sigma_g+$) + O_2 ($^3\Sigma_g^-$). In addition to this, the **S2** structure shows a significant N−N interaction, which could be the previous step in the formation of an N−N bond. This N−N bond is already formed in structures **S5** and **S6**, and thus, they might also be involved in the mechanism. Thermodynamic properties corresponding to the formation and decomposition of the most stable singlet structure **S1** are given in Table 4. Differences with other singlet structures (**S2**, **S5**, and **S6**) will be discussed in the text.

First of all, it can be observed that the formation of **S1** from ZCuO and two NO molecules is a very exothermic process ($\Delta H°_{298} = -54.0$ kcal mol^{-1}). If we consider that the reaction takes place in two steps, corresponding to the successive addition of the two NO molecules, it can be observed that almost all the exothermicity arises from the first step, that is, the formation of $ZCu(NO_2)$, given that the reaction enthalpy of the second step is only -0.5 kcal mol^{-1}. Our results are in contrast with those reported by Trout et al., according to which the formation of $ZCu(NO_2)NO$ was energetically unfavorable.[36]

As expected, the formation of $ZCu(NO_2)$ and $ZCu(NO_2)(NO)$ is not entropically favorable (Table 4). Consequently, high temperatures would destabilize both intermediates, specially $ZCu(NO_2)(NO)$. Nevertheless, in the presence of an excess of

TABLE 4: Energetics and Thermodynamics of $ZCu(NO_2)(NO)$ Formation and Decomposition

reaction	ΔE^a	$\Delta U_{0K}{}^a$	$\Delta H°_{298}{}^a$	$\Delta S°_{298}{}^b$	$\Delta G°_{298}{}^a$	$\Delta G°_{773}{}^a$
$ZCuO + 2NO \rightarrow ZCu(ONO)(NO)$	−57.0	−52.6	−54.0	−78.7	−30.5	+6.5
$ZCuO + NO \rightarrow ZCu(NO_2)$	−55.4	−52.5	−53.5	−42.6	−40.8	−20.4
$ZCu(NO_2) + NO \rightarrow ZCu(ONO)(NO)$	−1.6	−0.1	−0.5	−36.1	+10.3	+26.9
$ZCu(ONO)(NO) \rightarrow ZCuO + N_2 + O_2$	+13.7	+9.5	+10.9	+75.3	−11.6	−47.0

[a] In kcal mol^{-1}. [b] In cal mol^{-1}K^{-1}.

nitric oxide and at low temperatures, $ZCu(NO_2)(NO)$ might be produced in sufficient concentrations to be detected.[22]

For **S2**, **S5**, and **S6** the differences in $\Delta H°_{298}$ with respect to **S1** are very similar to the relative energies reported in Table 1. However, the entropic contribution is not equal for all singlet structures. Whereas **S1** and **S2** show a similar behavior, **S5** and **S6** are not as much destabilized by the increase of temperature as **S1** and **S2**. At 298 K the Gibbs energies of formation of **S5** and **S6** from ZCuO and two NO molecules are 7.3 and 7.4 kcal/mol, respectively, higher than that of **S1**. At 773 K these differences become 1.9 and 0.5 kcal mol^{-1}. Thus, at high temperatures, all these singlet structures would have similar Gibbs energies and their role in the mechanism would need to be considered.

Decomposition of **S1** to yield N_2 and O_2 is endothermic. This process is entropically favorable, and the corresponding $\Delta G°_{298}$ is −11.6 kcal mol^{-1}. Thus, high temperatures destabilize the $ZCu(NO_2)(NO)$ structure but favor its decomposition into N_2 and O_2. This would be in good agreement with the experimental studies, which detect $ZCu(NO_2)$ and $ZCu(NO_2)(NO)$ at low temperatures, whereas significant amounts of N_2 and O_2 only appear at high temperatures.[3,4,19,22,23] However, to know if such species are involved in the reaction mechanism, it would be necessary to localize the transition states corresponding to their formation and their decomposition. The study of the complete mechanism, including the localization of transition states, as well as other possible intermediates is currently in progress in our laboratory.

Finally, it should be mentioned that the cluster used to model the zeolite framework cannot obviously describe the specificity of ZSM-5. However, if one assumes that the local interactions on the active site are the most important ones, we expect the model used to provide reasonable results for the $ZCu(NO_2)(NO)$ complex that could help understand the nature of the species detected in the experimental studies.

IV. Conclusion

Several singlet and triplet state structures of $ZCu(NO_2)(NO)$ and $ZCu(N_2O_3)$ have been studied. All these structures are energetically more stable than the ZCuO + 2NO asymptote, and their relative energies are within a range of 12 kcal mol^{-1}.

The most stable structure (**T1**) is a triplet state in which Cu has square-pyramidal five-coordination with NO in the apical position, the bonding interaction between $ZCu(NO_2)$ and NO being mainly electrostatic. This structure is the only one that maintains a bidentate η^2-O,O coordination for NO_2.

The lowest singlet structure **S1** lies only 0.7 kcal mol^{-1} above **T1**. Its geometry and bonding interaction differs substantially from **T1**, since in **S1** the coordination around Cu is square planar and the $ZCu(NO_2)$−NO interaction has a significant covalent contribution.

The two $ZCu(N_2O_3)$ structures, **S5** and **S6**, present a η^1-O coordination for the N_2O_3 ligand, and the bonding is mainly electrostatic. These structures are less stable than the other singlet ones, the energy difference with respect to **T1** being 11−12 kcal mol^{-1}.

The computed vibrational frequencies are in good agreement with the known experimental data.

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