Theoretical analysis of N_2O to N_2 conversion during the catalytic decomposition of NO by Cu-zeolites

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Catalytic reactions of N_2O in Cu-exchanged silica zeolites (ZSM-5) have been investigated theoretically using first-principles density functional theory (DFT). We consider four possible reaction paths for the production of N_2, including (i) $ZCu + N_2O \rightarrow ZCuO + N_2$, (ii) $ZCuO + N_2O \rightarrow ZCuO_2 + N_2$, (iii) $ZCu + NO + N_2O \rightarrow ZCuNO_2 + N_2$ and (iv) $ZCu + NO_2 + N_2O \rightarrow ZCuNO_3 + N_2$ ("Z" refers to zeolites). Reactions (i) and (iii) are found to be the most favorable, whereas reactions (ii) and (iv) have much larger barriers. The implication for N_2O reactions in non-selective reduction of NO by CO is also discussed.

KEY WORDS: Cu-ZMS-5; zeolites; DFT; nitric oxide

1. Introduction

Developing efficient catalysts for treating exhaust produced from fuel-efficient "lean-burn" engines has been a major challenge in recent times. Traditional three-way catalysts (TWC), *i.e.*, supported Rh, Pd and Pt, are highly effective for treating automotive exhaust produced under stoichiometric combustion, but lose their activity for NO conversion in an oxygen-rich "lean" environment. Metal-exchanged zeolites, in particular Cu-ZSM-5, have received much attention due to their ability to act as a catalyst for selective catalytic reduction (SCR) of NO by hydrocarbons in O_2-rich exhaust [1–3].

The decomposition of NO into its elements is thermodynamically favorable, but the existence of a large activation barrier prevents spontaneous decomposition. Cu-ZSM-5 is effective in catalyzing NO conversion, but the reaction sites and reaction pathways for decomposition and SCR are not well understood. The likely reaction sites are single Cu sites and possibly oxocation pairs. It is unclear whether or not oxocation pairs exist, but indirect experimental reports indicate that they exist and may be active for NO decomposition [4]. Our recent theoretical results also show that Cu–O–Cu and Cu–O_2–Cu complexes can exist [5,6].

A variety of reaction mechanisms have been proposed, primarily involving single Cu sites [7]. In this paper we will only discuss reactions on single Cu sites, saving work on Cu pairs for a future investigation. However, we believe that most of the reactions that occur on isolated Cu sites can also occur on one Cu in a Cu pair. The Cu pairs probably also allow other reactions which cannot occur on an isolated Cu. Regardless, all proposed mechanisms agree with the fact that N_2O is formed as a gas phase intermediate [2,7–11], so this paper will focus on conversion of N_2O into N_2.

In our recent investigation [8], we proposed the following mechanism for NO decomposition where N_2O formation is a key step:

$$ZCu + NO \rightarrow ZCuON \tag{1}$$

$$ZCuON + NO \rightarrow ZCuONNO \tag{2}$$

$$ZCuONNO \rightarrow ZCuO + N_2O \tag{3}$$

$$ZCuO + N_2O \rightarrow ZCu + O_2 + N_2 \tag{4}$$

The activation barrier for reaction (4) was found to be $36\ \mathrm{kcal\,mol^{-1}}$, which is perhaps too high for this step to contribute significantly to the overall chemistry. The purpose of this paper is to investigate lower energy channels for subsequent reactions of N_2O leading to N_2. This paper presents some new theoretical results for such pathways and their activation barriers. The results suggest that there are several lower energy pathways for N_2O to N_2 conversion.

In the single active site model, an adsorbed gas molecule either decomposes directly or reacts with a molecule of the same or different type (Eley–Rideal mechanism). In the present work, we use an isolated active site (single T-site) to model N_2O reactions with other species that could be present during NO decomposition. We show how N_2O can participate in various reactions to produce N_2. We find that once N_2O is formed, it can react with ZCu, ZCuON, ZCuNO and NO to produce N_2.

One of the major challenges in modeling such catalytic processes with quantum mechanical methods, such as DFT, is the choice of an appropriate cluster model of the active site. Experimental reports [12] and theoretical calculations [8,9,13–19] have demonstrated that exchanged Cu^+ ions prefer a low coordination environment within the ze-

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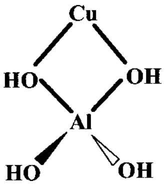
olite, and this coordination environment can be well represented by a single, hydrogen-terminated AlO_4^- framework (T-site).



The formal single negative charge on the $Al(OH)_4$ fragment ("Z") compensates the positive charge of Cu^+ to yield an overall neutral ZCu. It should pointed out that our model for a T-site does not contain any Si atom. Our previous work has shown that this simple model is capable of producing results that are comparable to those with large cluster models [20]. Moreover, this model allows one to examine a wide range of possible reactions that could contribute to its catalytic activity with high level *ab initio* calculations. We believe that calculations using this simple cluster model can produce results that would be valuable to understand, at least qualitatively, the mechanism of NO decomposition.

2. Computational methods

DFT calculations were performed using the Amsterdam density functional code (ADF) [21]. Geometry optimizations and vibrational frequencies were determined within the local (spin)density approximation [L(S)DA]. Single point energy calculations were performed on the L(S)DA optimized geometries with the Becke–Perdew exchange–correlation functional (BP86) [22,23]. A valence double-ζ plus polarization Slater-type basis set was used for all atoms except Cu, for which a double-ζ s and p, and triple ζ d basis set was used. Integration parameters were chosen to ensure that numerically evaluated integrals were accurate to five significant digits. Geometries were converged to maximum and root mean square gradients of 10^{-3} and 6.6×10^{-4} hartree bohr^{-1}, respectively, and energies to less than 10^{-5} hartree. Vibrational spectra were calculated by two-sided numerical differentiation of analytical energy gradients. Minimum energy and transition state structures were characterized by zero and one imaginary vibrational frequency, respectively, except for those involving state crossings, which are discussed in more detail individually. It should be pointed out that all transition structures were optimized without any symmetry constraints, which we find to be important for finding the true minimum of the transition state.

3. Results

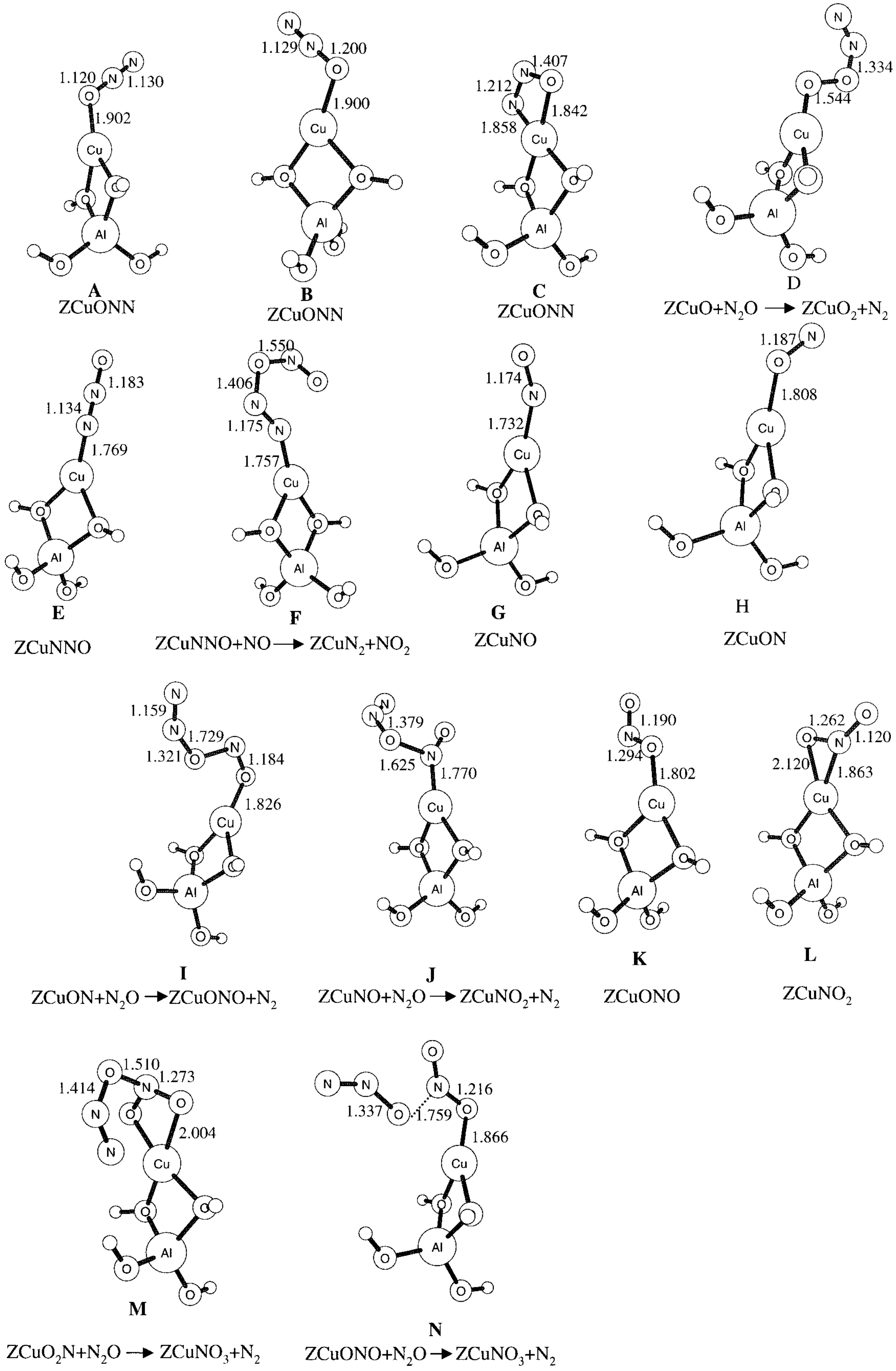
3.1. Direct decomposition of ZCuONN

A mechanism for direct conversion of N_2O into N_2 was proposed by Ayler *et al.* [7]. They suggested that the complex ZCuONN can directly dissociate to produce an oxidized site, ZCuO and N_2,

$$\mathrm{ZCuONN} \rightarrow \mathrm{ZCuO} + \mathrm{N_2} \tag{5}$$

Two different conformers for ZCuONN are possible (see figure 1, structures **A** and **B**). In ZCuONN the N_2O molecule still remains linear. The two conformers differ with respect to the orientation of the ONN fragment. In one confomer Cu–O–N–N is perpendicular to the Cu–O–Al–O ring (structure **A**) while in the other confomer it remains in plane (structure **B**). However, structure **A** is 2 kcal mol^{-1} more stable than **B**. Our calculations show that the above reaction is thermoneutral when structure **A** is considered as reactant. The lowest energy states of the reactant and products are singlet and triplet, respectively, and the potential energy surface of the reaction is therefore a combination of singlet and triplet electronic states (see figure 2) and the reaction is spin-forbidden. It is therefore difficult to to calculate the exact barrier for this type of reaction, but the activation barrier can be estimated as the difference in energies of the ground state reactant and the crossing point of the two electronic states. We previously studied a similar reaction [8] where the O atom of N_2O was directly abstracted by ZCu to produce the same products. The approximate barrier for this direct reaction was found to be 40 kcal mol^{-1}. However, that search included a linear constraint on the Cu–O–N–N portion of ZCuONN, and no geometry optimization was performed. Also, the transition state involved a short Cu–O bond and a long O–N bond, suggesting that the reaction proceeds first by formation of a ZCuONN intermediate, followed by desorption of N_2.

In this paper, we repeated the calculation while removing the linearity constraint, and carried out a more careful search starting from the ZCuONN intermediate. Initially, we calculated the energy of the singlet and triplet states as a function of ZCuO–NN distance of structure **A** and optimizing other geometrical parameters except those in ZCu without keeping any symmetry constraints. We found the Cu–O–N–N fragment turns in plane with the ring in ZCu before the crossing point is reached. In order to validate the right correlation between starting structure and the structure of the crossing point, we calculated the energy and the structure as a function of ZCuO–NN distance starting from the structure of the crossing point. The equilibrium structure thus obtained from this calculation is structure **B**. We think that the lower energy conformation near the crossing point resembles structure **B** while structure **A** is lower in energy at the equilibrium point. Our estimated activation barrier from the calculation without any symmetry constraint is 23 kcal mol^{-1}. We also performed similar calculations using structure **B** with C_s symmetry constraint. The orbital occupation patterns of the singlet reactant and triplet product were maintained in order to get a right orbital correlation. Energy calculations were performed as a function of ZCuO–NN distance while the ZCu–O and N–N distances were varied manually from their equilibrium (singlet ZCuONN) to the final values (ZCuO and N_2). The estimated activation



A ZCuONN

B ZCuONN

C ZCuONN

D $ZCuO+N_2O \rightarrow ZCuO_2+N_2$

E ZCuNNO

F $ZCuNNO+NO \rightarrow ZCuN_2+NO_2$

G ZCuNO

H ZCuON

I $ZCuON+N_2O \rightarrow ZCuONO+N_2$

J $ZCuNO+N_2O \rightarrow ZCuNO_2+N_2$

K ZCuONO

L $ZCuNO_2$

M $ZCuO_2N+N_2O \rightarrow ZCuNO_3+N_2$

N $ZCuONO+N_2O \rightarrow ZCuNO_3+N_2$

Figure 1. Selected geometrical parameters of all equilibrium and transition structures considered. Bond lengths and bond angles are in angstroms and degrees, respectively.

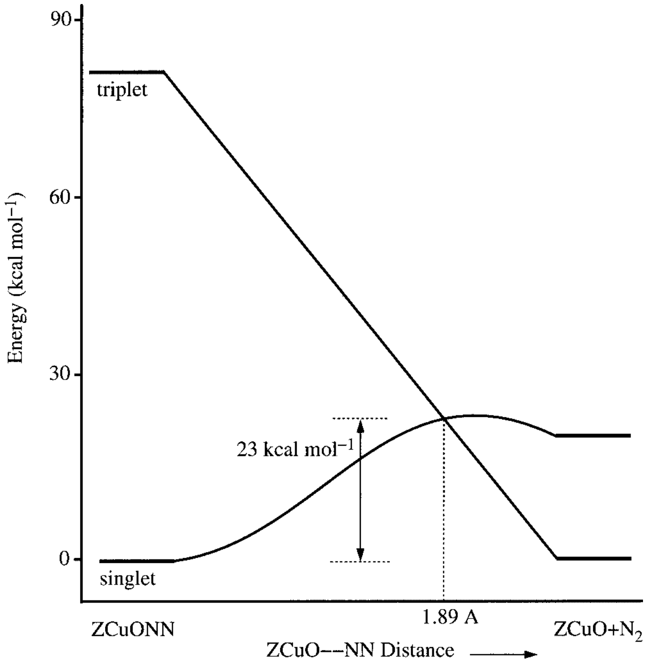


Figure 2. Schematic potential energy surfaces for singlet and triplet states of the reaction ZCuONN → ZCuO + N_2. The crossing point of the two curves indicates the approximate position of the transition state.

barrier for this reaction is found to be 24 kcal mol^{-1} (see figure 2). Adsorption followed by decomposition of N_2O over various Cu catalysts producing an oxidized species and N_2 was also proposed by Dandekar and Vannice [24].

We expect the efficiency of this reaction would be high, if coupling between singlet and triplet states is appreciable at the crossing point. It is important to compare reaction (5) with its analogous gas phase reaction, ONN → O + N_2 (note that O is a triplet, as is ZCuO, so the analogy is reasonable). Our DFT-calculated reaction energy of the gas phase reaction $N_2O \rightarrow N_2 + O$ is higher than the experiment (DFT 59 kcal mol^{-1} and experiment 40 kcal mol^{-1} [25]). This gas phase result suggests that the calculated energies for the analogous catalytic reaction could have a similar error, so that the actual barrier for our ZCu model may be lower than our calculated result.

3.2. Reaction of ZCuO and N_2O

The reaction of ZCuO with N_2O has been studied previously by us [8,9], and thought to be one of the possible mechanisms for N_2 and O_2 formation (reaction (4)). This reaction proceeds *via* direct abstraction of the O atom of N_2O by ZCuO. Several conformationally different transition structures were calculated. The lowest energy transition structure is shown in figure 1 (structure **D**). In this structure the O–O–N–N fragment is in *cis* position. At the transition state, the breaking O–N has increased to 1.334 Å, while the forming O–O distance is 1.545 Å. The activation energy for this reaction was calculated to be 36 kcal mol^{-1}, which suggests the reaction to be relatively slow compared to the others considered here.

3.3. Reactions of N_2O with NO

Reaction of N_2O with NO is another way of converting N_2O into N_2 with simultaneous formation of NO_2. This reaction could occur in the gas phase and in the zeolite. In the gas phase, reaction of N_2O with NO is an abstraction type of reaction where the N atom of NO directly abstracts the O atom of N_2O. The *ab initio* calculations of this gas phase reaction is reported by Mebel *et al.* [26]. Our calculated reaction energy (−32 kcal mol^{-1}) compares quite well with their reported value (−31.5 kcal mol^{-1}) at the B3LYP/6-311G(d,p) level and with experiment (−33.1 kcal mol^{-1}) [25]. However, our calculated activation barrier for this reaction (29 kcal mol^{-1}) is much lower than the value (40 kcal mol^{-1}) reported by Mebel *et al.* [26] using B3LYP exchange–correlation functional with all-electron 6-311G(d,p) basis set. Our transition structure is very close to theirs with bond lengths within 0.05 Å and bond angles within 5°. The source of discrepancy in activation barriers is unclear, although it appears to be a robust difference between the generalized gradient approximation (GGA) and hybrid B3LYP functionals; test calculations with a different GGA functional (BLYP) yielded a similar barrier of 29 kcal mol^{-1}. In this work, however, we compare the activation barriers and reaction energies of different reactions at the same level of theory, as mentioned in section 2. While the absolute value of the activation barriers and reaction energies may vary with the level of theory, we believe that the qualitative results based on the present level of theory would be independent of the theoretical methods.

In the zeolitic environment the reaction of N_2O with NO can occur in two ways: (i) N_2O is adsorbed at the active site and reacts with NO and (ii) NO is adsorbed first and reacts with N_2O. N_2O can bind either O down or N down (through the terminal N). For N_2O, the N-down complex (figure 1, structure **E**) is 15 kcal mol^{-1} more stable than the O-down complex ZCuONN. N_2O can also coordinate as a bidentate ligand through the terminal N and O forming a cyclic complex (figure 1, structure **C**). We find the bidentate complex is approximately 35 kcal mol^{-1} higher in energy than the most stable N-down complex and 12 kcal mol^{-1} unbound with respect to ZCu and N_2O. Thus ZCu–NNO is the most stable structure.

NO can abstract the terminal O atom of the ZCuNNO to form $ZCuN_2$ and NO_2. The N_2 can desorb to regenerate the reduced site, ZCu,

$$\mathrm{ZCuNNO} + \mathrm{NO} \rightarrow \mathrm{ZCuNN} + \mathrm{NO_2} \tag{6}$$

$$\mathrm{ZCuNN} \rightarrow \mathrm{ZCu} + \mathrm{N_2} \tag{7}$$

Reaction (6) proceeds with an activation barrier of only 17 kcal mol^{-1}, and hence we expect this to be a major pathway for N_2O to N_2 conversion. The lower activation barrier for this catalytic reaction compared to its gas phase analog could be due to the lowering of the N–O bond energy in the ZCuNNO complex. This is reflected in a slight increase in the N–O bond length (1.183 Å) of ZCuNNO compared to that in the gas phase N_2O (1.181 Å). The transition structure

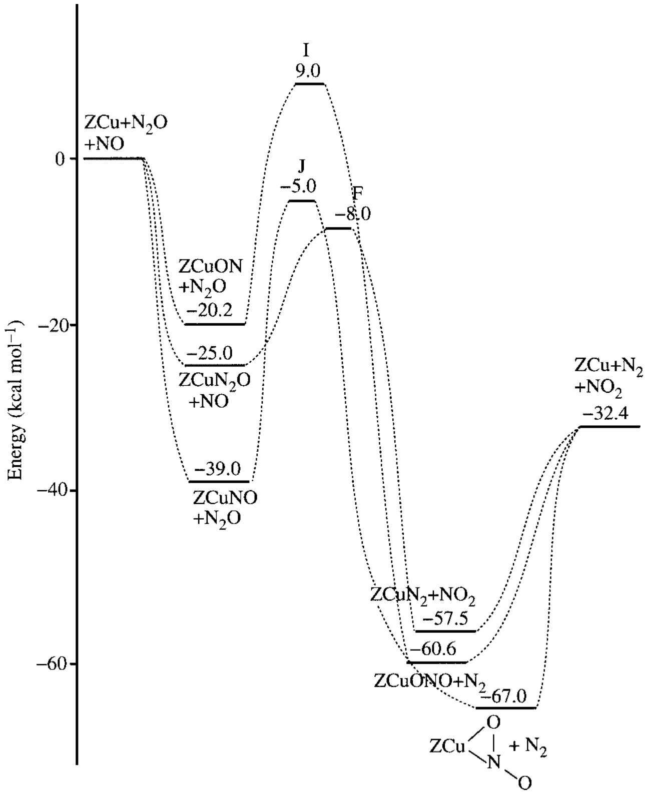


Figure 3. Schematic potential energy surfaces for three different pathways for ZCu + N_2O + NO reactions.

of this reaction is shown in figure 1 **F** while the potential energy surface is shown in figure 3. At the transition state, the breaking ZCuNN–ONO bond length is 1.406 Å, while the forming ZCuNNO–NO length is 1.550 Å, and Cu–N–N, unlike in ZCuNNO, is not linear (146.6°).

The binding of NO to the copper is possible in two different ways: N down (ZCuNO, figure 1, structure **G**) and O down (ZCuON, figure 1, structure **H**). Our DFT calculations show that ZCuNO is 19 kcal mol^{-1} more stable than the ZCuON complex. Once N_2O is formed, it can react with either the ZCuNO or ZCuON:

$$\text{ZCuON} + N_2O \rightarrow \text{ZCuNO}_2\ (\textit{cis}\text{-ZCuONO}) + N_2 \quad (8)$$

$$\text{ZCuNO} + N_2O \rightarrow \text{ZCuNO}_2\ (\eta^2\text{-NO}_2) + N_2 \quad (9)$$

Structures **G** and **H** in figure 1 show that both ZCuNO and ZCuON form non-linear complexes with Cu–N–O and Cu–O–N angles of 147.9° and 137.2°, respectively (figure 1). In reactions (8) and (9), the nitrogen centers of ZCuON and ZCuNO abstract the oxygen atom of N_2O and reduce N_2O into N_2. The activation barriers for reactions (8) and (9) are 29.6 and 33.6 kcal mol^{-1}, respectively, while the reaction energies are −41 and −27.8 kcal mol^{-1}, respectively (figure 3). The higher activation barrier for reaction (9) could be due to the lower spin density on the N atom (0.57) in ZCuNO compared to that in ZCuON (0.82). The forming ZCuON–ONN bond length at the transition state for reaction (8) is 1.729 Å (1.211 Å in free *cis*-ZCuONO), while the breaking ZCuONO–NN bond length is 1.321Å (1.181 Å in free N_2O). On the other hand, the forming ZCuN(O)–ONN bond length at the transition state for reaction (9) is 1.625 Å (1.196 Å in free ZCuη^2-NO_2), while the breaking ZCuN(O)O–NN length is 1.379 Å.

We expect that these two reactions, along with the gas phase reaction, will contribute towards the conversion of N_2O into N_2. The relative rates of reactions (8) and (9) would depend on the concentrations of ZCuON and ZCuNO. Since the concentration of ZCuNO should be higher than ZCuON due to the large binding of the former, reaction (9) likely out-competes reaction (8) in spite of its higher activation barrier.

Our reaction path calculations for reactions (8) and (9) confirm that two different $ZCuNO_2$ complexes are formed as products of these reactions. The *cis*-ZCuONO complex is a monodentate where the O of the NO_2 group is coordinated to the Cu, while in the bidentate η^2-NO_2 complex, N and one of the O atoms are coordinated to Cu. The bidentate complex is found to be approximately 6 kcal mol^{-1} more stable than the mono-dentate one. Binding energies of these two complexes are 28 and 34 kcal mol^{-1}. However, the most stable $ZCuNO_2$ is another bidentate complex ($ZCuO_2N$) where both O atoms are coordinated to Cu. The binding energy of this conformer is 39 kcal mol^{-1}. The structures of various complexes of ZCu with NO_2 and transition states for the above reactions are shown in figure 1.

3.4. Reaction of $ZCuNO_2$ with N_2O

Another possible way of converting N_2O into N_2 is *via* a direct abstraction of the O atom of N_2O by $ZCuNO_2$. This results in formation of a nitrate species, $ZCuNO_3$:

$$\text{ZCuNO}_2 + N_2O \rightarrow \text{ZCuNO}_3 + N_2 \quad (10)$$

After investigating the structures of various $ZCuNO_2$ complexes, we found that the bidentate $ZCuO_2N$ and ZCuONO complexes have the right conformation to abstract the O atom of the N_2O producing $ZCuNO_3$ and N_2:

$$\text{ZCuO}_2\text{N} + N_2O \rightarrow \text{ZCuNO}_3 + N_2 \quad (11)$$

$$\text{ZCuONO} + N_2O \rightarrow \text{ZCuNO}_3 + N_2 \quad (12)$$

Reactions (11) and (12) are exothermic by 30 and 41 kcal mol^{-1} (figure 4). The activation barrier for reaction (11) (47 kcal mol^{-1}) is less than that of reaction (12) (58 kcal mol^{-1}). The lower activation barrier for reaction (11) in spite of its lower exothermicity could be due to an electrostatic interaction between the positively charged Cu and the negatively charged N atom which are in close proximity at the transition state. These reactions are not likely to contribute significantly to the N_2O decomposition process, due to their high barriers compared with reactions (6), (8) and (9).

At the transition state (reaction (11)), the two Cu–O bonds in $ZCuO_2N$ fragments are relatively long (2.004 and 2.002 Å) compared to those in free $ZCuO_2N$ (1.903 Å). The distance between the terminal N atom of the N_2O fragment

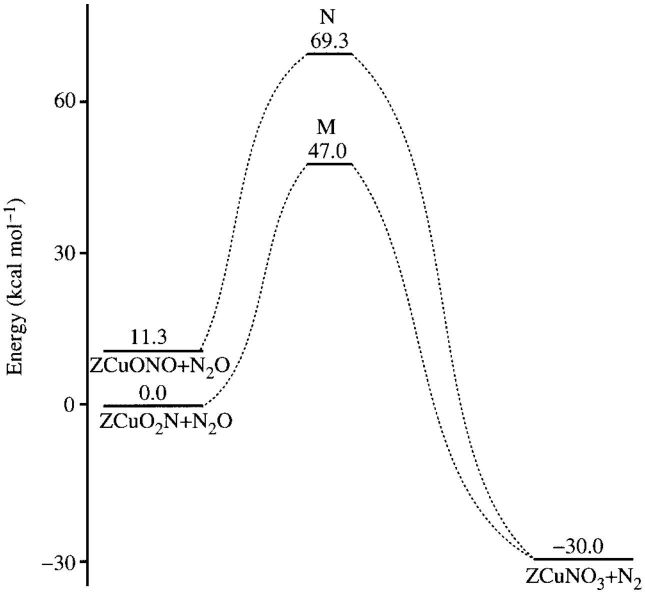


Figure 4. Schematic potential energy surfaces for two different pathways for $ZCuNO_2 + N_2O$ reactions.

from the Cu is only 2.134 Å. The forming $ZCuO_2N$–O bond is 1.510 Å, while the breaking $ZCuO_2NO$–NN bond is increased to 1.414 Å compared to that in free N_2O. The terminal N atom is in *cis*-conformation with respect to the Cu.

On the other hand, the transition structure for reaction (12) shows that the terminal N atom of the N_2O fragment is away from the Cu. The forming ZCuON(O)–ON_2 bond is 1.759 Å, while the breaking ZCuON(O)O–NN bond is increased to 1.337 Å compared to that in free N_2O. Comparing the breaking and forming bonds of the transition structures for reactions (11) and (12), we find that the latter transition state is "early" which is consistent with the larger exothermicity.

4. Discussion

The formation of N_2O could take place *via* the reaction of NO with the intermediate complex ZCuON on a single isolated Cu site [8,9]. Lei *et al.* [4] have also proposed the formation of N_2O with simultaneous formation of Cu pairs,

$$2CuNO \rightarrow ZCuOCuZ + N_2O \qquad (13)$$

Regardless of how N_2O forms, there are several ways it could react, and in this paper we investigated several possible reactions at single Cu sites. Figure 5 summarizes the reactions responsible for N_2O formation (reactions (1)–(3)) and the reactions responsible for N_2 and O_2 formation (discussed below). There are several reaction pathways *via* which N_2O can be converted into N_2. The reaction with the lowest activation barrier (17 kcal mol^{-1}) is reaction (6) where adsorbed N_2O reacts with NO to produce N_2. This reaction is very likely to contribute to N_2 formation, due to the low barrier. Reactions (8) and (9) are two alternative pathways to convert N_2O into N_2. These two reactions differ with respect to the mode of adsorption of NO on ZCu. It is interesting to note that though the N-down complex ZCuNO is inactive for N–N bond formation, it can participate in converting N_2O into N_2. Reactions (8) and (9) have comparable activation barriers (29.6 and 33.6 kcal mol^{-1}, respectively), but since NO strongly prefers to bind N down (by 15 kcal mol^{-1}), we believe that reaction (9) will usually dominate over reaction (8). Since the activation barrier for the gas phase reaction of N_2O with NO is comparable to those for reactions (8) and (9), the gas phase reaction is also likely to play a role in N_2 formation. A salient feature of reactions (5), (6), (8) and (9) is that, once N_2O is formed, the reaction to convert N_2O into N_2 only requires the reduced site (ZCu); there is no need for the oxidized site (ZCuO). It should pointed out that our conclusions are based on the comparison among the activation barriers of different reactions, and no pre-exponential factors have been calculated. Because the above reactions are all bimolecular atom transfers, it is reasonable to expect that their pre-exponential factors will be of similar orders of magnitude.

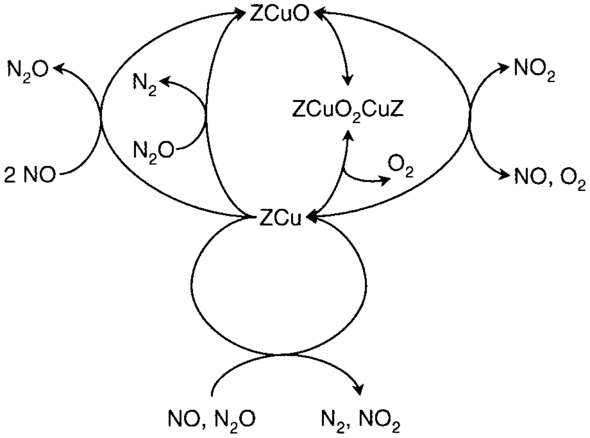


Figure 5. The catalytic cycle for various N_2O reactions during NO decomposition.

The direct decomposition of ZCuONN (reaction (5)) is a spin-forbidden reaction, but has a lower energy crossing point (23 kcal mol^{-1}) than we originally estimated [8]. This reaction is likely to contribute to N_2 formation provided that the transition probability at the crossing point is appreciable. The reactions $ZCuO + N_2O$ (reaction (4)) and $ZCuNO_2 + N_2O$ (reactions (11) and (12)) have higher activation barriers and are probably less important.

Thus, for single Cu sites, we conclude that reactions (5), (6), (8) and (9) are important reactions, with reaction (6) likely being the most important. These reactions involve O atom transfer from N_2O either to a reduced Cu site to form ZCuO (reaction (5)) or to NO to form NO_2 (reactions (6), (8) and (9)). To complete a catalytic cycle for NO decomposition, this O atom must be combined with a second to form O_2. Two possibilities present themselves. One is that two ZCuO combine to form an oxo-bridged Cu pair, which decomposes to yield O_2 and two reduced Cu sites:

$$2ZCuO \rightarrow ZCuO_2CuZ \qquad (14)$$

$$ZCuO_2CuZ \rightarrow 2ZCu + O_2 \qquad (15)$$

Such a process has been shown to be approximately thermoneutral for two Cu sites sufficiently proximate to allow pair formation [5,6], and is consistent with experimental evidence for Cu pair intermediates in NO decomposition. The second possibility involves combination of ZCuO and NO_2:

$$\mathrm{ZCuO} + \mathrm{NO_2} \rightarrow \mathrm{ZCuOO}\cdots\mathrm{NO} \tag{16}$$

$$\mathrm{ZCuOO}\cdots\mathrm{NO} \rightarrow \mathrm{ZCu} + \mathrm{O_2} + \mathrm{NO} \tag{17}$$

Previous work showed this pair of reactions to be slightly endothermic but to have no overall kinetic barrier [8]. Thus, both processes are expected to contribute to O_2 formation during NO decomposition.

It is also possible that Cu pairs are involved directly in the conversion of N_2O into N_2. For example, reaction (18) is exothermic by 49 $\mathrm{kcal\,mol^{-1}}$, although the detailed mechanism by which it would proceed is unclear,

$$\mathrm{ZCuO_2CuZ} + \mathrm{N_2O} \rightarrow \mathrm{ZCuOCuZ} + \mathrm{O_2} + \mathrm{N_2} \tag{18}$$

This reaction also provides an alternative path for O_2 formation.

Finally, it is worthwhile to mention the implication of our work for the non-selective reduction of NO by CO. Iwamoto and Hamada [2] carried out controlled experiments of NO reduction in the presence and absence of O_2 using CO as the reductant. They observed a marked increase in NO reduction by CO in the absence of O_2. Our recent studies on CO oxidation [27] over Cu-ZSM-5 reveal that CO can reduce ZCuO *via* the following reaction:

$$\mathrm{ZCuO} + \mathrm{CO} \rightarrow \mathrm{ZCu} + \mathrm{CO_2} \tag{19}$$

The above reaction has an activation barrier of only 9 $\mathrm{kcal\,mol^{-1}}$ and is expected to regenerate the reduced sites efficiently. We believe that in the presence of CO, the above reaction makes the reduced sites readily available to facilitate reactions (1)–(3) for N–N bond formation and reactions (5), (6), (8) and (9) for N_2O conversion into N_2.

5. Conclusions

The decomposition of N_2O over Cu-ZSM-5 has been studied using density functional methods. We find a number of kinetically favorable pathways that could convert N_2O into N_2. Most of these reactions do not need a direct cycling between oxidized and reduced species. However, the oxidized Cu sites formed during the N_2O formation can be reduced *via* several reactions with simultaneous production of O_2. The reaction

$$\mathrm{ZCu} + \mathrm{N_2O} + \mathrm{NO} \rightarrow \mathrm{ZCuN_2O} + \mathrm{NO} \rightarrow \mathrm{ZCuN_2} + \mathrm{NO_2}$$

seems to be the most favorable reaction among all the N_2 formation reactions we have studied here.

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References

[1] M. Shelef, Chem. Rev. 95 (1995) 209.
[2] M. Iwamoto and H. Hamada, Catal. Today 10 (1991) 57.
[3] Y. Li and W.K. Hall, J. Phys. Chem. 94 (1990) 6145.
[4] G.D. Lei, B.J. Adelman, J. Sarkany and W.M.H. Sachtler, App. Catal. B 5 (1995) 245.
[5] B.R. Goodman, W.F. Schneider, K.C. Hass and J.B. Adams, Catal. Lett. 56 (1998) 183.
[6] B.R. Goodman, W.F. Schneider, K.C. Hass and J.B. Adams, J. Phys. Chem. B 103 (1999) 10452.
[7] A.W. Aylor, S.C. Larsen, J.A. Reimer and A.T. Bell, J. Catal. 157 (1995) 592.
[8] W.F. Schneider, K.C. Hass, R. Ramprasad and J.B. Adams, J. Phys. Chem. B 102 (1998) 3692.
[9] W.F. Schneider, K.C. Hass, R. Ramprasad and J.B. Adams, J. Phys. Chem. B 101 (1997) 4353.
[10] Y. Li and J.N. Armor, Appl. Catal. 76 (1991) L1.
[11] F. Radtke, R.A. Koeppel and A. Baiker, Appl. Catal. 107 (1994) L125; 157 (1995) 592.
[12] R. Kumashiro, Y. Kuroda and M. Nagao, J. Phys. Chem. B 103 (1999) 89.
[13] W.F. Schneider, K.C. Hass, R. Ramprasad and J.B. Adams, J. Phys. Chem. 100 (1996) 6032.
[14] Y. Yokomichi, T. Yamabe, H. Ohtsuka and T. Kakumoto, J. Phys. Chem. 100 (1996) 14424.
[15] Y. Yokomichi, H. Ohtsuka, T. Tabata, O. Okada, Y. Yokoi, H. Ishikawa, R. Yamaguchi, H. Matusi, A. Tachibana and Y. Yamabe Catal. Today 23 (1995) 431.
[16] L. Rodriguez-Santiago, M. Sierka, V. Branchadell, M. Sodupe and J. Sauer, J. Am. Chem. Soc. 120 (1998) 1545.
[17] H. Kobayashi and K. Ohkubo, Appl. Surf. Sci. 121/122 (1997) 111.
[18] B.L. Trout, A.K. Chakraborty and A.T. Bell, J. Phys. Chem. 100 (1996) 17582.
[19] B.L. Trout, A.K. Chakraborty and A.T. Bell, J. Phys. Chem. 100 (1996) 4173.
[20] K.C. Hass and W.F. Schneider, Phys. Chem. Chem. Phys. 1 (1999) 639.
[21] E.J. Baerends, D.E. Ellis and P. Ross, Chem. Phys. 2 (1973) 41.
[22] A.D. Becke, Phys. Rev. A 38 (1988) 3098.
[23] J.P. Perdew, Phys. Rev. B 33 (1986) 8822.
[24] A. Dandekar and M.A. Vannice, Appl. Catal. B 22 (1999) 179.
[25] *CRC Handbook of Chemistry and Physics*, 78th Ed. (CRC Press).
[26] A.M. Mebel, M.C. Lin, K. Morokuma and C.F. Melius, Int. J. Chem. Kinet. 28 (1996) 693.
[27] D. Sengupta, W.F. Schneider, K.C. Hass and J.B. Adams, Catal. Lett. 61 (1999) 179.