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Why Is Silver Catalytically Active for NO Reduction? A Unique Pathway via an Inverted (NO)₂ Dimer

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Abstract: NO reduction on the noble metal Ag has been studied using density functional theory calculations. It was found that monomeric NO dissociation is subject to prohibitive barriers on Ag metal and is thus unlikely to account for the experimental observations for NO reduction over Ag-based catalysts. For the first time, a mechanism via an inverted (NO)₂ dimer is identified, which can explain both the high activity and the selectivity of this catalytic system. N₂O is the major reduction product of the inverted (NO)₂ dimer, in accord with experiment. The physical origin of the Ag metallic state as a good catalyst is furthermore identified: Ag surfaces, including small clusters, have little or no covalent bonding ability but can bond ionically with adsorbates. We conclude that the variation of the ionic bonding strength of Ag toward different reactants determines its catalytic selectivity.

Introduction

Platinum group metal catalysts such as Ru, Rh, and Pt often suffer from poisoning by oxygen at high temperatures and under oxidative conditions.^{1–2} The noble metals Ag and Au are, instead, well-known to be more resistant to oxygen poisoning.³ In recent years noble metals, when highly dispersed on oxides, have been discovered to exhibit high catalytic activity for selective NO reduction *in the presence of O₂*, a vital process for removing NO from industrial and car exhausts.^{1,4–8} However, it was also found that noble metal catalysts tend to suffer from sintering of the supported metal clusters. For NO reduction on Ag-based catalysts, the formation of large metal particles severely affects the product selectivity, which varies from N₂ to N₂O.^{1,5–8} To date, an understanding of the fundamental issues in NO reduction on noble metal-based catalysts remains elusive. Specifically, why are noble metals catalytically active at all, and why is the product selectivity sensitive to the metal morphology? In this contribution, we aim to provide insights into these questions through density functional theory (DFT).

Experimental studies in recent years have yielded some interesting and seemingly contradictory results.^{5–14} Ultrahigh

vacuum (UHV) experiments have shown that the Ag{111} surface can partially reduce NO to N₂O at very low temperatures, ~80 K.^{9–14} This finding is quite unexpected, showing that Ag can be more active than transition metals. Above 120 K and low NO pressures the reaction stops because of the low lifetime of the NO monomer on the surface. King and co-workers demonstrated using RAIRS,¹⁰ STM¹¹ and photoelectron¹³ experiments that this low-temperature reaction goes through a dimer intermediate, (NO)₂, which splits into N₂O and adsorbed O: 2NO → (NO)₂ → N₂O + O.^{9–11} The electronic structures of the NO monomer and dimer were evaluated in a preliminary DFT study.¹³ On the other hand, experiments under normal catalytic conditions, i.e., high temperatures (e.g., 600 K) and high NO pressure, demonstrate that the selectivity of NO reduction depends critically on the morphology of Ag on the oxide support (usually alumina (Al₂O₃)). Over highly dispersed catalysts, where Ag exists as separated atoms/ions, NO can be fully reduced to N₂.^{1,5–8} In contrast, over catalysts where Ag is present as metal particles, NO is mainly reduced to N₂O.^{5–8} To explain the variation of the selectivity with respect to the Ag morphology, it has been speculated^{1,5} that on the Ag metallic phase NO can dissociate into N and O atoms, and N₂O can then form through N + NO → N₂O, while on the single Ag atom/ion site the dissociation is hindered and the NO reduction is catalyzed by oxide surfaces with the Ag as promoter.

In this contribution, we present a comprehensive survey of different NO reduction pathways over Ag metals/clusters without the oxide support. This allows us to provide some insights into fundamental issues concerning the activity and selectivity of noble-metal-based catalysts. We show that NO monomer

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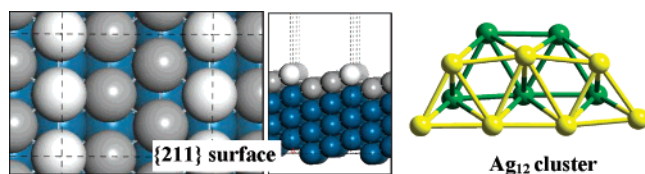


Figure 1. Structures of the {211} surface (a stepped surface) and the Ag_{12} cluster.

dissociation is impossible on Ag metals/clusters and is also unlikely over Ag/oxides catalysts. The selectivity can be explained using a mechanism involving an inverted $(\text{NO})_2$ dimer as the intermediate state.

Calculation Methods

Our calculations are based on the DFT-slab approach¹⁵ at the GGA-PBE (Perdew–Burke–Ernzerhof^{16a}) approximation level, as implemented in the CASTEP code.¹⁷ A variety of Ag surfaces have been studied, including Ag{111} (flat surface), Ag{211} (stepped surface), Ag-adatom on Ag{111}, and a 12-atom nonsupported Ag-cluster in neutral and positively charged forms (Ag_{12} and Ag_{12}^{2+}). It has been suggested from experiment^{5,6} that positively charged Ag clusters (i.e., the oxidized form) may be present in Ag/oxide systems due to the catalyst preparation procedure. These types of surfaces and clusters have been modeled in previous work to study reactions on Au,¹⁸ and illustrations of them are shown in Figure 1.¹⁸ Here we emphasize that the purpose in studying the Ag_{12} and Ag_{12}^{2+} forms is to examine the possible catalytic effects introduced by the small particle size and the oxidized Ag state and that the cluster size or the oxidation state here might be different from real supported Ag particles. The Ag_{12}^{2+} state is merely chosen as a presumably representative mildly oxidized example. All the exposed faces of the 12-atom Ag-cluster are {111}-like facets, having the lowest surface energy of all possible facets. The transition states (TSs) of all the reactions studied were sought using a constrained minimization technique.^{18,20–23} Previous work benchmarked against experiment has demonstrated that the above DFT setup affords good accuracy,¹⁹ even for the calculation of reaction barriers on metal surfaces.^{18–21}

Results and Discussions

To model the reactions, a sound knowledge of NO adsorption behavior on different Ag surfaces is essential. As a starting point, the adsorption of both monomer and dimer on several different Ag surfaces have been calculated, including Ag{111}, Ag{211}, Ag adatom on Ag{111}, Ag_{12} and Ag_{12}^{2+} clusters. The adsorption energy, E_{ad} of $(\text{NO})_n$ ($n = 1$ or 2) is defined to be $nE_{(\text{NO})} + E_{(\text{clean surf})} - E_{((\text{NO})n+\text{clean surf})}$, where E_X is the total energy of the X system. The calculated E_{ad} are summarized in Table 1, and the corresponding structures are shown in Figure 2. It can be seen that on neutral Ag surfaces the maximum

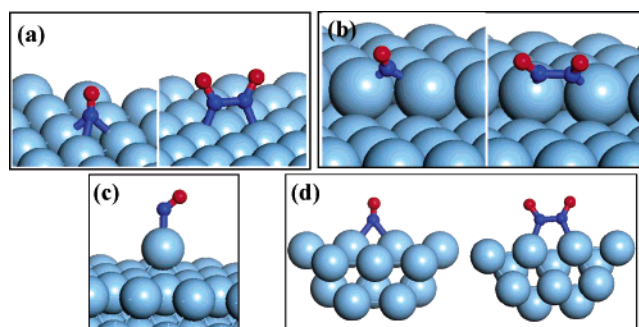


Figure 2. Optimized structures of NO and $(\text{NO})_2$ adsorption on (a) Ag{111}, (b) Ag{211}, (c) Ag-adatom, (d) Ag_{12} cluster. The adsorption configurations of NO and $(\text{NO})_2$ adsorptions on Ag_{12}^{2+} are similar to those on the neutral Ag_{12} .

Table 1. NO Monomer and Dimer Adsorptions on Different Ag Surfaces^a

	coordination (Ag)	E_{ad} (monomer)	E_{ad} (dimer)
Ag{111}	9	0.36 (1/4 ML) 0.15 (1/9 ML)	1.12 (1/9 ML)
Ag{211}	6	0.61 (1/2 ML)	1.57 (1/2 ML)
Ag-adatom	1	0.57 (1/9 ML)	
Ag_{12}	6	0.47	1.20
Ag_{12}^{2+}	6	0.71	1.35

^aThe coordination number of the Ag atom, to which NO bonds, is also listed. The coverages of the adsorbates are indicated in parentheses. The structures of them are shown in Figure 2. The energy unit is eV.

adsorption energy of NO monomers is 0.61 eV, which corresponds to 0.50 ML NO at the step edge of Ag{211}. There is an increase of NO adsorption energy when the Ag is positively charged, i.e. on going from a neutral Ag_{12} to Ag_{12}^{2+} ; however, the magnitude of the increase is small. From our results, NO only weakly adsorbs on Ag, irrespective of the morphology and the oxidation state of the substrate.

We found that $(\text{NO})_2$ can easily form on Ag as soon as two NO monomers approach each other, with a minimal barrier. In the dimer structure, as in the gas phase, the two NO molecules link to each other through the N atoms, the distance between these two being around ~ 1.5 Å. This is much shorter than in the gas phase $(\text{NO})_2$ dimer (1.97 Å). Importantly, the adsorption energy of the dimer is generally more than twice that of the NO monomer. The highest adsorption energy for $(\text{NO})_2$ is calculated to be 1.57 eV with respect to two free NO molecules. NO monomer adsorption on Ag is spin-polarized, but the dimer is spin nonpolarized, a result consistent with the previous theoretical calculation for NO on Ag surfaces.¹³

The possibility of monomeric NO dissociation ($\text{NO} \rightarrow \text{N} + \text{O}$) on metallic Ag is a key issue. For transition metals, NO dissociation is the most straightforward route toward NO reduction.¹ We have therefore examined NO dissociation on the flat Ag{111} and stepped Ag{211} surfaces. The transition states of the dissociation reactions have been located, and the reaction barriers were thus computed with respect to the NO molecule in the gas phase. The transition-state structures on the two surfaces are quite similar to those for diatomic molecules, such as NO and CO, dissociating on transition metal surfaces^{22,23} except that the N–O bond lengths in the transition states are remarkably long: 2.16 Å on Ag{111} and 2.56 Å on Ag{211}. This implies the transition states belong to the “very late” category.^{22–23} Next, we calculated the final states of the

- (15) The electronic wave functions were expanded in a plane wave basis set, and the ionic cores were described by ultrasoft pseudopotentials.^{16b} The vacuum region between slabs was 10 Å, and a cutoff energy of 340 eV was used. Monkhorst–Pack k-point sampling with approximately $0.07 \times 2\pi \text{ Å}^{-1}$ spacing in reciprocal lattice was utilized for all of the calculations (for example, for a $p(2 \times 2)$ Ag(111) slab, $3 \times 3 \times 1$ k-point sampling is used).
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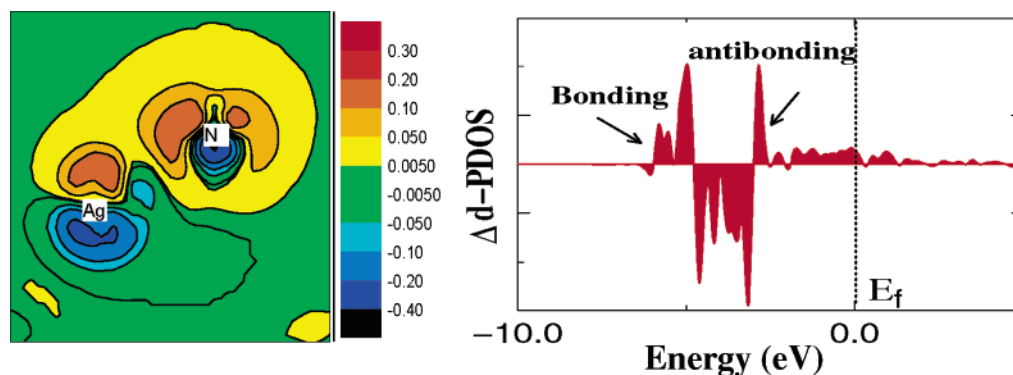


Figure 3. Bonding of N on Ag{111}. (a) Charge density difference contour plot (unit: $e^-/\text{\AA}^3$) cutting through the N–Ag bonding plane, constructed by subtracting the total charge densities of the adsorbed system from those of the separated N atom and clean Ag{111} surface. Positive values (red) represent an electron density increase. (b) The difference of the d-projected density of states (d-PDOS) of the Ag atom depicted in (a) before and after N adsorption.

reactions, i.e. the adsorbed N and O atoms, which are found to be much more unstable than the initial state by more than 2 eV per molecule (the NO bond energy of a free NO molecule is calculated to be 6.67 eV (expt 6.55 eV)). Consistent with the highly endothermic nature of the reaction, the calculated reaction barriers for NO dissociation are extremely high, 3.11 eV on Ag{111} and 2.70 eV on Ag{211}. We found that the instability of the final state is mainly due to the low adsorption energy of N atoms on Ag. For example with Ag{111}, the binding energy of N is 1.50 eV, much lower than for O atom adsorption (2.79 eV), and also significantly lower than that of a N atom on typical platinum group metals (more than 4 eV). To further check whether N adsorption behavior is different on small clusters, we also examined N atom adsorption on Ag₁₂ and Ag₁₂²⁺ clusters. In both cases, the calculated N atom adsorption energies remain low, 1.56 and 1.51 eV, respectively, which further confirms that NO dissociation is strongly disfavored on Ag metal because of its endothermic nature.

The low bonding energy of the N atom on Ag is thus of particular interest. To better understand how Ag bonds with the N atom, we first calculated the charge density difference for N adsorption on Ag{111}. The charge density difference is constructed by subtracting the total electron density of N/Ag{111} from the densities of the free N atom and clean Ag{111}, without modifying the atomic positions. Figure 3a represents the density difference cutting through the N–Ag bonding plane. The main feature of Figure 3a is the large electron density accumulation toward the N atom, which indicates significant ionic bonding in the N–Ag bond. Orbital mixing between the N p-like states and the Ag d-like states is weak. This p–d interaction yields an extra energy cost due to Pauli repulsion, evident from Figure 3b. Figure 3b is the difference in the d-projected density of states (d-PDOS) of the Ag atom (labeled in Figure 2a) before and after N adsorption. The Δ d-PDOS shows density depletion around -4 eV, along with density accumulation at two other regions, below -5 eV and near the Fermi level. Integrating the Δ d-PDOS ($g(\epsilon)$, y axis in Figure 3b) up to the Fermi level

$$E_d = \int_{-\infty}^{E_F} \epsilon g(\epsilon) d\epsilon$$

we found that the Ag occupied d-states are *destabilized* by 0.26 eV (i.e. $E_d = +0.26$ eV). This is opposite to N adsorption on transition metals, where the occupied metal d-states are generally *stabilized* by several eV due to the p–d covalent mixing. For

example for N on Ir{111}, $E_d = -3.94$ eV. From Ag–N bonding, we conclude that the low adsorption energy of N on Ag surfaces is mainly due to the absence of covalent bonding with Ag surfaces. It is weak bonding of the N atom that primarily determines the high barrier for NO dissociation on Ag.

Apart from the NO dissociation pathway, we have searched for the pathways initiated from the adsorbed (NO)₂ dimer. Ag{111} is chosen as the model surface since N₂O formation on Ag{111} has been observed at ~ 80 K.^{9–12,14} As shown in Figure 4, we have located three different pathways, two leading to N₂O formation (Pathways I and II) and one leading to N₂ formation (Pathway III). The overall energy diagram of the NO reduction process is shown in Figure 5.

Pathway I is a straightforward pathway for (NO)₂ decomposition. The TS (TS1 in Figure 4) is achieved when one NO leans away from its partner down to the surface and the other NO moves away from the surface. The barrier of this pathway is 0.80 eV with respect to the dimer initial state. *Pathway II*, however, is the lowest-energy route and is initiated when the (NO)₂ dimer first flips from the upright N-down geometry to a parallel geometry and thence to an upright O-down geometry. The O-down dimer is a precursor state (**P** in Figure 4), which can readily lose one of its O atoms (TS2 in Figure 4) with a 0.27 eV barrier and finally yields an N₂O molecule and an adsorbed O atom. It should be mentioned that the potential energy surface of the (NO)₂ on Ag{111} is very flat, which enables it to invert on the surface with surprisingly little energy cost (the barrier to flipping is below 0.2 eV from our calculation). In fact, the O-down dimer is slightly more stable than the initial N-down dimer by 0.09 eV. Compared to Pathway I, Pathway II is strongly kinetically favored and is also consistent with the low-temperature UHV experiment. Finally, *Pathway III* is the only pathway that can produce N₂. The pathway is, in fact, quite similar to Pathway II except that the O-down precursor simultaneously loses *both* of its O atoms to produce an N₂ molecule. In this route, as two N–O bonds have to be stretched simultaneously, the achieved saddle point (**S** in Figure 4) possesses more than one imaginary mode and therefore is not a conventional TS. Nevertheless, the determined barrier of Pathway III is 0.71 eV, which is much higher than Pathway II.

It should be mentioned that both the normal and the inverted (NO)₂ dimer species have been observed previously in discrete organic²⁴ and organometallic²⁵ complexes. In particular, ref 25 discusses a reaction of the dinitrosyl complex to react with CO to form N₂O and CO₂ through an inverted (NO)₂ dimer. The

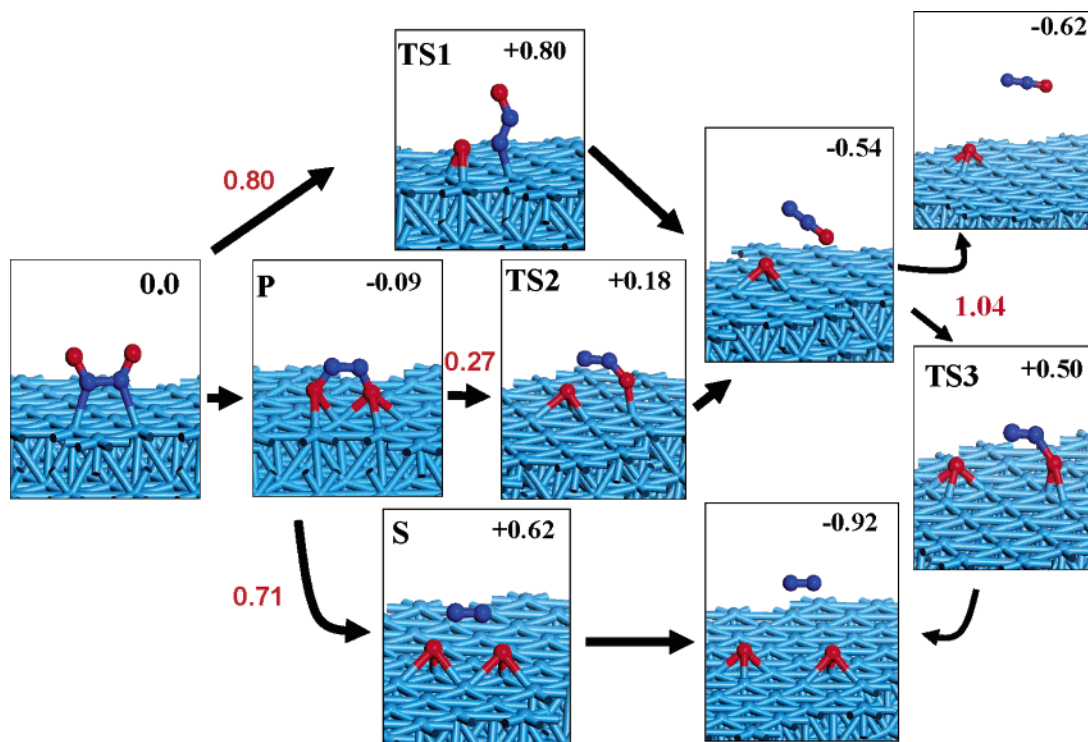


Figure 4. Reaction pathways initiated from the $(\text{NO})_2$ dimer. The energy cost (unit: eV) at each step is labeled. TS1, TS2 are the transition states leading to N_2O formation. S is a high-index saddle point leading to N_2 formation. The relative energy of each state with respect to the initial state is labeled in the top-right corner (also see the overall energy diagram in Figure 5).

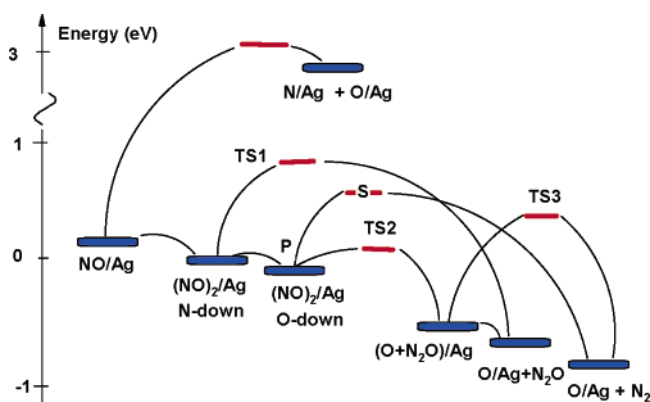


Figure 5. Overall energy diagram of the NO reduction process on Ag. The P, TS1, TS2, S, TS3 states are the same as those labeled in Figure 4.

determined structure of the ONNO in their case is very close to what we found for it on the Ag metal surface. For example, in their case the N–N bond length is 1.21 Å, and in our case it is 1.26 Å. We are not aware of any such mechanism being proposed for a surface reaction, however.

Knowing how N_2O is produced from $(\text{NO})_2$, it is natural to ask whether N_2O can further decompose to N_2 . We therefore calculated the pathway and the energetics of the $\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}$ reaction on Ag{111}. The calculated adsorption energy of N_2O on clean Ag{111} is found to be very small, only 0.02 eV, while in the presence of adsorbed O the adsorption of N_2O is slightly endothermic. The N_2O bonds with Ag surfaces through its O-end, as shown in Figure 4. At the TS (TS3 in Figure 4), the O of N_2O is passing to the surface with the N–O

bond stretched to 1.55 Å and the N–N–O angle bent to 127.5°. In the final state, an adsorbed O atom and a gas-phase N_2 molecule are produced. Although the reaction is exothermic by 0.38 eV, the barrier of the reaction is 1.04 eV (see Figure 4). Obviously, N_2O is easier to desorb than to decompose. To produce N_2 , a direct dissociation of N_2O is expected, which may occur at temperatures high enough to overcome the barrier. The above results show that N_2O is the immediate product from $(\text{NO})_2$ dimer and N_2 production is hindered kinetically. This is consistent with the general finding for NO reduction over noble metal catalysts that N_2O starts to form at low temperatures while N_2 is only produced at higher temperatures.^{1,4–6}

The above results show that NO reduction on Ag intrinsically favors N_2O production. There are two apparent reasons: first, the $(\text{NO})_2$ dimer adsorption energy on Ag is larger than that of either NO or N_2O , and second, the barrier of the $(\text{NO})_2 \rightarrow \text{N}_2\text{O} + \text{O}$ reaction (0.27 eV) is much lower than that of $\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}$ (~1 eV) although both reactions are exothermic by a similar extent. To understand the reactivity difference among the species, we have examined the electronic structures of the $(\text{NO})_2$ dimer, NO, and N_2O on Ag. Similar to the N atom adsorption shown in Figure 3, we found that the bonding between the molecules and Ag is largely ionic bonding. Basically, the Ag surface donates electrons to the molecules, and then an electrostatic attraction is developed between the negative molecules and the positive surface. By performing Mulliken charge analysis, we indeed found the accumulated net charges on $(\text{NO})_2$, NO, and N_2O are –0.56, –0.37, –0.04, respectively, which follows the same trend as the adsorption energy of the molecules on the surface: $(\text{NO})_2 > \text{NO} > \text{N}_2\text{O}$. The differences in the electron-accepting ability of the molecules on the surface can be associated with the electron affinities of the molecules in the gas phase. Using DFT, we have calculated

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the electron affinity of $(\text{NO})_2$, NO, and N_2O , which are -1.50 , -0.55 , and $+0.15$ eV, respectively (negative value means energy gain upon adding an electron). It is evident that $(\text{NO})_2$ is the best electron acceptor and N_2O is the worst. More importantly, we found that the extra electron added into $(\text{NO})_2$ enters into the 2π antibonding state of the N–O bonds but enters into the bonding state of the N–N bond, which modifies the structure of the dimer dramatically, represented by the shortened N–N distance in $(\text{NO})_2^-$ (1.45 Å compared to 1.97 Å in $(\text{NO})_2$) and the lengthened N–O distances. This structural variation can be understood according to molecular orbital theory. For each NO molecule the frontier orbitals are two $2\pi^*$ antibonding orbitals, which are occupied by only one electron. These two $2\pi^*$ orbitals can interact with their counterparts in another NO molecule to form two $2\pi^*-2\pi^*$ ON–NO bonding orbitals. In the neutral $(\text{NO})_2$ only one such bonding orbital is occupied, while in $(\text{NO})_2^-$ the second will also be half occupied. This leads to an increase in the N–N bonding, but a further decrease in the N–O bonding, explaining why electron donation into $(\text{NO})_2$ assists its reduction. In contrast, the extra electron added into N_2O enters into the nonbonding state, which only leads to a small structural change (within 0.01 Å in bond lengths).

In conjunction with experimental observations, we may now address some implications of our theoretical results. First, we have shown that NO monomers do not adsorb strongly on Ag surfaces, including small clusters. Therefore, one would anticipate that oxide supports play critical roles in enhancing the NO adsorption in the high-temperature and high-pressure experiment of NO reduction over Ag/oxide catalysts. Recent DFT studies^{18,21} have found, for instance, that O_2 adsorption can be greatly enhanced at the Au/ TiO_2 interface (O_2 does not adsorb well upon either Au or TiO_2). Fundamentally, this is due to the fact that the Ti^{4+} ion on the oxide surface (acid site) promotes electron transfer from the supported Au to O_2 sitting at the metal/oxide interface. This physical picture is expected to carry over for NO or $(\text{NO})_2$ dimer adsorption at the Ag/oxide interface. Second, NO dissociation is highly energetically disfavored over Ag surfaces because of the lack of a suitable covalent binding site for the dissociated N atom on Ag. This situation may not be altered in the presence of the oxide support since the oxides typically used, such as alumina, are known to be redox inactive (Al^{3+} needs to be oxidized to bond with N atoms). Therefore, a mechanism involving NO dissociation is unlikely to account for the experimentally observed NO reduction. Third, if the $(\text{NO})_2$ dimer is present in the catalytic system, N_2O production

is intrinsically easier compared to N_2 production. The presence of $(\text{NO})_2$ is very likely under real catalytic conditions as the high NO pressure will increase the lifetime of the NO monomer on the surface and thus enhance the formation of the $(\text{NO})_2$ dimer. Furthermore, the dimer formation mechanism identified in the present work requires the involvement of at least two adjacent Ag metal atoms (see Figures 2 and 4). It is implied, therefore, that when Ag is present as separated single atoms/ions, the dimer pathway may be suppressed, and N_2 formation becomes the only possible route.

Conclusions

Our DFT calculations have identified, for the first time, an entire pathway for NO reduction over Ag metal, which involves an inverted $(\text{NO})_2$ dimer on the surface as the precursor for N_2O formation. The results affirm the previous conclusion from UHV experiments that NO reduction on $\text{Ag}\{111\}$ must go through a $(\text{NO})_2$ dimer state.^{9–11} The barrier to the process is 0.27 eV, which agrees well with the experimental observation of the process at ~ 80 K. The further dissociation of N_2O to N_2 is kinetically hindered, due to the adsorption energy of N_2O on the surface being lower than its dissociation barrier. Crucially, we rule out the possibility that monomeric NO dissociation occurs on bare Ag because the barrier of the process is far too high (more than 2.7 eV). This is mainly due to the extremely low adsorption energy of the N atom on Ag. An examination of the electronic structures reveals that Ag surfaces, including small clusters, have little or no covalent bonding ability, but can bond ionically with adsorbates. This determines the low adsorption energy of adsorbates, such as N atoms, which strongly favor covalent bonding. For the same reason, we conclude that NO dissociation is also unlikely on irreducible oxides such as alumina. Furthermore, the $(\text{NO})_2$ dimer has a larger electron affinity in the gas phase (compared to NO and N_2O) which gives rise to its stronger ionic bonding with Ag. Electron donation from Ag to the dimer occurs into the N–O antibonding states, weakening the N–O bond and directly facilitating the decomposition of the dimer.

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