

# First-Principles Characterization of NO<sub>x</sub> Adsorption on MgO

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Alkaline earth oxides are leading candidates as NO<sub>x</sub> ( $x = 1, 2$ ) sorbents; however, the understanding of adsorption and reaction of NO<sub>x</sub> on these surfaces is currently limited. In this paper, Mg(001) terrace cluster models and density functional theory (DFT) are used to characterize the adsorption properties of neutral and charged NO, NO<sub>2</sub>, and NO<sub>3</sub>. Neutral NO and NO<sub>2</sub> molecules weakly adsorb on the MgO terrace, while neutral NO<sub>3</sub> adsorbs more strongly through oxidation and significant acid–base coordination with the surface. Chemisorbed nitrite can be formed either from adsorption of Lewis acidic NO<sup>+</sup> on Lewis base surface sites (O<sub>s</sub><sup>2-</sup>) or from adsorption of Lewis basic NO<sub>2</sub><sup>-</sup> on Lewis acid surface sites (Mg<sub>s</sub><sup>2+</sup>). Similarly, chemisorbed nitrate can form from NO<sub>2</sub><sup>+</sup> adsorption on O<sub>s</sub><sup>2-</sup> sites or NO<sub>3</sub><sup>-</sup> adsorption on Mg<sub>s</sub><sup>2+</sup> sites. These charged adsorbates are not expected to exist in isolation on the MgO surface but rather are expected to form oppositely charged, cooperatively bound pairs with enhanced adsorption energy over the isolated neutrals. While results are demonstrated for adsorption on MgO, they have application to NO<sub>x</sub> adsorption on a wide range of oxide surfaces.

## Introduction

The development of after-treatment and abatement technologies for NO<sub>x</sub> ( $x = 1, 2$ ) is a current challenge in environmental chemistry and emission control. Presently, new catalyst materials are being explored for the effective removal of NO<sub>x</sub> from vehicle exhaust containing excess oxygen. Because traditional three-way catalysts do not effectively remove NO<sub>x</sub> under these “lean” conditions, new combinations of durable, poison-resistant materials are being pursued for effective lean NO<sub>x</sub> abatement.<sup>1</sup>

One solution being explored is NO<sub>x</sub> storage catalysts or “traps” that hold, release, and reduce NO<sub>x</sub> through operation in alternating fuel-lean (NO<sub>x</sub>-oxidizing) and fuel-rich (NO<sub>x</sub>-reducing) modes.<sup>2</sup> The trapping mechanism is thought to involve NO oxidation to NO<sub>2</sub> on a precious metal constituent and subsequent adsorption on an alkaline earth oxide constituent as nitrate (NO<sub>3</sub><sup>-</sup>).<sup>3–45</sup> However, the precise roles of both the precious metal and the metal oxide in the formation of nitrate are not well understood. To help unravel the questions behind this complex adsorption behavior, NO, NO<sub>2</sub>, and NO<sub>3</sub> have been separately characterized on several representative alkaline earth metal oxide surfaces using both experiment and theory.

Temperature-programmed desorption (TPD) experiments indicate that NO desorbs in two peaks from alkaline earth oxide surfaces,<sup>6–13</sup> which have been attributed to two types of surface adsorbates.<sup>12</sup> TPD experiments with isotopically labeled oxygen show exchange between NO and MgO, CaO, and SrO surfaces prior to desorption, which has been proposed to occur via nitrite (NO<sub>2</sub><sup>-</sup>) or nitrate surface intermediates.<sup>11,12,14</sup> Similarly, several in situ Raman and FTIR studies of NO + O<sub>2</sub> reaction on alkaline earth oxides propose metal–nitro, nitrite, or monodentate and bidentate nitrate intermediates or a combination of these as precursors to NO decomposition.<sup>4,15–19</sup>

Computational studies suggest that a single NO molecule weakly adsorbs on the (001) terraces of MgO and CaO, forming neither nitrite nor nitrate. Density functional theory (DFT) cluster calculations show NO to very weakly physisorb atop surface Mg cations (Mg<sub>s</sub><sup>2+</sup>) of MgO(001) with an energy of  $\sim 0^{13}$  and  $-0.3$  kcal/mol,<sup>20</sup> where here and throughout this paper, negative energies indicate exothermic reaction and adsorption. DFT supercell calculations give a somewhat greater physisorption energy of  $-6$  to  $-7$  kcal/mol for NO on MgO terraces with adsorption atop surface O anions (O<sub>s</sub><sup>2-</sup>)<sup>21</sup> or Mg<sub>s</sub><sup>2+</sup> sites.<sup>22</sup> Binding at steps is reported to be only a few kcal/mol more favorable than that at terraces.<sup>22</sup> These DFT results generally agree with the experimental binding energies of  $-5.1$  kcal/mol for NO adsorption on a Mg(001) single crystal<sup>7</sup> and  $-3.4 \pm 0.4$  kcal/mol for NO on bulk MgO(001) powders.<sup>23</sup> Similar to MgO, CaO cluster calculations indicate NO to physisorb on the terrace surface with an adsorption energy of  $-6$  kcal/mol.<sup>24</sup>

NO<sub>2</sub> adsorption experiments exhibit more complex behavior. Rodriguez et al. characterize adsorption of NO<sub>2</sub> on MgO powders and (001) thin films as NO<sub>2</sub> adsorbed as nitrite, which, as temperature is increased, transforms partially to nitrate.<sup>25</sup> Nitrite and nitrate both remain on the surface up to 670–770 K. The nitrite to nitrate transformation is also consistent with the behavior of NO<sub>2</sub> adsorption on ZnO,<sup>26,27</sup> CuO,<sup>28</sup> Fe<sub>2</sub>O<sub>3</sub>,<sup>28</sup> TiO<sub>2</sub>,<sup>29</sup> and alumina-supported BaO.<sup>30</sup> NO<sub>2</sub> was determined through X-ray adsorption near-edge spectroscopy (XANES) experiments to bind more substantially atop lattice O rather than lattice Mg.<sup>26</sup> In contrast, computational results suggest that isolated NO<sub>2</sub> physisorbs on the MgO(001) terrace<sup>21,26</sup> and weakly chemisorbs on the BaO(001) terrace.<sup>31</sup> These computational results suggest that more complicated phenomena account for the experimental observation of chemisorbed surface nitrite and nitrate upon NO<sub>2</sub> exposure.

More recent computational work reveals a large enhancement effect when NO<sub>2</sub> molecules are paired on an alkaline earth oxide surface, leading to a mixture of chemisorbed nitrite and

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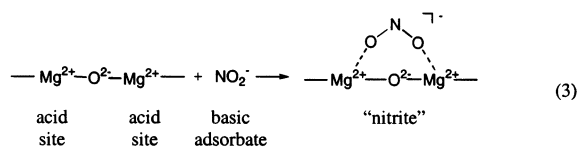
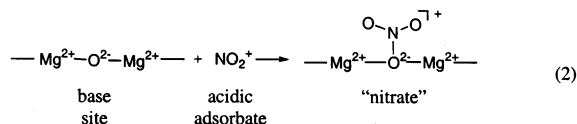
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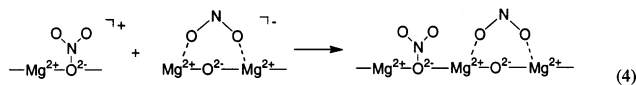
nitrate.<sup>21,31</sup> This “cooperative” adsorption enhancement has been explained in terms of a one-electron transfer between adsorbates yielding charged species with increased adsorption strengths.<sup>21</sup> Cooperative chemisorption of NO<sub>2</sub> on MgO(001), for example, is decomposed in a thermochemical cycle into charge transfer between two gas-phase NO<sub>2</sub>,



adsorption of the resulting charged species on surface Lewis base (O<sub>s</sub><sup>2-</sup>) and acid (Mg<sub>s</sub><sup>2+</sup>) sites,



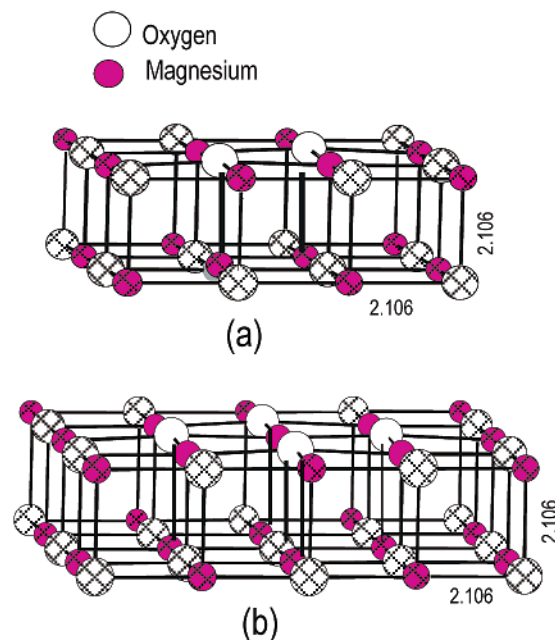
and combination of the locally charged adsorbates to form a cooperative pair,



The cooperative mechanism appears to resolve the main discrepancies between experiment and theory regarding NO<sub>2</sub> chemisorption on MgO. On the basis of this model, cooperative adsorption is expected to occur in situations in which (i) the gas-phase charge-transfer energy requirement (reaction 1 and its analogues) is small and (ii) the charged species thus produced have greater absolute adsorption energies than their neutral parents.

The Lewis base anion sites (O<sub>s</sub><sup>2-</sup>) dominate the surface chemistry of the alkaline earth oxides,<sup>32</sup> which have a lesser contribution from the Lewis acid cation sites (M<sub>s</sub><sup>2+</sup>) sites. Odd-electron NO, NO<sub>2</sub>, and NO<sub>3</sub> are weak to moderately strong Lewis acids and thus would be expected to bind at base sites. NO and NO<sub>2</sub> have relatively low ionization potentials (9.26 and 9.59 eV, respectively),<sup>33</sup> and one-electron oxidation produces closed-shell cations (NO<sup>+</sup> and NO<sub>2</sub><sup>+</sup>) that are potentially much more potent Lewis acids than their neutral parents. Similarly, NO, NO<sub>2</sub>, and NO<sub>3</sub> have moderately large electron affinities (0.03,<sup>34</sup> 2.27,<sup>35</sup> and 3.91 eV,<sup>36</sup> respectively), and reduction by one electron produces the closed-shell anions NO<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup> that are strong electron pair donors.

These one-electron oxidized or reduced adsorbates are not readily studied in isolation via supercell calculations. However, DFT cluster calculations can be used to investigate the differences between single-molecule neutral and ionized nitrogen oxide adsorption on oxide surfaces. In this work, we use cluster models specifically to compare the intrinsic adsorption tendencies of the neutral and charged nitrogen oxides on Lewis acid (Mg<sub>s</sub><sup>2+</sup>) and base (O<sub>s</sub><sup>2-</sup>) sites of model MgO(001) surfaces. We find that the charged adsorbates are stronger Lewis acids and bases than their neutral counterparts, that they bind strongly to the MgO(001) surface, and that they generate structures consistent with supercell calculations<sup>21</sup> of cooperatively bound surface nitrite or nitrate. This determination of NO, NO<sub>2</sub>, and



**Figure 1.** Clusters used in calculations: (a) Mg<sub>16</sub>O<sub>16</sub>; (b) Mg<sub>25</sub>O<sub>25</sub>. Crosshatching designates atoms that were constrained at experimental bulk locations.

NO<sub>3</sub> chemisorption driven by redox processes and acid/base pairing provides a new chemical bonding perspective for NO<sub>x</sub> adsorption on ionic surfaces. The key role of coupled redox and acid–base interactions in driving strong chemisorption of NO, NO<sub>2</sub>, and NO<sub>3</sub> highlights the power of these electronic bonding concepts in describing chemistry at metal oxide–gas interfaces. While the results presented here are focused on the MgO(001) terrace surface, the concepts provide a useful framework for describing the adsorption of amphiphilic molecules on oxides and other ionic surfaces.

## Computational Methods

To treat the neutral and charged adsorbates even-handedly and to facilitate analysis, we employ cluster models of the MgO(001) surface. These models have been used successfully in the past to study NO<sub>x</sub> adsorption on alkaline earth oxide surfaces.<sup>20,25,37</sup> As will be discussed, they provide adsorption geometries and energetics comparable to published supercell calculations of NO<sub>x</sub> adsorption on MgO.<sup>21</sup> While an embedding field of point charges is sometimes used to simulate the electrostatic potential of the extended ionic lattice (e.g., see ref 38), such embedding was not found here to be necessary to obtain reliable results.

All-electron local orbital DFT calculations were performed using a commercial version of DMol<sup>3</sup>.<sup>39</sup> Energies and forces were calculated within the generalized gradient approximation (GGA)<sup>40,41</sup> using the PW91 exchange and correlation functional. For odd-electron systems, calculations were performed spin-unrestricted, while all others were performed spin-restricted. A double numerical plus polarization atom-centered basis set was used. Charge and spin distributions were determined using a Mulliken analysis.

Two different cluster models were employed depending on the position of the adsorbate to take full advantage of symmetry (Figure 1). A Mg<sub>16</sub>O<sub>16</sub> cluster (four ions by four ions by two ions, Figure 1a) was employed for adsorbates bridging two lattice atoms (e.g., the bidentate bridging shown in Figures 2c,d and 3c,d), while a Mg<sub>25</sub>O<sub>25</sub> cluster (five ions by five ions by

two ions, Figure 1b) was used for all other geometries. Top, central surface atoms were allowed to relax, while atoms on the bottom face of the cluster and along the edges were constrained in space at their bulk locations. For all initial geometries, adsorbates were placed in the center above the top face of the cluster. Therefore, all lattice atoms in the immediate vicinity of the adsorbate are pentacoordinated. To promote self-consistent field (SCF) convergence in cases of small HOMO–LUMO gaps, level shifting of the virtual orbitals was applied.<sup>42</sup>

To determine the MgO cluster lattice constant, GGA periodic supercell energy minimization calculations were performed using DMol with the same basis set. The calculated Mg–O separation was 2.116 Å (corresponding to a lattice constant of 4.232 Å), larger than experiment by only 0.010 Å. The experimentally determined Mg–O separation was used in all cluster calculations.

The neutral adsorbate binding energies reported in this work (NO, NO<sub>2</sub>, and NO<sub>3</sub> on MgO) were calculated as the total energy of the energy-minimized adsorbate-on-cluster minus the total energies of the neutral bare cluster and neutral gas-phase adsorbate:

$$E_{\text{binding energy}} = E_{\text{adsorbate and cluster}} - E_{\text{cluster}} - E_{\text{adsorbate}} \quad (5)$$

The binding energies of charged adsorbates (i.e., NO<sup>+</sup>, NO<sub>2</sub><sup>+</sup>, NO<sub>2</sub><sup>−</sup>, and NO<sub>3</sub><sup>−</sup>) were calculated in the same way except using the total energy of the charged gas-phase adsorbate:

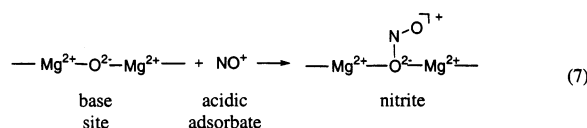
$$E_{\text{binding energy}} = E_{\text{adsorbate and cluster}} - E_{\text{cluster}} - E_{\text{charged adsorbate}} \quad (6)$$

For each NO<sub>x</sub> adsorbate/cluster system numerous starting geometries were examined. The energy-minimized geometries presented in this paper are the configurations that yielded the lowest (most negative) binding energy of all those investigated. Other converged energy-minimized arrangements yielded higher (less favorable) binding energies and will be discussed separately.<sup>43</sup>

As points of reference, Table 1 lists calculated structures and vibrational frequencies of the neutral and charged gas-phase NO<sub>x</sub> species. As shown, the results are consistent with available experimental information.

## Results and Discussion

The role of coupled redox and acid–base processes in controlling the chemisorption of NO<sub>x</sub> species on basic oxide surfaces is demonstrated in this work. The lowest-energy configurations for adsorbed neutral and charged NO, NO<sub>2</sub>, and NO<sub>3</sub> on a model MgO(001) terrace surface are identified, and their bonding modes are characterized. Neutral NO and NO<sub>2</sub> molecular species adsorb weakly with long surface/adsorbate separations and little change in internal structure. One-electron oxidation or reduction strongly modifies the adsorption properties, resulting in species characteristic of chemisorbed nitrite and nitrate. The adsorption reactions can be thought of as Lewis acid–base reactions in which the cationic nitrogen oxides act as strong acids and the anionic ones as strong bases. Thus, chemisorbed nitrite (NO<sub>2</sub><sup>−</sup>) can be thought of as forming either through acidic NO<sup>+</sup> adsorption on basic O<sub>s</sub><sup>2−</sup> sites

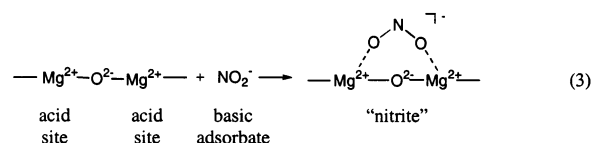


**TABLE 1: Computed Spin-Polarized GGA Bond Lengths (Å), Angles (deg), and Stretch Frequencies (cm<sup>−1</sup>) vs Experimental Values**

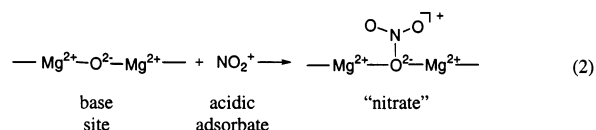
	N–O bond length	O–N–O angle	frequency	ref
		NO		
computed	1.162		1680	
experimental	1.15		1870	44, 45, 46
		NO <sub>2</sub>		
computed	1.208	133.3	1646	
experimental	1.197	134.3	1621	44, 45
		NO <sub>3</sub>		
computed	1.246	120	1791	
experimental	1.236	120		<i>a</i>
		NO <sup>+</sup>		
computed	1.074		2375	
experimental	1.063		2376	47
		NO <sub>2</sub> <sup>+</sup>		
computed	1.132	180	2427	
experimental	1.15	180	2375	44, 48
		NO <sub>2</sub> <sup>−</sup>		
computed	1.283	115.1	1292	
experimental	1.236	115.4	1243	44, 49
		NO <sub>3</sub> <sup>−</sup>		
computed	1.272	120	1354	
experimental			1356	50

<sup>a</sup> The gas-phase structure of NO<sub>3</sub> is the subject of some debate. The comparison here is to results from accurate ab initio calculations assuming a *D*<sub>3h</sub> structure.<sup>51</sup>

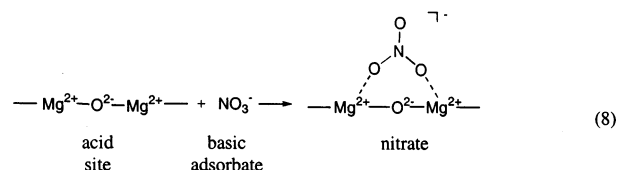
or through NO<sub>2</sub><sup>−</sup> adsorption on acidic Mg<sub>s</sub><sup>2+</sup> sites



Similarly, chemisorbed nitrate (NO<sub>3</sub><sup>−</sup>) forms either via adsorption of NO<sub>2</sub><sup>+</sup> on the O<sub>s</sub><sup>2−</sup> basic sites



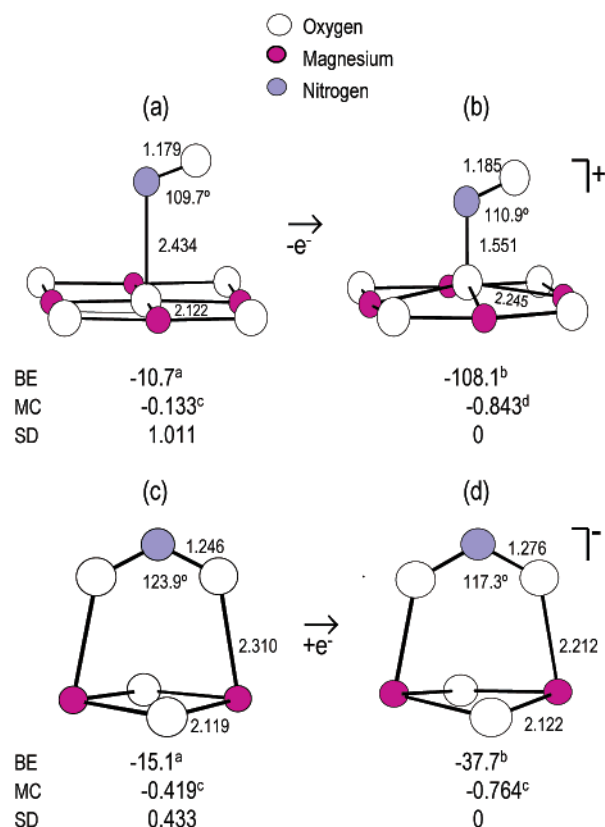
or through adsorption of NO<sub>3</sub><sup>−</sup> on acidic Mg<sub>s</sub><sup>2+</sup> sites



The substantial increase in binding energy of the charged species compared to their neutral counterparts underpins the phenomenon of cooperative chemisorption of NO<sub>x</sub> species.<sup>21</sup>

In what follows, we first compare adsorption of neutral and oxidized NO on the MgO clusters. Next, neutral NO<sub>2</sub> is compared to reduced and oxidized NO<sub>2</sub> for the formation of nitrite and nitrate, respectively. Neutral NO<sub>3</sub> adsorption is investigated and then compared with adsorbed reduced NO<sub>3</sub> for the formation of nitrate. Last, the implications of this work with respect to experiments and cooperative adsorption are examined.





<sup>a</sup> Binding Energy calculated using equation 5

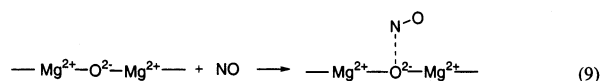
<sup>b</sup> Binding Energy calculated using equation 6

<sup>c</sup> Mulliken charge of adsorbate only

<sup>d</sup> Mulliken charge of adsorbate plus nearest O<sub>s</sub><sup>2-</sup>

**Figure 2.** Adsorption on MgO of (a) NO, (b) NO<sup>+</sup>, (c) NO<sub>2</sub>, and (d) NO<sub>2</sub><sup>-</sup>. Computed spin-polarized GGA adsorbate bond lengths (Å), angles (deg), binding energies (kcal/mol), Mulliken charges (MC), and adsorbate spin densities (SD) are listed. Only atoms nearest to the adsorbate are shown for clarity.

**NO vs NO<sup>+</sup> as Lewis Acids.** The molecular topology necessary for a chemisorbed nitrite can be satisfied by placing NO on an O<sub>s</sub><sup>2-</sup> site:



If the Lewis acidity of neutral NO is substantial enough to facilitate electron transfer from the O<sub>s</sub><sup>2-</sup> site, then chemisorption will occur. In line with previous results, the DFT cluster calculations indicate that the Lewis acidity is not sufficient for chemisorption. NO physisorbs on the Mg<sub>25</sub>O<sub>25</sub> terrace cluster with a binding energy of -11 kcal/mol (Figure 2a). To determine the most favorable geometry, NO adsorption was considered on both Mg<sub>s</sub><sup>2+</sup> and O<sub>s</sub><sup>2-</sup> sites in numerous orientations. The preferred location of NO is bent N-down atop an O<sub>s</sub><sup>2-</sup> site with an adsorbate-surface separation of 2.434 Å. This large N-O<sub>s</sub> separation and minimal perturbation of the adsorbate N-O bond compared to free NO reflect the weak interaction between neutral NO and MgO. In agreement with the small electron affinity of NO, Mulliken analysis indicates transfer of only -0.133 electron from the surface to the adsorbate and localization of the unpaired electron density on the adsorbate (Figure 2a).

Previous DFT calculations are in agreement with physisorption of NO on MgO. Recent supercell calculations indicate NO physisorbs atop O<sub>s</sub><sup>2-</sup> ions with a binding energy of -7.2 kcal/mol and a N-O<sub>s</sub><sup>2-</sup> separation of 2.27 Å.<sup>21</sup> Other recent supercell calculations have predicted NO to sit linearly atop Mg<sub>s</sub><sup>2+</sup> cations with Mg-N and N-O bond lengths of 2.42 and 1.16 Å, respectively, and a binding energy of -6 kcal/mol.<sup>22</sup> B3LYP embedded cluster calculations predict the lowest energy configuration to be a bent atop Mg<sub>s</sub><sup>2+</sup> cations with Mg-N and N-O bond lengths of 2.66 and 1.159 Å, respectively, and a binding energy of -0.3 kcal/mol.<sup>20</sup> The variability of these results reflects the weak surface-adsorbate interaction and its sensitivity to details of the surface model chosen.

The physisorption of NO on the MgO terrace is a result of the weak acid/base interactions between the surface and adsorbate. Electron counting suggests that the O<sub>s</sub><sup>2-</sup>-N-O fragment has one too many electrons to form a nitrite anion (NO<sub>2</sub><sup>-</sup>). Removal of one electron, that is, by adsorbing NO<sup>+</sup> rather than NO, should result in enhanced chemisorption and the formation of nitrite (reaction 7). Indeed, when an electron was removed from the neutral NO-MgO adsorbate cluster and the system was allowed to relax, the adsorbate binding energy increased markedly (Figure 2b).

The most energetically favorable arrangement found for O<sub>s</sub><sup>2-</sup>-NO<sup>+</sup> is similar to that of neutral NO adsorption on MgO but with a much shorter adsorbate-surface separation. The binding energy for NO<sup>+</sup> is a dramatic -108 kcal/mol by eq 6. Additionally, the lattice oxygen closest to the adsorbate is pulled up from the surface, the O<sub>s</sub><sup>2-</sup>-N bond length shortens from 2.434 Å for neutral NO on MgO to 1.551 Å, and the O<sub>s</sub><sup>2-</sup>-N-O angle widens to 110.9° (Figure 2a). The geometric modifications of the O<sub>s</sub><sup>2-</sup>-NO<sup>+</sup> fragment are consistent with a transformation from physisorption to chemisorbed nitrite (Table 1). The Mulliken charge of the O<sub>s</sub><sup>2-</sup>-N-O fragment is -0.843 electron, consistent with a monoanion, and, as will be shown later, is similar to the Mulliken charge of chemisorbed nitrite of a different geometry (Figure 2d). Taken together, these results indicate that strong Lewis acid/base interactions between NO and O<sub>s</sub><sup>2-</sup> can be induced by oxidation. These interactions result in enhanced bonding and the formation of chemisorbed nitrite. Therefore, NO<sup>+</sup> adsorbed on O<sub>s</sub><sup>2-</sup> provides one model for chemisorbed nitrite on MgO.

**NO<sub>2</sub> vs NO<sub>2</sub><sup>-</sup> as Lewis Bases.** Like NO, NO<sub>2</sub> is a potential precursor for surface nitrite formation. In this case, additional oxygen is not necessary to produce the nitrite stoichiometry, but an additional electron is required. As with NO, numerous starting geometries were explored in search of the most energetically favorable orientation for NO<sub>2</sub> on MgO. In its most favorable configuration, neutral NO<sub>2</sub> adsorbs on the MgO cluster O-down and bridging two Mg<sub>s</sub><sup>2+</sup> cations along a [110] diagonal relative to the (001) surface, having an adsorption energy of -15 kcal/mol and a surface-adsorbate separation of 2.310 Å (Figure 2c). The adsorbate Mulliken charge of -0.419 electron suggests greater surface-adsorbate charge transfer than with neutral NO (Figure 2a), commensurate with the increase in binding energy. The decrease in adsorbate spin density to 0.433, compared to 1.011 for NO, further indicates some transfer of charge from the adsorbate to the surface. The greater ability of NO<sub>2</sub> than NO to withdraw electron density from the MgO surface is a consequence of its greater electron affinity (2.273 eV).<sup>35</sup> However, both the small absolute binding energy and large surface-adsorbate separation suggests that adsorbed NO<sub>2</sub> more resembles gas-phase NO<sub>2</sub> than chemisorbed nitrite. DFT

supercell calculations give qualitatively the same structure for physisorbed  $\text{NO}_2$  as that reported here.

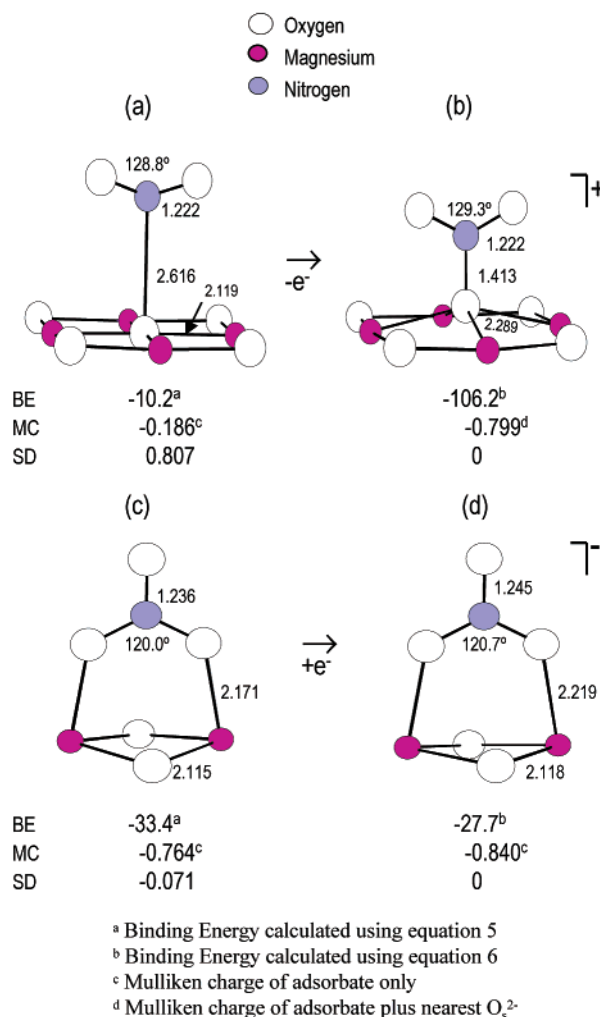
The above results show that neutral  $\text{NO}_2$  does not have sufficient Lewis basicity to strongly chemisorb to  $\text{MgO}$ . Neutral  $\text{NO}_2$  is one electron short of a nitrite ion, and its electron affinity is not great enough to withdraw that extra electron from  $\text{MgO}$ . Supplying an additional electron to  $\text{NO}_2$  should enhance its basicity and its surface adsorption, and in fact, such an enhancement is observed (Figure 2d). The lowest energy configuration for  $\text{NO}_2^-$  is similar to that for neutral  $\text{NO}_2$  (Figure 2c) except that the surface–adsorbate distance decreases by 0.1 Å and the binding energy increases to  $-38$  kcal/mol. Because the cationic sites of  $\text{MgO}$  are not strongly acidic, this increase is not as great as that observed above for  $\text{NO}^+$  adsorption on base sites. The  $\text{NO}_2$  fragment Mulliken charge of  $-0.764$  electron is comparable to the  $\text{O}_s^{2-}$ – $\text{NO}$  fragment Mulliken charge of  $-0.843$  electron observed for  $\text{NO}^+$  adsorption on  $\text{O}_s^{2-}$  (Figure 2b). Furthermore, this increase in Mulliken charge is an indication of increased ionic character of the adsorbate. The  $\text{O}$ – $\text{N}$ – $\text{O}$  angle decreases to  $117^\circ$ , similar to that of  $\text{NO}_2^-$  in the gas phase (Table 1). The increase in adsorbate–surface interaction indicates that one-electron reduction makes  $\text{NO}_2$  a better Lewis base, which facilitates better interaction with acidic  $\text{Mg}_s^{2+}$  ions.  $\text{NO}_2^-$  on  $\text{Mg}_s^{2+}$  sites thus provides a second model for chemisorbed nitrite.

**$\text{NO}_2$  vs  $\text{NO}_2^+$  as Lewis Acids.** As discussed in the previous section, the most favorable configuration for neutral  $\text{NO}_2$  on  $\text{MgO}$  is an O-down and bridging two  $\text{Mg}_s^{2+}$ . Neutral  $\text{NO}_2$  is also found to physisorb N-down atop  $\text{O}_s^{2-}$  sites, but with a less favorable binding energy of  $-10.2$  kcal/mol (Figure 3a). The large surface–adsorbate separation of  $2.616$  Å is characteristic of physisorption, and the small adsorbate Mulliken charge and large spin density are consistent with a weak surface–adsorbate interaction. Under these conditions,  $\text{NO}_2$  is a weak Lewis acid atop a basic  $\text{O}_s^{2-}$  site unable to undergo sufficient charge transfer to facilitate chemisorption.

Electron counting shows that the  $\text{O}_s^{2-}$ – $\text{NO}_2$  fragment possesses one too many electrons for a nitrate ( $\text{NO}_3^-$ ). As shown in Figure 3b, removal of this excess electron by oxidation of the neutral  $\text{NO}_2$ – $\text{MgO}$  cluster causes a dramatic change in structure and energetics (Figure 3b) consistent with conversion to surface nitrate (reaction 2).  $\text{NO}_2^+$  binds to the cluster by  $-106$  kcal/mol. The surface–adsorbate separation decreases to  $1.412$  Å and, like the oxidized  $\text{O}_s^{2-}$ – $\text{NO}$  system (Figure 2b), the lattice oxygen is noticeably pulled up from the surface. The Mulliken charge for the  $\text{O}_s^{2-}$ – $\text{NO}_2$  fragment is  $-0.799$  electron and suggests much stronger surface–adsorbate electron transfer compared to that of neutral  $\text{NO}_2$  adsorption. Furthermore, as will be shown below, it is similar to the Mulliken charge observed for chemisorbed nitrate in a different geometry (Figure 3c). Oxidation enhances the adsorption of  $\text{NO}_2$  on a Lewis base site, and the resultant structure provides one model for chemisorbed nitrate on  $\text{MgO}$ .

**$\text{NO}_3$  vs  $\text{NO}_3^-$  as Lewis Base.** Gas-phase  $\text{NO}_3$  is a strongly oxidizing, highly reactive species that may play an important role in surface reactions involving  $\text{NO}_x$  in oxidizing environments. As with other adsorbates, the strength of the  $\text{NO}_3$ –surface interaction depends on the Lewis acid/base properties of the adsorbate and the surface.

Numerous starting geometries were explored to find the most energetically favorable adsorption geometry for neutral  $\text{NO}_3$ . In its lowest energy configuration, neutral  $\text{NO}_3$  adsorbs on the  $\text{MgO}$  surface O-down and bridging two  $\text{Mg}_s^{2+}$  sites along the  $[110]$  diagonal (Figure 3c), similar to neutral  $\text{NO}_2$  but with a



**Figure 3.** Adsorption on  $\text{MgO}$  of (a)  $\text{NO}_2$ , (b)  $\text{NO}_2^+$ , (c)  $\text{NO}_3$ , and (d)  $\text{NO}_3^-$ . Computed spin-polarized GGA adsorbate bond lengths (Å), angles (deg), binding energies (kcal/mol), Mulliken charges (MC), and adsorbate spin densities (SD) are listed. Only atoms nearest to the adsorbate are shown for clarity.

much larger binding energy of  $-33$  kcal/mol. The surface–adsorbate separation is only  $2.171$  Å, compared with  $2.310$  Å for neutral  $\text{NO}_2$ . The significantly negative adsorbate Mulliken charge and small spin density both indicate a significant oxidation of the  $\text{MgO}$  surface by  $\text{NO}_3$ . This Mulliken charge is comparable to that for chemisorbed nitrate formation via  $\text{NO}_2^+$  adsorption on  $\text{O}_s^{2-}$  (Figure 3b).

Neutral  $\text{NO}_3$  thus behaves qualitatively differently than neutral  $\text{NO}$  or  $\text{NO}_2$  on the  $\text{MgO}$  surface.  $\text{NO}_3$  has sufficient electron affinity ( $3.91$  eV)<sup>36</sup> to oxidize the  $\text{MgO}$  surface by nearly a full electron, and the resultant  $\text{NO}_3^-$  binds readily to  $\text{Mg}_s^{2+}$  acid sites. Supercell calculations give nearly identical structures and energetics for  $\text{NO}_3$  adsorption,<sup>21,25</sup> further demonstrating the robustness of the cluster models used here. Unlike neutral  $\text{NO}$  and  $\text{NO}_2$ , isolated  $\text{NO}_3$  is able to satisfy its valency and to become nitrate-like through oxidation of the  $\text{MgO}$  surface.

The strongly oxidizing  $\text{NO}_3$  becomes nearly fully reduced by interaction with the  $\text{MgO}$  surface. Reduction of  $\text{NO}_3$  by one electron does not enhance this surface–adsorbate interaction. The adsorption of  $\text{NO}_3^-$  on the  $\text{MgO}$  cluster is found to be  $6$  kcal/mol less favored than is that of neutral  $\text{NO}_3$ , and the surface–adsorbate separation ( $2.219$  Å) increases by  $0.05$  Å (Figure 3d). In this case, the additional electron does not enhance the basicity of  $\text{NO}_3$  but rather is delocalized over the cluster,

neutralizing the positive charge induced by NO<sub>3</sub>. As evidence, the adsorbate Mulliken charge in the reduced system is only slightly more negative than that in the neutral one.

This result illustrates the importance of adsorbate electron affinity in controlling chemisorption. When an adsorbate has sufficient Lewis acidity or basicity, oxidation or reduction is not necessary to promote acid–base pair formation between the surface and adsorbate. Because NO and NO<sub>2</sub> are weak Lewis acids, they must be oxidized or reduced by one electron to effectively chemisorb: strongly bound nitrite was formed only after NO<sup>+</sup> or NO<sub>2</sub><sup>−</sup> adsorption and strongly bound nitrate was formed from NO<sub>2</sub><sup>+</sup> on O<sub>s</sub><sup>2−</sup> sites. Neutral NO<sub>3</sub> is a strong enough oxidant to form NO<sub>3</sub><sup>−</sup> by direct oxidation of MgO and does not require an additional electron to promote adsorption on MgO. However, if more ready electron sources are available than the MgO surface itself, for example, a nearby NO or NO<sub>2</sub>, the electron will be withdrawn from these stronger donors rather than from the surface itself.<sup>21</sup>

## Conclusions

These results provide new insight into the molecular nature and energetics of nitrite and nitrate formation on alkaline earth oxide surfaces. We have shown that it is conceptually useful to consider NO<sub>x</sub> chemisorption on MgO to occur via one-electron oxidations or reductions that produce strong Lewis acids and bases. Thus, two types of chemisorbed nitrite can be considered to derive from acidic NO<sup>+</sup> adsorption on basic O<sub>s</sub><sup>2−</sup> sites (Figure 2b) or basic NO<sub>2</sub><sup>−</sup> adsorption on acidic Mg<sub>s</sub><sup>2+</sup> sites (Figure 2d). Similarly, chemisorbed nitrate can be considered to derive from acidic NO<sub>2</sub><sup>+</sup> adsorption on basic O<sub>s</sub><sup>2−</sup> sites (Figure 3b) or from basic NO<sub>3</sub><sup>−</sup> adsorption on Mg<sub>s</sub><sup>2+</sup> sites (Figure 3c). While in the first three cases the charged adsorbates must be formed by addition or subtraction of an electron from the system, in the last case NO<sub>3</sub> itself has sufficient electron affinity to abstract an electron from the model MgO cluster to form the anionic adsorbate. These nitrite and nitrate types should exhibit distinct vibrational and electronic spectra, and their identification remains a challenge.

These charged adsorbates are models for nitrite and nitrate species possible on an oxide surface. They are not expected to exist in isolation; rather, the enhanced chemisorption properties of the cationic and anionic species suggest that they pair on the surface to form locally neutral and strongly bound adsorbates. In fact, just such “cooperative” adsorption has been demonstrated using supercell DFT calculations.<sup>21,31</sup> Within this model, NO<sub>2</sub> chemisorption can be thought of as arising from pairing of NO<sub>2</sub><sup>+</sup> and NO<sub>2</sub><sup>−</sup>:



where MO could represent any alkaline earth oxide. Similarly, other NO<sub>x</sub> combinations can produce cooperative pairs of nitrite



or of nitrate



The cluster DFT results, by showing that oxidation or reduction does enhance the adsorption properties of the NO<sub>x</sub> species and by demonstrating that the resultant structures are entirely consistent with the cooperative pairs predicted from supercell calculations, reinforce the cooperative chemisorption model.

These findings provide a new framework for understanding the formation of chemisorbed surface NO<sub>x</sub> on all oxide surfaces in terms of adsorbate oxidizing strength, acid–base pair formation, and redox processes. They may well have ramifications for the adsorption of other amphoteric, odd-electron species, such as the halogen oxides, on metal oxide surfaces.<sup>21</sup>

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## References and Notes

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