NO_x Storage on BaO(100) Surface from First Principles: a Two Channel Scenario

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 NO_2 adsorption at a BaO(100) surface is investigated by means of spin polarized GGA density functional theory. A periodic supercell procedure is employed, and two redox reaction channels are mapped out, involving two chemisorbed NO_2 molecules per supercell. The chemisorption is studied in two subsequent steps. The reaction paths are initiated by NO_2 adsorption in the form of a nitrite over a Ba^{2+} site. This generates an electron hole among the surrounding surface oxygen atoms. A reaction path branching occurs as the second NO_2 either (a) acts as surface oxidant, forming a surface nitrite—peroxide pair by releasing NO(g), or (b) binds to an O^-_{surf} site to form a formal surface nitrate. A redox reaction involving surface nitrite—nitrate interconversion is also addressed. The computed results are employed to interpret experimental observations of surface nitrites, peroxides, NO(g) desorption, and surface $Ba(NO_3)_2$ formation. The understandings are discussed in the context of the NO_x storage concept of lean-burn catalysis.

1. Introduction

The demand for lower fuel consumption in gasoline engines has led to the introduction of lean-burn engines where the engine is operated at oxygen excess.¹ This concept yields a more efficient combustion and reduces the fuel consumption in comparison to "stoichiometric combustion". Increased combustion efficiency implies reduced CO₂ emissions in conjunction with effectively eliminating CO and hydrocarbon emissions. A drawback of the lean-burn engine is that NO_x cannot be efficiently removed with a catalytic converter. One possible solution to this problem comprises the NO_x storage concept, where a storage function in the catalytic converter is combined with mixed operation conditions of the engine.² During lean periods NO_x is trapped by the storage material, while during short fuel-rich intervals it is regenerated by NO_x release and subsequent reduction with hydrocarbons H₂ and CO to form N₂, H₂O, and CO₂. Detailed mechanistic knowledge of the interaction of NO_x with the storage component is of vital importance for optimizing this concept. Key parameters to investigate include, e.g., temperature stability, NO_x storage capability, regeneration times, and hindering of sulfur deactivation.

Several investigations regarding NO_x storage on aluminasupported barium oxide are found in the literature.^{2–9} Experiments with simplified gaseous compositions and model catalysts have been employed in order to gain knowledge of various aspects of the real system.^{6,7} Thus, influence of, e.g., carbonate and hydroxyl formation has been removed in order to obtain knowledge of the interplay between NO_x and the storage compound alone. Indeed, competition between CO₂ and NO₂ for the same adsorption sites has previously been demonstrated.⁹ Also relevant is the finding that, in case of NO, the NO_x storage capacity is crucially dependent on an intermediate NO oxidation step to NO₂ before the storage can take place under lean conditions.^{7–9} This initial oxidation step, employing a Pt catalyst, limits the storage rate for the temperature range below where the storage capacity displays its maximum, i.e., T < 380 °C. At T > 450 °C, the stored compounds are found to decompose rapidly.^{7,8}

When a storage catalyst is exposed to NO₂, both trapping of NO₂ and release of NO can be observed. This tells of a redox process involving oxidation of either the oxide surface or an adsorbed species upon NO₂ reduction. Fridell et al.⁸ discuss this NO release in view of two different possible processes, either surface nitrites are converted to nitrates, or, formation of surface peroxides result from oxidation of the oxide surface, predominantly BaO, by NO₂. FTIR studies of the interaction of NO₂ with BaO/Al₂O₃ samples show formation of surface nitrites and nitrates. Experiments at 100 °C indicate that the formation of nitrites precedes the formation of nitrates. Formation of bulk nitrates is not observed on the relevant time scales for NO_x storage. Thus, a plausible mechanism for NO_x storage becomes one where the oxidation of NO to NO₂ over Pt is followed by formation of surface nitrites on the BaO surface. These are further oxidized to nitrates by NO₂ with desorbing NO as a result. However, a mechanism involving BaO₂ cannot be ruled out. Kinetic modeling of NO_x storage on Pt/Al₂O₃ and Pt/BaO/ Al₂O₃ has been undertaken based on these two mechanisms.⁷

The present work aims at complementing the available experimental work with a theoretical study. In this paper we have chosen to focus on the interaction between NO_x and barium oxide. NO_x in the form of NO_2 is employed, as experiments conclude that the oxidation of NO to NO_2 precedes the actual storage of NO_x . The storage compound, barium oxide, is in the form of a clean BaO(100) surface, cleaved from the geometry optimized BaO bulk structure. The (100) surface is generally considered to be the most stable one for BaO(s). It consists of five coordinated Ba and O atoms in the top layer of atoms. The complexity of surface properties due to steps, oxygen vacancies, etc. is not considered in this paper. Enhancement effects of surface defects such as kinks and steps have been demonstrated on CaO surfaces¹⁰ where it may be of great importance for NO_x

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adsorption. Below, we demonstrate that the BaO (100) surface is highly reactive toward NO_2 adsorption, and activation becomes unnecessary. Similar ideas have been proposed by Pettersson et al.¹¹

The interaction between NO₂ and BaO(100) is studied using periodic supercell density functional theory (DFT) within the gradient corrected local density approximation (GGA). Pseudo potentials are employed to describe the inert core electrons.¹² Key steps in the NO₂ adsorption on a BaO(100) surface are generated from first-principles, and an NO₂ storage scenario is formulated. Possible connections to the proposed storage mechanism by Fridell et al.⁸ are highlighted.

2. Method

2.1. Theoretical Method and Computational Details. Structures and binding energies were produced for NO₂, NO₂⁻, NO₃⁻, and NO bound at the barium surface site (Ba^{2+}_{surf}) and oxygen surface site (O^{2-}_{surf}) of BaO(100). All calculations were performed using the commercial version of CASTEP¹² as implemented in Cerius^{2,13} A large body of existing work indicates that CASTEP is indeed useful for predicting structural properties and energy changes associated with chemical transformations involving oxides (see, e.g., refs 14–16).

CASTEP employs a plane wave expansion of the wave functions associated with the valence electrons. This basis set is determined by selecting a kinetic energy cutoff, E_{cut} . The tightly bound core electrons are represented by nonlocal ultrasoft pseudopotentials as proposed by Vanderbildt.¹⁷ Reciprocal space integration over the Brillouin zone is approximated through a careful sampling at a finite number of k points using the Monkhorst-Pack scheme.¹⁸ The exchange-correlation contribution to the total electronic energy is treated in the spin polarized generalized gradient approximation (GGA) extension to the local density approximation (LDA) by Perdew et al.,19 as implemented in the CASTEP software package (GGS-PBE).12 In all calculations, the kinetic energy cutoff and the density of the Monkhorst-Pack k-point mesh were chosen high enough so as to ensure convergence of the computed structures and energetics. The E_{cut} was set to 300 eV and the k-point spacing was set to 0.05 \AA^{-1} . The methodological accuracy in adsorption energies and molecular bond distances were converged to within ± 0.05 eV, and ± 0.01 Å respectively. This was deemed sufficient for the present investigation.

To model the BaO(100) surface, a two-layer slab was cleaved from the geometry optimized bulk structure and modeled by a periodic supercell. A $\sqrt{2} \times \sqrt{2}$ supercell was employed in conjunction with a 9 Å vacuum thickness. Tests on convergence of adsorption energies were performed by using a three-layer slab and by varying the vacuum thickness in the interval 9–15 Å. Insignificant differences in binding energies were obtained. Following usual convention, the adsorption energies E_{ads} were calculated according to the following expression:

$$E_{\rm ads} = E_{\rm slab + molecule} - (E_{\rm slab} + E_{\rm molecule}) \tag{1}$$

where E_{molecule} is the energy of the isolated adsorbate in its equilibrium configuration, E_{slab} is the total energy of the isolated slab, and $E_{(\text{molecule+slab})}$ is the total energy of the adsorbate + slab supersystem. Negative adsorption energies denote an exothermic adsorption process.

The purpose of this study is to produce information regarding structures and relative stabilities for the different NO₂ derivatives on the surface. Therefore, all calculations were performed with a fixed surface, while the sorbate geometries were optimized.



Figure 1. Position of chemisorbed NO_2 with N centered over a surface oxygen site. (a) Top view and (b) side view with bond length [Å] and angle [degrees] indicated.

In case of chemisorption involving a surface oxygen, the position of the latter was included in the geometry optimization. Earlier studies addressing surfaces of the alkaline earth metal oxides MgO and CaO have shown the surface not to change significantly upon chemisorption when allowing the initial bulk parameters to relax.^{10,20} Such secondary relaxation may be larger in case of the BaO substrate due to the weaker restoring Madelung potential. Such effects will be quantified in a future study.

2.2. Experimental Method. NO₂ adsorption and NO/NO₂ desorption from a BaO/Al₂O₃ monolith catalyst were monitored by TPD experiments in a flow reactor system. The monolith catalyst was prepared by wet deposition methods as described in ref 5, and the resulting washcoat consisted of 20 wt % BaO and 80 wt % γ -Al₂O₃. In situ detection of NO and NO₂ in the flow reactor was made with a chemiluminescence detector as described in ref 21. TPD measurements were performed by first conditioning the sample at 600 °C in Ar and then cooling it to the adsorption temperature in Ar for 1 min. 500 ppm NO₂ in Ar was subsequently introduced for 10 min, and after another min in Ar, a temperature ramp from the adsorption temperature up to 600 °C with 20 °C/min in Ar was commenced.



Figure 2. Position of chemisorbed nitrite over a surface barium site. (a) Top view and (b) side view with bond lengths [Å] and angle [degrees] indicated.

3. Results and Discussion

Electronic structure calculations and geometry optimizations were performed in order to determine the relative stabilities of the most relevant species formed when a clean BaO(100) surface is exposed to NO₂(g). The scenario is unravelled as follows: in section 3.1 initial adsorption of NO₂ on a surface oxygen site is considered; section 3.2 contrasts the former by the initial adsorption of NO2 on a surface barium site; section 3.3 addresses chemisorption of two NO2 molecules as nitrite-nitrate pairs, where the nitrite adsorbs on a barium site and the nitrate involves a surface oxygen. Section 3.3 addresses also subsequent redox reactions among the adsorbates to form nitrate-nitrite pairs and the stability of an all-nitrate surface phase at 25% coverage resulting from NO₂(g) reduction to NO(g). Section 3.4 describes a competing reaction channel to that described in section 3.3 as it involves the formation of transient nitrite-peroxynitrite pairs, followed by disproportionation of the Osurf-O-NO species into NO(g) and a surface peroxide.

The theoretical findings are discussed in detail below and are used to interpret experiments.



Figure 3. (a) Spin density plot for NO_2 adsorbed over a barium site. The spin is seen to delocalize over the adsorbate and the surrounding surface oxygen ions. (b) Spin density plot for NO_3 adsorbed over a surface barium site. The spin density is seen to delocalize over the surface oxygens alone. (c) Charge density plot emphasising the electrostatic nature of the bond between the $NO_2(ads)$ and the Ba^{2+} -site, i.e., nonoverlapping adsorbate/surface charge distributions.

3.1. Initial Adsorption of NO₂ at an O_{surf} Site. When molecular NO₂ approaches a clean BaO(100) surface at low



Figure 4. Optimized structure of the surface nitrite–nitrate pair on BaO(100). (a) Top view and (b) side view with bond lengths [Å] indicated.

coverage, electrostatic interactions guide the positive nitrogen of NO₂ toward a surface oxygen site. An initial O_{surf}–NO₂ bond distance of 2.39 Å is obtained for the adsorbate/substrate compound and it is depicted in Figure 1. This suggests a physisorbed species, but binding energies in the range of 0.8 ± 0.05 eV in conjunction with the structure of the adsorbate approaching that of NO₂⁻ imply the adsorbate to be chemisorbed. Indeed, the experimental 1.24 Å N–O bond length in the nitrite ion and the 115.4° O–N–O bond angle²² compare reasonably with the 1.25 Å and 121° obtained here for the surface species. The latter result is also reflected in the spin density map, which has the spin to a great extent delocalized over the adsorption site, i.e., O_{surf}, indicating a partial electron transfer from the oxygen site to the adsorbed NO₂ molecule.

The fact that NO₂ is found to chemisorb weakly with a long O_{surf} -N bond distance is chemically intuitive, since it amounts to the formation of an "NO₃²⁻" surface species, which has the unpaired electron in the antibonding O_{surf} -N orbital. The alternative would be the formation of an NO₃⁻ surface species, but the extra electron would then have to reduce Ba²⁺, which is not observed in the calculations.

3.2. Initial Adsorption of NO₂ on a Ba_{surf} Site. Crucial to the NO₂ loading is the adsorption configuration whereby a single NO₂ is found to bind at a Ba²⁺_{surf} site, see Figure 2. Similar to the description in section 3.1, also here NO₂ chemisorbs as a



Figure 5. Optimized structure of the surface nitrate-nitrite pair on BaO(100). The two NO_2 molecules in Figure 4 have undergone a disproportionation (redox) reaction. (a) Top view and (b) side view with bond lengths [Å] indicated.

surface nitrite, i.e., (i) an electron transfer from substrate to adsorbate occurs, (ii) the structure approaches that of NO2⁻, and (iii) a 0.7 eV adsorption energy is obtained. Although apparently trivial, this surface species is decisive to the mechanism for further NO₂ storage. Given a priori that $NO_2(g)$ has an unpaired electron, it implies that the BaO surface becomes partially oxidized when forming a nitrite at the Ba site. This feature can be demonstrated by performing spinpolarized calculations and plotting the spin density, see Figure 3. It is clearly seen how this density is delocalized over both adsorbate and adjacent substrate oxygen ions. Thus, while the NO₂ adsorption energy could be interpreted to result from electrostatic interactions between an ionic surface site and a neutral but polar molecule, the spin density distribution and indeed also the NO₂(ads) structure ($R_{\rm N-O} = 1.26$ Å, V(O–N– $O = 118^{\circ}$ both clearly infer electron transfer. Thus the bonding must be described as a chemisorption rather than a physisorption event.

The degree to which the Ba^{2+}_{surf} - NO_2^- interaction is noncovalent can be appreciated from the fact that binding energies in the range 0.5–0.7 eV are obtained for the four most stable chemisorption arrangements, comprising the monodentate structures Ba-NO₂ and Ba-O-NO, in conjunction with the bidentate structures Ba-O₂N and Ba-ON-O. Still, the latter



Figure 6. Optimized structure of the surface nitrate-nitrate pair on BaO(100). (a) Top view and (b) side view with bond lengths [Å] indicated.

is found to display the global minimum on the potential energy surface. In this structure, the molecule binds with the molecular plane orthogonal to the surface plane. The atomic arrangement is such that one oxygen atom points away from the surface, while the molecule binds to the surface with the doubly occupied highest occupied molecular orbital of local π symmetry with respect to the remaining NO bond. The low electron density between N and Ba (see Figure 3c) supports the understanding of an ionic bond.

The net stability of the surface nitrite species can be understood to result from three contributions, including (a) the significant electron affinity of NO₂ (2.27 eV),²³ (b) the resulting Ba^{2+}_{surf} to NO₂⁻ electrostatic interaction, and (c) the loss of lattice energy as an O²⁻ is effectively oxidized to O⁻. To the extent that the Madelung potential is decisive for the stability of the formal doubly charged oxygen anions in the alkaline earth oxides, the lattice constant must be deemed critical for the initial formation of surface nitrites.

3.3. Further NO₂ Storage and Surface Nitrite–Nitrate Redox Reaction. The increasingly undressed columbic interactions among the adsorbates with increasing nitrite coverage would be the main mechanism for controlling the NO₂ storage along the initial adsorption channels outlined above. It is found that a channel for additional loading comes into play already before this limit is reached. Indeed, it was stressed above, that



Figure 7. Optimized structure of a single surface nitrate ion over a Ba^{2+} -site on BaO(100). (a) Top view and (b) side view with bond lengths [Å] indicated.

the initial nitrite formation channel, described in section 3.2, is associated with the formation of a delocalized unpaired electron on the surface oxygens in the vicinity of the Ba^{2+}_{surf} - $NO_2^$ site. This result suggests that initial formation of surface nitrites over barium sites activates new chemisorption sites comprising the adjacent O⁻_{surf} sites. Thus, a key intermediate step in the NO₂ loading on BaO(s) involves the pairwise formation of nitrate analogues [O_{surf}-NO₂]⁻ and surface Ba nitrites.

To test this possible understanding, a second NO₂ molecule was introduced into the supercell and placed on a surface oxygen adjacent to the Ba^{2+}_{surf} -NO₂⁻ site. Geometry optimization was performed and an additional 1.0 eV adsorption energy is obtained, which is slightly greater than what was found for a single NO₂ at a barium site. This result supports possible formation of transient nitrite-nitrate pairs at intermediate initial nitrite coverages. The resulting bonding configuration for the nitrite-nitrate pair is depicted in Figure 4, where the proximity between adjacent nitrite and nitrate ions can be appreciated. The distance between O on the nitrate and N on nitrite is approximately 3 Å, which limits the NO₂ loading at the BaO-



Figure 8. Structure of the surface nitrite—peroxynitrite pair transient, which may lead to surface peroxide formation and NO(g) release. (a) Top view and (b) side view with bond lengths [Å] indicated.

(100) surface. In principle, it would be possible for the nitrite and nitrate to switch sites, and one possible rearrangement comprises nitrate-to-nitrite oxygen transfer. Indeed, an additional 0.3 eV stability gain is observed upon such a rearrangement (see Figure 5). The resulting nitrite ion formed by this redox reaction can be understood to consist of an NO molecule bound to a surface O⁻ site. This species in the (nitrate on Ba)–(nitrite) pair displays slightly greater stability toward NO desorption than does NO₂ in the (nitrite on Ba)–(nitrate) pair (1.1 eV vs 1.0 eV for the latter). Introduction of a third NO₂ molecule allows oxidation of the NO at the O⁻_{surf} site, whereby a nitrate–nitrate surface pair is formed and an NO(g) molecule is released. This reaction comes out marginally endothermic by 0.2 eV. The resulting structure is depicted in Figure 6.

To complete the picture, we describe the situation resulting from a nitrate sitting at the Ba^{2+}_{surf} site, depicted in Figure 7, when first removing NO/NO₂ from the O⁻_{surf} site. As expected, the Ba^{2+}_{surf} nitrate is found to be more stable toward desorption of an NO₃(g) species than is Ba^{2+}_{surf} nitrite toward desorption of NO₂, i.e., 0.9 eV vs 0.7 eV. This is reflected in the greater



Figure 9. Optimized structure of the surface nitrite species and peroxide on BaO(100). (a) Top view and (b) side view with bond lengths [Å] and angle [degrees] indicated.

electron affinity (EA) of NO₃ than that of NO₂, i.e., 3.91 eV^{24} vs 2.27 eV,²³ respectively. An efficient illustration as to the significance of this EA difference is found in the spin density distribution for the Ba²⁺_{site}-NO₃⁻ surface compound (see Figure 3b), where the spin density is seen to delocalize exclusively on the surface oxygens. This is in contrast to the nitrite formation at the barium site, where significant spin density is found to remain on the adsorbate (see Figure 3a).

3.4. Peroxide Formation on BaO(100). A surface reaction competing with the formation of surface nitrite-nitrate pairs comprises the nitrite-peroxynitrite channel. When an oxygen site has been activated by nitrite formation at an adjacent barium ion, a second NO₂ can form an O_{surf} -O-NO transient (see Figure 8), which subsequently dissociates into an O_{surf} -O species and NO(g) (see Figure 9). Loss in stability of ~0.4 eV is associated with this reaction. Analysis of the electronic spin density reveals that a surface peroxide is formed as no spin density is found on this species. Rather, the spin is located on the nitrite and the remaining O_{surf} sites. This NO(g) release is thus understood to reactivate the surface, although some O_{surf} sites are replaced by surface peroxides. The fact that the unpaired electron is shared among fewer O_{surf} sites results in a more NO₂-



Figure 10. Diagram summarizing the relative stabilities of the species considered in the present study. Transient species 1 and 2 correspond to initial adsorptions of single NO_2 molecules. Two channels for further NO_2 storage, indicated A and B, refer to intermediate peroxide formation and direct pairwise NO_2 loading, respectively. Adsorption energies are given in eV; triplet excited state in brackets, denoted *.

TABLE 1:	Results from	Geometry O	ptimization	Calculations
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reaction	cf. Figure 10	$\Delta E [eV]$
$NO_2(g) + BaO \rightarrow Ba^{2+} - [O_{surf} - (NO_2)]^{2-}$	0→1	-0.8
$NO_2(g) + BaO \rightarrow Ba^{2+}(NO_2^{-}) - O_{surf}^{-}$	0→2	-0.7
$NO_2(g) + Ba^{2+}(NO_2^{-}) - O_{surf}^{-} \rightarrow Ba^{2+}(NO_2) - [O_{surf}^{-} - O]^{2-} + NO(g)$	2 → 4A	0.4
$Ba^{2+}(NO_2)-[O_{surf}-O]^{2-} \rightarrow Ba^{2+}(NO_3^{-})-O_{surf}^{-}$	4A→5	-0.6
$NO_2(g) + Ba^{2+}(NO_2^{-}) - O^{-}_{surf} \rightarrow Ba^{2+}(NO_2^{-}) - [O_{surf} - (NO_2)]^{-}$	2 → 3B	-1.0
$Ba^{2+}(NO_2^{-}) - [O_{surf} - (NO_2)]^{-} \rightarrow Ba^{2+}(NO_3^{-}) - [O_{surf} - (NO)]^{-}$	3B→4B	-0.3
$Ba^{2+}(NO_3^-) - [O_{surf} - (NO_2)]^- \rightarrow Ba^{2+}(NO_3^-) - O_{surf}^- + NO_2(g)$	3B→5	0.8
$NO_2(g) + Ba^{2+}(NO_2^{-}) - [O_{surf} - (NO_2)]^{-} \rightarrow Ba^{2+}(NO_3^{-}) - [O_{surf} - (NO_2)]^{-} + NO(g)$	3B→6	-0.1
$Ba^{2+}(NO_3^{-}) - [O_{surf}^{-}(NO)]^{-} \rightarrow Ba^{2+}(NO_3^{-}) - O_{surf}^{-} + NO(g)$	4B→5	1.1
$NO_2(g) + Ba^{2+}(NO_3^-) - [O_{surf}^-(NO)]^- \rightarrow Ba^{2+}(NO_3^-) - [O_{surf}^-(NO_2)]^- + NO(g)$	4B→6	0.2
$NO_2(g) + Ba^{2+}(NO_3^{-}) - O^{-}_{surf} \rightarrow Ba^{2+}(NO_3^{-}) - [O_{surf} - (NO_2)]^{-}$	5→6	-0.9

^{*a*} The corresponding reaction scheme is depicted in Figure 10. ΔE is calculated according the expression: $\Delta E = E_{ads}$ (products) – E_{ads} (reactants). Negative ΔE corresponds to an exothermic reaction.

like species at the Ba site. This is seen in the slight shortening of the bond length (0.01 Å) and the slightly increased bond angle (119.5°) for this species.

The detailed energy balance in the peroxide formation channel is emphasized. Such a bond displays a typical stability of 2.5 eV.²⁵ The simultaneous N–O bond dissociation in the NO₂ molecule, whereby NO(g) is formed, results in an accidental approximate cancellation of energy contributions.

Finally, the oxidative power of the surface peroxy species toward oxidation of the Ba²⁺ associated nitrite ion was tested. The results give that a Ba²⁺ associated nitrate is the energetically more favorable surface species by 0.2 eV. This property can be taken to infer that spurious peroxides at the BaO surface do not inhibit NO_x loading at lean combustion conditions, since as long as NO₂⁻ ions are present at the Ba²⁺ sites, these will act to reduce the surface.

3.5. Results and Interpretation of Experiment. The theoretical results, presented in sections 3.1-3.4, are summarized in Figure 10 and in Table 1. These findings are used to explain the experimental results, depicted in Figure 11.

The NO(g) and NO₂(g) concentrations during NO₂ storage at 400 $^{\circ}$ C are depicted in Figure 11a. As learned from other

studies,^{6,8} an initial NO(g) release is observed during this process. Three contributions to the experimentally observed initial NO(g) desorption during NO₂ loading (see Figure 11a) were discussed above. These comprise NO₂ reduction by surface peroxide formation (see transient from 3A to 4A in Figure 10), heterogeneous $Ba^{2+}-NO_2^-$ oxidation (see transient from 3B to 6 in Figure 10), and heterogeneous oxidation of $[O_{surf}-NO]^-$ (see transient from 4B to 6 in Figure 10). Both the latter reactions along the reaction path B produce the formal surface $Ba(NO_3)_2$ compound.

Temperature programmed desorption (TPD) measurements of NO_x (see Figure 11b) are determined to come from two contributions. For a heating rate of 20 °C/min from 300 to 600 °C, NO₂ is seen to desorb with a peak at 470 °C (see Figure 11b) in conjunction with an NO desorption peak at 530 °C. This ordering is understood from the computed coverage dependence of initial NO₂ adsorption found in the range 0.7– 1.0 eV (see transient species 2 and 3B in Figure 10). When considering the NO release, two sources contribute from transient species 4B and one from the surface Ba(NO₃)₂ end product. Direct NO release from transient species 4B produces transient species 5 with an energy cost of 1.1 eV, while the



Figure 11. (a) Concentration of NO and NO₂ during exposure of 500 ppm NO₂ to a BaO/Al₂O₃ sample at 400 °C. Note the appearance of an NO peak at t = 100 s and its exponential decay with time. (b) Concentration of NO and NO₂, detected during temperature programmed desorption experiment after exposure of 500 ppm NO₂ to a BaO/Al₂O₃ at 300 °C. Note the NO₂ peak at 1250 s (460 °C) followed by an NO peak at 1580 s (540 °C).

subsequent indirect dissociation/decomposition of NO₃ costs 0.9 eV. Similarly, NO₂ release from Ba(NO₃)₂ costs 0.9 eV. This implies a 0.7-1.0 eV stability range for the NO₂(g) producing surface species. The corresponding range for the NO(g) producing surface species is 0.9-1.1 eV. This can be taken to explain the observed desorption ordering in Figure 11b.

Having said this, a contributing factor to the appearance of the NO curve in Figure 11b originates to some extent from desorbing NO₂, which is converted to NO at, e.g., reactor walls, since NO is thermodynamically favored in the experimental temperature range. Support for the fact that at least part of the NO(g) observed originates from direct desorption is found from experiment on an Al₂O₃ system under similar conditions to those employed here.²⁶

4. Summary and Conclusions

The NO_x storage process on BaO(s) is initiated by the adsorption of one NO₂ on a clean BaO(100) surface, as shown in Figure 10. There are two different adsorption sites and several different adsorption configurations for NO₂(ads). The corre-

sponding adsorption energies range from 0.5 to 0.8 eV. The adsorbate becomes more nitrite like with increasing adsorption energy in the case of adsorption over a Ba²⁺ site. The initial adsorption step involves the binding of one NO₂ molecule over either a surface O^{2-} or a surface Ba^{2+} site. The former is formally an NO₃²⁻ ion but is better understood as a [O_{surf}-NO2]2- species with the extra unpaired electron mainly localized in an O_{surf}-NO₂ antibonding orbital. This configuration displays a binding energy of 0.8 eV, see Figure 1 and transient species 1 in Figure 10. The competing Ba^{2+} associated nitrite species, see Figure 2 and transient species 2 in Figure 10, opens the route toward surface Ba(NO₃)₂ formation. This is so because it oxidizes the substrate, thus generating a delocalized electron vacancy among the adjacent surface oxygen. The unpaired Osurf electron, which results from NO₂ binding at the Ba^{2+} site, provides bonding for a second NO₂ molecule, which can react with the surface oxygen in two ways, depicted channel A and B in Figure 10. Either a metastable peroxynitrite species corresponding to channel A is formed, i.e., [O_{surf}-O-NO], or a straightforward formation of surface nitrate species follows (see channel B), i.e., [O_{surf}-NO₂]⁻. The latter binds by 1.0 eV to the surface, while the former constitutes an endothermic transient species (see 3A in Figure 10). Interestingly, though, the peroxynitrite is unstable toward surface peroxide formation in conjunction with the evolution of NO(g). This surface peroxide, in turn, is seen to be unstable toward decomposition by oxidation of the nitrite located over the barium site, forming a nitrate (see transient from 4A to 5 in Figure 10). This reaction comes out exothermic by 0.6 eV, which implies that inhibition of the NO_x loading capacity of BaO(s) due to spurious surface peroxides is deemed unlikely. Peroxide decomposition by oxidizing a Ba^{2+} nitrite in the presence of a [O_{surf} -NO₂]⁻ surface nitrate (see Figure 4) leads to the allnitrate end product (see surface species 6 in Figure 10 and Figure 6).

If the second NO₂ molecule approaches O^{-}_{surf} with the nitrogen end, then reaction channel B follows (see transient species 3B in Figure 10) and a stable nitrite—nitrate pair is formed. Redox reactions among the nitrite—nitrate pairs lead to the 0.3 eV more stable transient species 4B. Two additional paths to nitrite oxidation at the surface Ba²⁺ site come about from (i) the above surface peroxide acting as oxidant or (ii) an additional NO₂ molecule acting as oxidant toward the Ba²⁺ surf—NO₂⁻ species. The latter corresponds to the transient from 3B to 6 (see Figure 10).

Some straightforward observations regarding the initial NO-(g) release observed experimentally during NO₂ storage (see Figure 11a) are highlighted. There are two different sources for NO(g) evolution along the route to the all-nitrates end product. These involve either an $NO_2(g)$ oxidant toward surface nitrite oxidation or the channel for surface peroxide formation. Naively, the probability for choosing the peroxide forming channel A is twice that for choosing channel B. This observation exaggerates the importance of this reaction channel due to the short lifetime of the $[O_{surf} - O - NO]^{-}$ species, because it has an unreacted desorbing NO₂ molecule as a likely product. Still, this source of NO(g) is expected to dominate at low temperatures and sufficiently high coverages, as longer residence times and availability of O⁻_{surf} sites are necessary prerequisites. The sole reducing agents at high coverages comprise the surface nitrites $[O_{surf} - NO]^-$, which are oxidized by $NO_2(g)$ to form surface Ba(NO₃)₂ under NO(g) release.

In conclusion, a first-principles semiquantitative mechanistic investigation regarding the NO_x loading property of BaO(s) has

been undertaken and used to interpret experimental TPD data. Signatures of the proposed mechanism include (a) initial pairwise NO₂ chemisorption at Ba^{2+} and O_{surf} sites to form surface nitrites and nitrates, respectively, (b) a surface redox step to form nitrate-nitrite pairs, and (c) subsequent heterogeneous oxidation of the remaining nitrite to form an all-nitrate final product.

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