N₂O Decomposition over BaO: Including Effects of Coverage

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We have used embedded clusters to model the abstraction of oxygen from N₂O over the (001) terraces of BaO. At low coverage, we find a very low barrier (16 kcal/mol) in strong contradiction with experiment (33 kcal/mol). Regeneration of the surface through surface diffusion of oxygen and recombination is excluded by high barriers. At low coverage, the direct reaction of N₂O with surface peroxide ion through an Elay−Rideal (ER) mechanism has a computed barrier of 20.6 kcal/mol, which at full coverage increases to 34.3 kcal/mol. The reaction will use the lower-barrier direct abstraction as long as there are free anions available and will switch to the ER mechanism at high coverage of peroxide ions.

Introduction

Since BaO has the same rock-salt structure as MgO, CaO, and SrO, one would expect the mechanism for the decomposition of N₂O over the terrace sites to be similar in this sequence. The reaction over MgO and CaO has previously been studied by several authors and, from both experimental and theoretical work, there is agreement that the abstraction takes place at an oxygen site and leaves a peroxide ion at the surface.[1−4] Xie and Lunsford[4] have investigated the decomposition of N₂O over barium oxide and obtained a steady-state barrier to decomposition very similar to that found earlier for MgO by Snis and Miettinen,[1] that is, 33 kcal/mol for BaO versus 36 kcal/mol for decomposition over MgO. The barrier was proposed to relate to the direct reaction with anion sites at the BaO surface. In terms of O(−2) chemistry, which relates the charge-donating ability of the oxygen anion to the lattice parameter and the resulting stabilizing crystal potential, this is a surprising result. The basic idea of O(−2) chemistry, or basicity of the anions, has been proposed in earlier works by Pettersson et al.[3,5] and by Pacchioni et al.[6] and has been applied to a discussion of N₂O decomposition over MgO and CaO by Snis and Miettinen.[1] A similar reasoning should be applicable also to BaO.

Since the lattice parameter of BaO (5.52 Å) is much larger than for MgO (4.21 Å),[7] one would expect the anion in the BaO surface to be more reactive, which would result in a more stable peroxide ion product and thus, as a consequence, in a lower barrier to the abstraction considering that reactants and mechanism are the same. If one compares the determined activation energies for MgO and CaO, 36 and 26 kcal/mol, respectively, the expected trend is true; CaO with a lattice parameter of 4.81 Å has a substantially lower barrier to decomposition. Why is that not true for the reaction over BaO?

To shed some light on this problem, we have performed a series of calculations on embedded cluster models of the BaO crystal surface. We have considered the abstraction reaction in analogy with earlier work on MgO(001) and CaO(001)[1,3] but have here in particular focused on the problem of regenerating the surface. In accordance with preceding studies of this reaction over the rock-salt alkaline-earth oxides, we have chosen to consider the five-coordinated regular terrace sites of the (001) face of the BaO crystal. We find that the mechanism for direct abstraction at a terrace site is the same as earlier reported for MgO and CaO and follows the trends expected from O(−2) chemistry. The regeneration of the active surface, however, has a more complicated behavior and proceeds along different mechanisms for the different oxides. For MgO and CaO, recombination of surface perox*ide* species to form O₂ has been proposed,[8] but for BaO the substantially larger lattice parameter excludes this mechanism. In the following, we would like to focus on an alternative mechanism for BaO.

Methods

The surface is modeled using embedded clusters where the ab initio Model Potential (AIMP)[9,10] embedding approach, together with an explicit representation of the full Madelung potential of the lattice, has been used to represent the crystal outside the cluster. Ions out to a distance of 11.3 Bohr from any cluster ion are represented by complete ion model potentials. These provide an approximate description of the short-range Coulomb (incomplete screening), exchange, and orthogonality interactions, as well as a representation of relativistic effects, on the basis of the frozen ions.[9,10] This AIMP embedding approach has proven to be successful in representing the lattice effects in several studies including ionic crystals.[9,11,12] The nuclear attraction integrals over the Madelung potential (assuming a fully ionic lattice) were computed through the proper Ewald summation using the approach of Parry.[13,14] These integrals and the AIMP (core and embedding) potential integrals have been implemented in the ECPAIMP program[15] and have been interfaced by Nygren and Hall[16] to the Gaussian98[17] package which is used in this work.

For the O₂²⁻ species formation step, a Ba₅O₅ cluster model was used. For the surface regeneration step, the central cluster model ranges in size from Ba₉O₉ in the low-coverage case up to Ba₈O₁₈ for the high-coverage studies. All geometries and energies were obtained at the B3LYP level. For the oxygen in the BaO lattice, we have applied the double-ζ basis set of Dunning[18] extended with an extra diffuse s-function and where the diffuse p- and d-functions have been reoptimized for the negative ions. No extra s-functions were added for the adsorbate. For barium, the relativistic core potential and the valence basis

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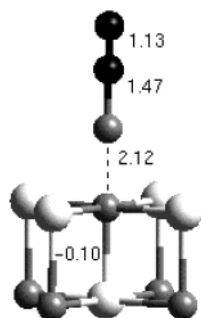† Oil and Energy Research Centre Porsgrunn.
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Figure 1. Transition-state structure for the oxygen abstraction step in the N_2O decomposition reaction over BaO(001) surface. Oxygen is colored gray, nitrogen black, and barium white. Only the central cluster is displayed. Bond distances are given in Å.
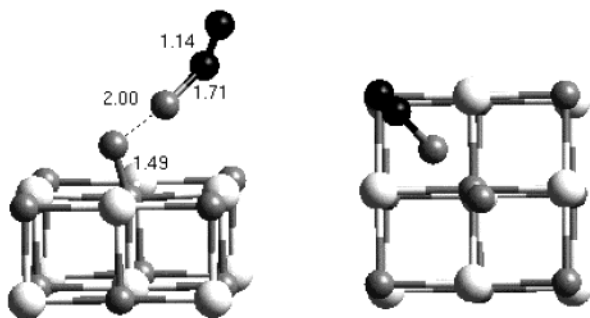

Figure 2. Side and top view of the transition-state structure of N_2O reacting with peroxide ion at low peroxide ion coverage on the BaO-(001) surface. Nitrogen is shown in black, oxygen in gray, and barium in white. Only the central cluster is displayed. Bond distances are given in Å.

set were taken from Hay and Wadt.[19] Since we are not able to obtain the Hessian matrix in these calculations, we have assumed as reaction coordinate the bond distance between the oxygen in N_2O and the surface oxygen or peroxide ion, where energy and gradient calculations were performed along this reaction path. We will, however, denote these obtained possibly higher order saddle points as transition states in this work. For the Ba_5O_5 cluster model, the central oxygen was kept free during the geometry optimization, whereas for Ba_8O_8 and Ba_8O_{18}, the two central peroxide ions were allowed to relax. The remaining peroxide ions in Ba_8O_{18} were kept fixed in the geometry determined by optimizing a single peroxide ion on Ba_5O_5.

Results and Discussion

The transition state in the abstraction reaction occurs for a linear approach of the N_2O onto a surface oxygen anion. This is in agreement with earlier studies on MgO and CaO and seems to be a general behavior for the terrace sites. The obtained geometrical parameters for BaO are indicated in Figure 1.
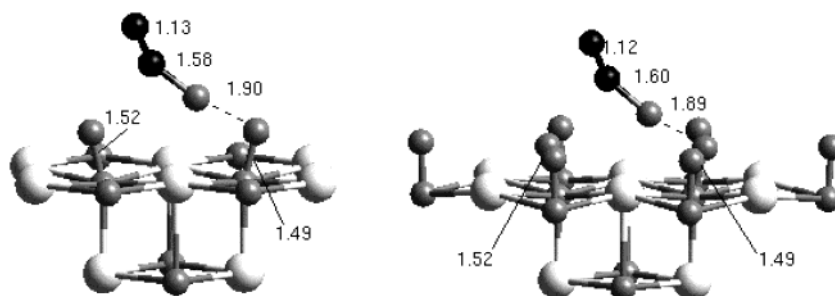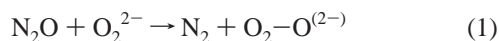
The computed barrier for the BaO reaction of 16 kcal/mol is substantially lower than what is found for the other oxides and is at strong variance with the experimental determination of 33 kcal/mol. A substantially lower barrier is in line with the expectations from O(−2) chemistry since the stability of the product, that is, a surface-bound O_2^{-2} will be determined by the charge sharing between the two oxygens. Because the doubly negative oxygen anion is unstable without the crystal potential and the distance between the charges determines the strength of this potential, it follows that a larger lattice parameter will lead to a less stabilized anion. Thus, the oxygen in MgO ($a = 4.21$ Å) will be a harder, more Neon-like ion than the oxygen in BaO ($a = 5.52$ Å). Furthermore, the lattice in BaO is more open, allowing larger relaxation effects such that the surface oxygen in the resulting O_2^{-2} on BaO relaxes inward by 0.27 Å, while on MgO it relaxes by only 0.11 Å. This effect further enhances the stability of the peroxide ion on BaO. With the increased stabilization of the products for BaO compared to MgO, we must expect a substantially lower barrier for BaO than for MgO, contrary to what has been found experimentally.

For steady-state conditions to apply, some mechanism to eliminate the resulting surface peroxide ion must also be active. On MgO and CaO, it has been suggested that oxygen can diffuse over the surface and recombine to form O_2, which then desorbs.[8] The diffusion path is on the direct line connecting two surface anions and the barrier is located at the midpoint between two surface cations. On BaO, however, we find that the surface diffusion is completely hindered because of the substantially larger lattice parameter; the binding to the first anion is completely broken before the bond to the next anion can be formed. This leads to a prohibitively high barrier for diffusion, and the only way to obtain two oxygens at neighboring anions is through deposition, that is, at high coverage of peroxide ions. An alternative mechanism for the oxygen desorption is through the recombination path leading to oxygen desorption for the case of two oxygens at neighboring sites. On CaO, an asymmetric pathway has been suggested to lead to the lowest barrier.[8] In this case, one oxygen retains its bonding to its anion while the other crosses over the midpoint between the cations and loses its bond while forming the bond to the other oxygen. On CaO, this leads to a computed barrier in reasonable agreement with experiment.[8] However, for BaO the lattice parameter is again such that this recombination mechanism cannot be active; the distances are too large and bonds cannot be continuously formed and broken leading to exceedingly high barriers. Thus, some other mechanism to regenerate the surface must be sought for BaO.

The decomposition reaction has been determined by Xie and Lunsford to be first-order in N_2O.[4] One possible reaction scheme, which takes this into account, would be for N_2O to react directly with a surface peroxide ion to give gas-phase N_2

Figure 3. Transition-state structure of N_2O adsorbed on peroxide with additional two peroxide ions (left) and full peroxide ion coverage on the BaO(001) surface (right). Nitrogen is shown in black, oxygen in gray, and barium in white. Only the central clusters are displayed. Bond distances are given in Å.

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and surface singlet-bound O$_2$:

$$N_2O + O_2{}^{2-} \rightarrow N_2 + O_2{-}O^{(2-)} \qquad (1)$$

At the transition state for reaction 1, we investigated coordination of the N$_2$ moiety of N$_2$O toward both the surface oxygen and barium, and the lowest energy pathway is reported in Figure 2.

There are several interesting aspects with this transition-state structure. The transition state is found for a configuration where there is a favorable electrostatic interaction with the substrate. The internal charge distribution in the N$_2$O at the TS is negative oxygen, somewhat positive nitrogen bound to the oxygen, and a negative outer nitrogen; this is stabilized with the positive nitrogen moving down toward the next surface oxygen anion. After the dissociation into N$_2$ and surface-bound O$_2$, the resulting [O$-$O$_2$]$^{2-}$ species is bound by 8.6 kcal/mol, which is in line with the observation that O$_2$ inhibits the abstraction. The computed barrier for the reaction is 20.6 kcal/mol, which still is substantially lower than the experiment. However, it is also higher than the barrier for direct abstraction and so this pathway should not open up until at higher coverage where it will be difficult to find free surface anion sites to react with. We must thus consider the effects of coverage on the reaction to regenerate the surface. As a first step, we have considered the effect of reducing the electrostatic stabilization by assuming a peroxide ion also at the anion, which interacts with the positively charged nitrogen. The resulting TS structure is shown in the left part of Figure 3.

The transition-state structure reported here is restricted in the sense that the adsorbate was not allowed to move out of the plane. However, test calculations where N$_2$O is coordinated to surface barium gave a higher energy path resulting in movement of N$_2$O away from the surface.

The effect of the additional peroxide ion is to give a steric repulsion and to reduce the stabilizing charge available to interact with the positive nitrogen since this charge now is shared between the two oxygens. To improve the interaction, we find that the two peroxide ions bend away from the reaction site. The computed barrier is now increased to 31.2 kcal/mol, and clearly the reaction over any free anion site will be strongly preferred, which leads us to consider the situation with a fully peroxide-covered surface as indicated in the right part of Figure 3. Increasing the coverage now reduces the possibility for the peroxide ions to relax away from the reaction site and increases the barrier somewhat to 34.3 kcal/mol. This is within the error bars of the 33 kcal/mol barrier determined by Xie and Lunsford,[4] and we would suggest that this is the rate-limiting step in this reaction.

Conclusions

We have presented results of N$_2$O decomposition over the BaO(100) surface. As for MgO and CaO, O($-$2) chemistry is applicable for the initial abstraction step for BaO. The calculated activation barrier follows the expected trend, where it decreases along the series MgO, CaO, and BaO. For CaO, the rate-limiting step is the recombination of surface peroxide to form O$_2$.[8] However, the distance between neighboring anions in the BaO surface is too long to allow this process. Instead, we have investigated the direct reaction of N$_2$O with a surface peroxide ion, which becomes possible only at high coverage of peroxide. We propose that this is the barrier that has been determined experimentally.

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