

Oxygen vacancies and peroxo groups on regular and low-coordinated sites of MgO, CaO, SrO, and BaO surfaces

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Abstract

The formation of an oxygen vacancy and the simultaneous re-adsorption of an oxygen atom on regular and low-coordinated (LC) sites (edges and corners) of the surface of alkaline-earth oxides with cubic rock salt structure, MgO, CaO, SrO, and BaO, has been investigated using DFT cluster model calculations. The process corresponds to the formation of a surface Frenkel defect when the vacancy formation energy is partially compensated by the energy gained in the formation of a peroxo group. The structural and electronic properties of vacancies and peroxo groups along the series of alkaline-earth oxides have been analyzed. We found that the role of low-coordinated sites on the surface chemistry of alkaline-earth oxides is of crucial importance for MgO, but decreases for the heavier members. For instance, on BaO the formation of a peroxo group is practically site-insensitive. This is not the case of the vacancy formation, which is always favored on the low-coordinated sites.

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1. Introduction

The reactivity of oxide surfaces is very dependent on the level of defectivity and composition [1]. Not surprisingly, sub-stoichiometric surfaces are more reactive than the regular stoichiometric ones. One of the mechanisms leading to sub-stoichiometric surfaces is the release of oxygen under various conditions like high thermal treatment [2,3], electron bombardment [4,5], photo-irradiation [6], dehydroxylation at high temperature [7], single-crystal cleavage in UHV [8], etc. All these processes result in the formation of oxygen vacancies, di-vacancies or vacancy aggregates. The formation of oxygen vacancies, V_{O} , on the surface of inorganic oxides has attracted a considerable attention in the last decade and the number of studies on this topic is continuously increasing [9,10]. Usually, the formation

energy of an oxygen vacancy, defined as the cost to remove an $\text{O}^{3\text{P}}$ atom and to bring it to infinite distance from the oxide, is quite high, being of 4–9 eV depending on the material [9,11]; furthermore, the oxygen formation energy can vary substantially with the position of the removed oxygen atom, bulk, sub-surface, surface, or low-coordinated sites [12,13]. The formation energy of O vacancies is generally obtained from first principles calculations [14–18] being a difficult quantity to access experimentally. However, the global energy cost for the defect formation decreases when the removed O atom is re-adsorbed on another surface site, thus keeping the whole stoichiometry unaltered. The atomic adsorption energy partially compensates the cost of formation of the defect. This process is the surface equivalent of the formation of a Frenkel defect in the bulk, where an ion is displaced from its lattice position and accommodated at an interstitial site. It could also be classified as a Schottky defect where an anion (or cation) is displaced from a bulk lattice site to the surface of the crystal. However, bulk Schottky defects usually indicate the presence of equal numbers of positive and negative

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ion vacancies, a situation which is not that represented here for the MgO surface. In this respect, the pair described is more reminiscent of a bulk Frenkel defect. This paper is devoted to the study of this process on the surface of alkaline-earth oxides. We investigate the thermodynamic aspects of the displacement of an O atom and search the configuration of lowest energy of an oxygen vacancy and ad-atom pair on regular and low-coordinated sites of MgO, CaO, SrO, and BaO surfaces. Of course, this implies the constraint that the O adsorption does not occur on the vacancy; in fact, a vacancy-peroxo pair corresponds to a metastable state.

The abstraction of an oxygen atom from the MgO(100) surface has been investigated by several authors (besides the references mentioned above see, e.g., Refs. [19–23]) and the presence of oxygen vacancies on the surface of MgO after electron bombardment has been confirmed experimentally very recently [4,24]. Less attention has been dedicated to the heavier members of the series [25]. The removal of a neutral oxygen atom reduces the surface by generating a neutral F^0 center, with two electrons trapped in the cavity. O adsorption on the perfect surface of alkaline-earth oxides occurs by formation of a peroxo compound. Adding an O atom to the stoichiometric surface implies that two O atoms have the oxidation state -1 and hence are bound as an O_2^- ion. This process has been investigated theoretically by several authors. Kantorovich and Gillan have studied peroxo groups formed at terrace and low-coordinated sites of MgO [26,27]; this was reconsidered recently by Geneste et al. [28]. Peroxo groups formed at the (100) surface of CaO have been investigated by Snis, Panas, and Strömberg [29] while systematic studies of peroxo groups formed on the terrace sites of the MgO–BaO or MgO–SrO series have been reported by Karlsen et al. [30] and by Abdel Halim and Shalabi [31], respectively. O adsorption on BaO has also been discussed by Broqvist et al. [32,33] in the context of the decomposition reaction of N_2O . No studies seem to exist on the formation of peroxo groups on the low-coordinated sites of CaO–BaO. While the properties of the isolated defects, V_O and O_2^- , have been studied in detail, in particular for MgO, the combined formation of pairs of defects has only been addressed for MgO, and restricted to terrace sites [11].

In our study, we assumed that the V_O and the peroxo group are formed at two different non-interacting sites, separated by large distances. No attempt has been done to study the vacancy and the peroxo group on the same cluster model, which implies a close vicinity of the two defects. When this is done, the lowest state is not necessarily that corresponding to a neutral vacancy, F^0 , and a peroxo group. A recent study on this topic [11] has shown that the lowest energy is found in correspondence of the formation of two paramagnetic species, a F^+ center and O^- ion adsorbed on a Mg^{2+} cation (triplet state). This configuration is about 0.4 eV lower in energy than the F^0/O_2^- pair investigated here. However, the formation of F^+/O^- pairs benefits from an additional electrostatic stabilization

between the two charged centers which vanishes for very large distances.

After the introduction, in Section 2 we describe the computational methods and the surface models. We present in the first part of Section 3 the energetics of a vacancy formation, then the energy gain associated to the formation of a peroxo group, and finally we consider various possibilities of simultaneous removal of the O atom and readsorption on a given site. Trends along the MgO, CaO, SrO, and BaO series are discussed in the concluding section.

2. Computational details

All the calculations are based on the density functional theory (DFT) approach using the gradient corrected Becke's three parameters hybrid exchange functional [34] in combination with the correlation functional of Lee et al. [35] (B3LYP).

The surface of MgO, CaO, SrO and BaO was represented by finite clusters embedded in ± 2 point charges (PC) to reproduce the Madelung potential (MP) at the adsorption site [36]. The positive PCs at the interface are replaced by effective core potentials (ECPs) [37] to account for the finite size of the cation and to remove spurious polarization effects. The interface cations are denoted as M^* . No basis functions are associated to these atoms. For the (100) terraces of MgO, CaO, SrO, BaO, the cluster used is $M_{13}O_{13}M_{16}^*$. Edge and corner sites have been modeled by $M_{12}O_{12}M_{14}^*$ (edge) and $M_{10}O_{10}M_9^*$ (corner) clusters. All the atoms of the cluster which are not in direct contact with the PC's are let free to relax in the geometry optimization, while the others are fixed to their bulk positions. The O ions have been described with a 6-31+G* basis set. The Mg^{2+} cations have been treated with a 6-31G basis, except for the Mg^{2+} ions nearest neighbors of the peroxo groups where a 6-31G* basis has been employed. The Ca^{2+} , Sr^{2+} and Ba^{2+} cations have been treated with a small core effective core potential (ECP, lanl2) and a lanl2dz basis [38].

We have determined the 1s core level binding energies (CLBE) of the surface oxide anions as well as of the peroxo groups. In general, the shifts of the core levels provide a qualitative, not a quantitative, measure of the charge on a given atom. Several effects contribute to the final shift and this cannot be simply related to the amount of charge transfer [39–41]. We used changes of the Kohn–Sham eigenvalues, $-\epsilon_i$, as a measure of the shifts in CLBEs occurring upon adsorption. In this way final state effects are not included. The quantity is reported as $\Delta\epsilon_{1s}(O)$ where the difference is assumed to be positive when the shift is to smaller CLBEs. Since we are interested in relative shifts for a series of systems, the approximation of considering initial state effects is justified and provides an internally consistent measure of the core level shift. This quantity in turn is related to the experimental XPS measurements.

Vibrational frequencies of the peroxo groups formed at the terrace sites of the four oxides have been computed by determining the second derivatives of the total energy with

respect to the internal coordinates. The calculations have been done with the Gaussian98 program package [42].

3. Results

3.1. O vacancies formation energies

The removal of an O atom from the terrace sites of alkaline-earth oxides results in an impurity state in the gap and in a trapped electron pair [14–16]. The level of localization changes along the series. The energy gap of the MgO(100) surface is predicted to be 5.7 eV, i.e., about 1 eV lower than the experimental one [15] because of the well known problem of DFT in reproducing band gaps and also because of

the use of a cluster model. The creation of a surface vacancy introduces a state 3.6 eV above the top of the valence band, well separated (more than 2 eV) from the bottom of the conduction band. Going down the series, the gap decreases, being 3.8 eV in CaO, 3.0 eV in SrO, and 2.3 eV in BaO. The position of the one-electron energy level corresponding to the trapped electrons moves towards to bottom of the conduction band going to the heavier oxides. In CaO it is 1.1 eV below the conduction band, in SrO and BaO the distance is reduced to about 0.4 eV. As the impurity level gets closer to the conduction band, the electron pair becomes less localized. This is clearly shown in Fig. 1 where the density contour plot of the mid-gap level associated to the *F* center is shown for the terrace site of the four oxides. It is apparent that the electron density in the cavity is highest in MgO and decreases in CaO, SrO, and BaO, as the consequence of the reduced ionicity and Madelung potential along the series [43].

The formation energy, E_F , of an oxygen vacancy, V_O , created at the surface of alkaline-earth oxides is reported in Table 1 (the values are with respect to an isolated O 3P atom). The general trend that emerges is not unexpected: going from MgO to BaO, E_F for an oxygen vacancy on terrace decreases by about 1.6 eV. However, the change is not monotone. MgO and CaO have approximately the same formation energy, 9.3 eV; on SrO the cost is reduced by 0.6 eV only, while a large reduction of 1 eV is found going from SrO to BaO, Table 1. These changes are related to the expansion of the lattice parameter and to the consequent decrease of the Madelung potential going down the series. This is associated also to a reduction of ionicity of the crystal and to an enhanced surface basicity, as discussed in the literature [43].

The second trend which clearly emerges from the calculations is the easier formation of oxygen vacancies on the low-coordinated sites of alkaline-earth oxides, as already found for MgO by Kantorovich et al. [12] and by Pacchioni and Pescarmona [13]. Recently, the preference for generation of oxygen vacancies on steps, edges, and corners of MgO crystalline thin films has been confirmed experimentally

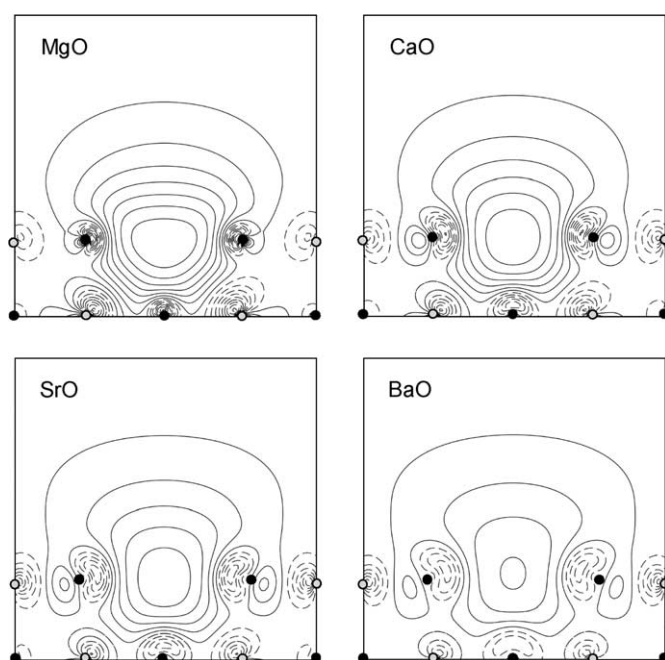


Fig. 1. Charge density contour plots of the doubly occupied mid-gap state associated to the oxygen vacancy on the (100) surface of alkaline-earth oxides. The lines are drawn in intervals of 0.012 e/a.u.³.

Table 1

Formation energies of oxygen vacancies, $E_F(V_O)$, formation energy of peroxo groups, $E_F(O_2^{2-})$, O–O distance, $r(O-O)$, net charge on external atom, $q(O_a)$, and vibrational frequency, $\omega_e(O-O)$, of surface peroxo groups formed on various sites of the MgO, CaO, SrO, and BaO surfaces

| | Site | $E_F(V_O)$, eV | $E_F(O_2^{2-})$, eV | $r(O-O)$, Å | $q(O_a)$ | $\omega_e(O-O)$, cm ⁻¹ |
|-----|---------|-----------------|----------------------|--------------|----------|------------------------------------|
| MgO | Terrace | 9.26 | -1.91 | 1.52 | -0.21 | 907 |
| CaO | Terrace | 9.24 | -2.81 | 1.50 | -0.75 | 953 |
| SrO | Terrace | 8.62 | -3.18 | 1.49 | -0.94 | 937 |
| BaO | Terrace | 7.67 | -3.56 | 1.49 | -0.90 | 907 |
| MgO | Edge | 8.42 | -2.44 ^a | 1.51 | -0.61 | 898 |
| CaO | Edge | 8.23 | -3.05 | 1.51 | -0.69 | – |
| SrO | Edge | 7.58 | -3.30 | 1.50 | -0.84 | – |
| BaO | Edge | 7.05 | -3.57 | 1.50 | -0.82 | – |
| MgO | Corner | 7.70 | -2.63 | 1.52 | -0.55 | – |
| CaO | Corner | 7.06 | -3.26 | 1.51 | -0.75 | – |
| SrO | Corner | 6.54 | -3.43 | 1.50 | -0.81 | – |
| BaO | Corner | 6.32 | -3.43 | 1.50 | -0.73 | – |

^a The value refers to the asymmetric complex, see text.

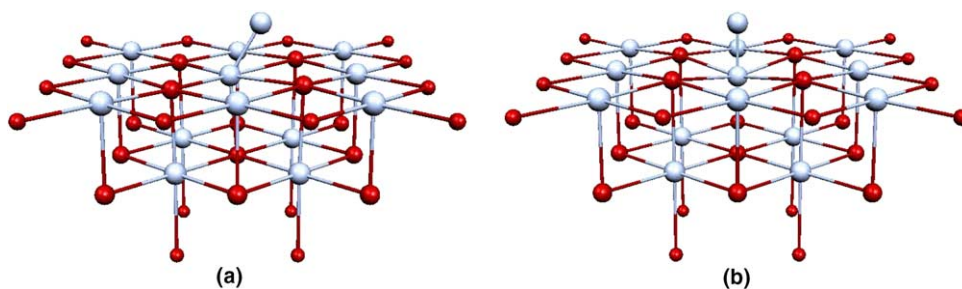


Fig. 2. (a) Structure of a peroxo group on the (100) terrace of the MgO surface. (b) Structure of a peroxo group on the (100) terrace of CaO, SrO, and BaO surfaces.

by a combined EPR and STM study in UHV [24]. The changes in vacancy formation energy on low-coordinated sites are rather similar on the various alkaline-earth oxides. On MgO the reduction of E_F moving from a terrace to an edge is of 0.84 eV, and of 0.72 eV going from an edge to a corner site. On BaO the corresponding ΔE_F values are 0.62 eV (terrace to edge) and 0.73 eV (edge to corner). In absolute terms, the lowest formation energy is that required to create a vacancy on a corner site of BaO, 6.32 eV, and still represents a quite high energy expense. The reason for the lower cost to remove an oxygen from the low-coordinated sites is the same illustrated above: at edges, steps, and corners the Madelung potential is considerably reduced compared to the terrace sites or to the bulk. Furthermore, the coordination is lower, so that even when the covalent effects become more pronounced, as in BaO [44], the O atom is more tightly bound to the rest of the surface.

3.2. Surface peroxo complexes

In this section we analyze the structure and the bond strength of surface peroxo groups formed on regular and low-coordinated sites of the MgO, CaO, SrO, and BaO surfaces. On MgO(100) the peroxo complex is tilted by about 30° with respect to the surface normal, Fig. 2(a), and the O–O bond length is 1.52 Å; the ground state is singlet and the adsorption energy, 1.91 eV, in line with that of previous studies, taking into account that the B3LYP exchange-correlation functional usually gives smaller binding energies than other functionals [45].

On CaO terrace sites the peroxo group has a similar O–O distance, 1.50 Å, but is oriented normal to the surface, Fig. 2(b). The structure is the same also for the other two oxides, SrO and BaO. This suggests that the tilting found on MgO, Fig. 2(a), is determined by electrostatic effects. The adsorbed O atom, O_a , feels the attractive potential generated by the two nearest Mg^{2+} cations and bends towards them. On CaO, where the distances are longer, the electrostatic attraction is not sufficient to induce this bending. Furthermore, the O–O bond strength on CaO is considerably higher than on MgO, 2.81 eV against 1.91 eV, Table 1, thus resulting in a larger cost for the tilting. In fact, the O–O bond has a considerable covalent character, which typically corresponds to strong bond directionality. The surface oxygen atom, O_s , undergoes a significant downward relaxation. This is between about 0.1 Å in MgO and 0.42 Å in BaO as already found in [30]; the inward relaxation is of 0.27 Å in CaO and 0.34 Å in SrO. The origin of the larger binding in CaO compared to MgO is again due to the larger basicity of the former oxide [43]. The tendency to form more strongly bound peroxo groups is observed also for SrO and BaO, where the adsorption energies are 3.18 and 3.56 eV, respectively, Table 1. The bond strength in surface peroxo groups computed here is close to that determined by Karlsen et al. [30], in particular for the heavier members of the group. Small differences can be attributed to the cluster size dependence of this quantity [30].

The structure of the peroxo complex is quite different when formed at an edge site of MgO, Fig. 3. Here the formation of a relatively strong O–O bond, 2.48 eV, leads to a

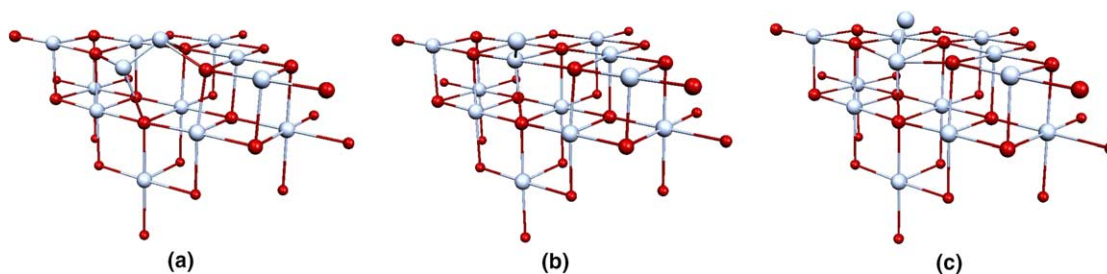


Fig. 3. (a) Structure of a peroxo group on the edge site of the MgO surface, symmetric isomer. (b) Structure of a peroxo group on the edge site of the MgO surface, asymmetric isomer. (c) Structure of a peroxo group on the edge site of the CaO, SrO, and BaO surfaces.

substantial structural relaxation. The O_{4c} ion moves outwards, and in the final structure the two O atoms are equivalent and directly bound to lattice Mg atoms. We call this structure symmetric peroxo group (Fig. 3(a)). The O–O distance 1.51 Å, is similar to that found on a terrace site, Table 1, although the topology is quite different. On MgO a second minimum exists in correspondence of a structure which is reminiscent of that found for a terrace peroxo group. Here the lattice O atom remains at the edge site while the second O protrudes outside the surface, Fig. 3(b). We call this second minimum asymmetric peroxo. This latter structure in MgO is about 0.1 eV higher in energy than the symmetric one. We cannot exclude that the presence of the two minima, and their relative energy difference, are related to the limited geometrical relaxation allowed in our models where only few atoms of the cluster can relax, the rest being fixed at the ideal truncated bulk positions. It is possible that a full relaxation in a larger portion of the surface leads to a single minimum or changes the order of stability of the two minima. The existence of two minima for a peroxo group formed at an edge is peculiar of MgO and is not observed on the other alkaline-earth oxides. On CaO, SrO, and BaO the structure of the peroxo group formed at an edge site is similar to the asymmetric one of MgO. However, on MgO the external oxygen points towards the nearest Mg_{4c}^{2+} cation, Fig. 3(b) so that the external oxygen is “bridging” the O–Mg bond. On the other oxides the peroxo group stands almost normal to the (100) plane, Fig. 3(c), and exhibits no tilting, as for the complex formed on the terrace sites Fig. 2(b).

The surface O_s atom undergoes a substantial relaxation as a consequence of the peroxo formation in CaO–BaO, Fig. 3(c), as found also for the terrace sites. This relaxation occurs also on corner sites, where a different structure is found for MgO with respect to the other oxides. On corners of MgO, Fig. 4(a), the peroxo has practically the same structure as the asymmetric peroxo group formed at an edge site, with the adsorbed O_a atom pointing towards a vicinal Mg_{4c}^{2+} cation. On CaO we have identified two minima, one similar to that observed for MgO and shown in Fig. 4(a), and one, more stable by 0.4 eV, where the O_a

atom is lying up, nearly along the normal to the (100) plane, Fig. 4(b). On SrO and BaO the geometry optimization leads to the same structure found for the most stable isomer of CaO, with the O_a atom normal to the (100) plane, Fig. 4(b).

Being more reactive, the lattice oxygens at edge and corner sites of the alkaline-earth oxides form stronger peroxo complexes compared to their terrace counterparts. On an edge and a corner of MgO ΔE is -2.44 eV and -2.63 eV, respectively. These values are 0.5–0.7 eV higher in absolute value than on a terrace site, Table 1. On CaO the peroxo formation energy goes from -2.81 eV on a terrace to -3.05 eV and -3.26 eV on edges and corners, respectively. The difference between regular and low-coordinated sites is thus smaller than on MgO. This trend is further confirmed by the results on SrO and BaO, Table 1. On SrO the peroxo complex has rather similar adsorption energies on the three sites, -3.18 eV (terrace), -3.30 eV (edge), -3.43 eV (corner). On BaO the adsorption of an O atom on a terrace or an edge leads practically to the same energy gain, about -3.6 eV, even larger than on a corner, -3.43 eV. This provides a clear indication that while a completely different reactivity is expected for fully or partially coordinated oxide anions on MgO, this effect is much less dramatic when one goes to SrO and almost absent in BaO.

We have computed the vibrational frequencies for the peroxo groups formed at various oxides. On the terraces of MgO the stretching mode of the O–O bond occurs at 907 cm^{-1} ; on CaO the value is higher, 953 cm^{-1} , then it decreases regularly to 937 cm^{-1} on SrO and to 907 cm^{-1} in BaO, Table 1. On an edge site of MgO the vibrational mode is found at 898 cm^{-1} , suggesting that peroxo groups formed at various sites of the alkaline-earth oxides will have very similar vibrational signatures. For this reason, no further calculation of the vibrational frequency of peroxo groups formed on low-coordinated sites has been done. The computed values are consistent with some experimental values reported in the literature. Nakamura et al. reported a value of 880 cm^{-1} for peroxo groups formed on the surface of CaO by reaction with N_2O [46]; Hess and Lunsford suggest that a band at 930 cm^{-1} is due to peroxo groups formed on the surface of BaO [47]. In general, surface peroxides are expected to exhibit vibrational frequencies in the 800 – 900 cm^{-1} region. The calculated values, Table 1, also show that the vibration of this defect is not diagnostic of the oxide nor of the site where the complex is formed.

The formation of a surface peroxo group leads to a charge redistribution. Formally, when a neutral O atom is adsorbed on-top of an O^{2-} anion (oxidation state-II), the two O atoms of the peroxo complex, O_2^{2-} , are in $-I$ -oxidation state. Charge flows from the surface oxygen, O_s , to the adsorbed oxygen, O_a , as shown by the data of Mulliken population analysis reported in Table 1. Notice that these values have no absolute meaning, but provide a trend within the series of the oxides considered. The amount of charge transfer, however, is not the same on all oxides

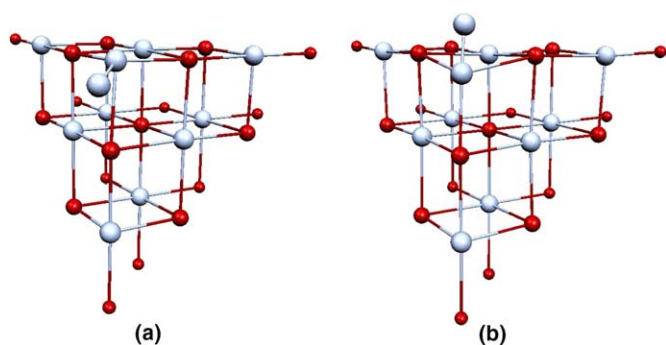


Fig. 4. (a) Structure of a peroxo group on the corner site of the MgO surface. (b) Structure of a peroxo group on the corner site of CaO, SrO, and BaO surfaces.

and on all sites. Let us consider the terrace sites first. There is a clear difference between MgO, where the charge flow is of $0.21 e^-$ only, and the other oxides where it is of 0.7 – $0.9 e^-$. This reflects the lower basicity of MgO five-coordinated oxide anions compared to the CaO, SrO, and BaO counterparts [43]. There are substantial differences between peroxo groups formed at terrace sites and at low-coordinated sites of MgO: the charge associated to O_a is of about $0.6 e^-$ for both edges and corners, Table 1, i.e., about three times larger than on a terrace. The difference in charge transfer between terrace and low-coordinated sites is much less pronounced or even absent on the other oxides where is always between 0.7 and $0.9 e^-$.

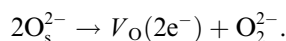
Indirect information about the charge state of a given atom in a solid is provided by the corresponding core level binding energy, CLBE, a quantity directly accessible in XPS measurements. In the first column of Table 2 we give the CLBE of the 1s level of the surface oxygen before adsorption, O_{5c} , of the same atom after O adsorption, O_s , and of the adsorbed oxygen, O_a . For the terrace sites the highest value is that of the O_s ions of MgO, 517.1 eV, consistent with the higher value of the Madelung potential. The value decreases regularly for the other oxides, 515.9 eV for CaO, 515.5 eV for SrO, 515.1 eV for BaO. Moving from terrace to low-coordinated sites the CLBE's change less regularly. This is because beside the change in Madelung potential, there is a change in coordination and local relaxation that lead to a global shift of the CLBE.

By forming the peroxo complex one observes a clear trend. The CLBE of the O_s atom is shifted to higher values, sign of a reduced charge in the valence of the atom. The shift is very pronounced, being always larger than 2 eV, often close to 3 eV, Table 2, in agreement with previous findings [28]. This shift considerably exceeds the sensibility of commercial XPS instruments, making the detection of peroxo groups possible, provided that their concentration is sufficiently high. In fact, a shoulder in the XPS spectra of MgO films grown on metal substrates has been inter-

preted as due to water adsorption or peroxo groups formation [48–50]. The new band is consistent with the CLBE's shift found here. On terrace sites the shift is of 2.5 eV for MgO, and of 2.9 eV for CaO, SrO and BaO, consistent with the charge transfer analysis based on the Mulliken population of Table 1. This trend is found also for peroxo groups formed at edges and corners. Finally, we notice that while on the MgO terrace the CLBE's of the two atoms of the peroxo group, O_a and O_s , differ by 0.5 eV, on the other oxides this difference is of 0.2 eV only, indicating that the two atoms of the peroxo group are nearly equivalent.

3.3. Frenkel pairs formation energies

In the last section we consider the energy required to create a Frenkel defect consisting of an oxygen vacancy and a peroxo group. The total process is thus



We have seen before that the energy involved in creating an oxygen vacancy and forming a peroxo group varies as function of the site where the O atom is removed and read-sorbed and, of course, of the alkaline-earth oxide. In Table 3 we report the formation energies of the Frenkel defects for all possible situations considered in this work: creation of a vacancy on a terrace, edge, or corner site and formation of a peroxo group on various sites. Clearly, the most favorable situation is when both the vacancy and the peroxo group are formed on low-coordinated sites. On MgO, while the formation of a Frenkel pair of defects on the (100) terrace costs 7.35 eV, the creation of a vacancy on a corner with oxygen readsorption on a corner or edge sites costs about 5 eV, Table 3.

As one moves to the heavier members of the series one observes two trends: first of all, the formation energy of a Frenkel pair, ($V_O + O_2^{2-}$), decreases considerably. On BaO the formation of a V_O center and of a peroxo group

Table 2
Oxygen 1s core level binding energies and corresponding shifts for oxide anions and peroxo groups on various sites of the MgO, CaO, SrO, and BaO surfaces

| Site | Oxide | Peroxo group | | $\Delta(O_s - O_{5c})$, eV | |
|------|---------|---------------|------------|-----------------------------|------------|
| | | O_{5c} , eV | O_s , eV | | O_a , eV |
| MgO | Terrace | 517.1 | 519.6 | 519.1 | 2.5 |
| CaO | Terrace | 515.9 | 518.8 | 518.6 | 2.9 |
| SrO | Terrace | 515.5 | 518.4 | 518.2 | 2.9 |
| BaO | Terrace | 515.1 | 518.0 | 517.8 | 2.9 |
| MgO | Edge | 517.7 | 519.8 | 519.7 | 2.1 |
| CaO | Edge | 516.2 | 518.9 | 518.7 | 2.7 |
| SrO | Edge | 515.6 | 518.3 | 518.0 | 2.7 |
| BaO | Edge | 515.3 | 518.2 | 518.0 | 2.7 |
| MgO | Corner | 516.1 | 518.4 | 517.7 | 2.3 |
| CaO | Corner | 514.7 | 517.6 | 517.3 | 2.8 |
| SrO | Corner | 514.4 | 517.2 | 516.9 | 2.8 |
| BaO | Corner | 514.9 | 517.5 | 517.1 | 2.5 |

Table 3
Formation energies (in eV) of Frenkel defects at the surface of MgO, CaO, SrO and BaO^a

| | | O_2^{2-} (terrace) | O_2^{2-} (edge) | O_2^{2-} (corner) |
|-----|-----------------|----------------------|-------------------|---------------------|
| MgO | V_O (terrace) | 7.35 | 6.82 | 6.63 |
| | V_O (edge) | 6.51 | 5.98 | 5.79 |
| | V_O (corner) | 5.79 | 5.26 | 5.08 |
| CaO | V_O (terrace) | 6.43 | 6.19 | 5.98 |
| | V_O (edge) | 5.42 | 5.18 | 4.97 |
| | V_O (corner) | 4.25 | 4.01 | 3.80 |
| SrO | V_O (terrace) | 5.44 | 5.32 | 5.19 |
| | V_O (edge) | 4.40 | 4.28 | 4.15 |
| | V_O (corner) | 3.36 | 3.24 | 3.12 |
| BaO | V_O (terrace) | 4.11 | 4.10 | 4.24 |
| | V_O (edge) | 3.49 | 3.48 | 3.62 |
| | V_O (corner) | 2.76 | 2.75 | 2.89 |

^a Defined as the sum of the formation energy of V_O at a given site and the adsorption energy of an O atom at a terrace, edge, or corner site.

on a terrace site costs 4.11 eV, i.e., about 3 eV less than on MgO. The other two oxides are in between, with a cost of about 6 eV for CaO and about 5 eV for SrO. The second trend is that the role of the various sites involved is important only as far as the oxygen vacancy is concerned, since the formation energy varies significantly from high to low-coordinated sites, Tables 1 and 3. Much less important from an energy point is the position where the peroxy group is formed. This means that once a vacancy is formed on the terrace of BaO, it is quite irrelevant where the removed O atom is readsorbed. In this respect, the formation of O vacancies on the edges of BaO with peroxy groups formed on terraces, edges or corners costs about 3.5 eV, a value which is further reduced to about 2.8 eV when the vacancies are created at corner sites.

These data show a large variation in the formation energy of Frenkel defects along the series of alkaline-earth oxides, since this goes from the very high cost on the MgO(100) terraces, 7.35 eV, to the relatively low cost on the BaO low-coordinated morphological sites, 2.8–3.5 eV. This suggests that depending on the sample preparation, the number of defects in thermodynamic equilibrium can be much higher on the heavier oxides.

4. Conclusions

In this study we have investigated the properties of two defects which can simultaneously occur on the surface of oxide materials, thus leading to a more reactive surface without changing its stoichiometry: an oxygen vacancy and a peroxy groups. Taken individually, these two defects are typical of reduced (oxygen vacancy) and oxidised (peroxy group) materials, respectively. When simultaneously present, they form a pair of defects created by moving one lattice ion from its original position to another site where it is readsorbed. In this respect the vacancy-peroxy pair can be assimilated to a Frenkel defect in the bulk of oxide materials. In the process of creating this defect, the cost for the vacancy formation, which is rather high in alkaline-earth oxides, is partially compensated by the formation of the O–O bond of the peroxy group. The situation is further complicated by the fact that the surfaces of ionic oxides present a complex and rich morphology, with a number of irregularities like steps, edges, kinks, corners, reverse corners, etc. Clearly, both the cost of oxygen removal and the gain in oxygen adsorption depend on the local environment of the site involved.

In this work we have analyzed the properties of individual V_O centers and O_2^{2-} groups: formation energies, structure, vibrational modes and core level shifts have been discussed along the series of the alkaline-earth oxides. Not surprisingly, the degree of localization of the trapped electron pair in a vacancy decreases going from MgO (more ionic) to BaO (more covalent). At the same time, the bond strength of the peroxy group increases going from the less basic MgO to the more basic BaO surface. The combined effect is that while the formation of a vacancy-

peroxy pair on the terrace sites of MgO costs 7.35 eV, this cost is reduced to 4.11 eV on the terrace sites of BaO, with the other two oxides exhibiting intermediate behavior.

The other aspect investigated is that of the role of the low-coordinated sites in this process. This seems to be very pronounced on MgO: if we assume to create a vacancy on a corner, and to form a peroxy group on another kink or corner, the whole cost for the process is 5.08 eV, much lower than when all the sites involved are on the terraces. On BaO the formation of a vacancy still depends on the site where the O atom is removed but the formation of the peroxy group is site-insensitive, as it leads to virtually the same energy gain on terraces, edges, and corners. This behavior is observed, in a less pronounced way, also for the other members of the series, CaO and SrO. In this respect, the role of surface area and surface morphology of the sample on the concentration of defects is expected to be much more pronounced on MgO than on the other oxides of the group.

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