

## EPR Study of the Surface Basicity of Calcium Oxide. 3. Surface Reactivity and Nonstoichiometry

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High surface area polycrystalline calcium oxide forms ozonide  $\text{O}_3^-$  ions upon  $\text{O}_2$  adsorption and  $\text{NO}_3^{2-}$  anions under low pressures of NO. Both radical anions, detected by electron paramagnetic resonance (EPR), are not observed in the case of the homologous magnesium oxide. This behavior reveals the presence, in CaO, of anomalies with respect to the ideal composition of an ionic oxide which are identified in terms of two main types of defects. The first type consists of positive holes dispersed in the bulk and originated by the unavoidable presence of  $\text{Na}^+$  ions in the composition of the solid. The decomposition of the surface ozonide shows the formation of a transient surface stabilized  $\text{O}^-$  (the chemical notation of a positive hole associated to an oxide ion) which is for the first time reported at the surface of CaO. The second type of defect consists of surface peroxide groups (present at particular surface sites where they are formed by pairing of two distinct  $\text{O}^-$ ) which react with nitric oxide (NO) yielding  $\text{NO}_3^{2-}$  radical anions. The presence of peroxide is not related to the presence of impurities but, rather, to a certain propensity of the solid to form such ions at the surface along the dehydration process.

### Introduction

The surface reactivity of calcium oxide, despite the important applications of this solid in the field of the automotive exhaust purification,<sup>1,2</sup> is far less known than that of the homologous magnesium oxide which represents the prototype of a binary ionic oxide for both surface science and surface chemistry.<sup>3,4</sup> While magnesium oxide has been the object of systematic investigation over the years, only recently the number of papers devoted to specific aspects of the CaO physical properties and surface reactivity has increased.<sup>5–8</sup> It is generally believed that the properties of CaO, which has the same rock-salt structure of MgO, parallel those of this latter oxide scaled by its higher basicity. The basicity of an oxide is related, in general terms, to the effects of the Madelung potential at specific surface sites on the electron donor capability of  $\text{O}^{2-}$  surface ions. This point has been addressed by Pacchioni et al.<sup>9</sup> in a seminal theoretical paper about this subject which was indeed devoted to a comparison of the surface basicity of MgO and CaO monitored through the reactivity with carbon dioxide and sulfur dioxide.

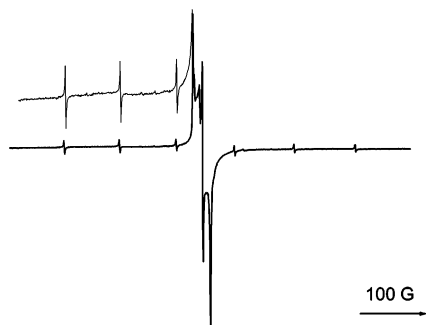
The higher basicity of CaO is the reason, as pointed out in the two previous papers of this series,<sup>10,11</sup> why the specific reactivity of this oxide was not observed for MgO like, for instance, the surface dissociation of saturated hydrocarbons. The high basicity of CaO however is not conflicting with the accepted description of polycrystalline alkaline earth oxides, which are usually made up of cubes of variable size exposing  $\text{Me}^{2+}$  and  $\text{O}^{2-}$  ions having three types of distinct coordination states (5c for plane (100) faces, 4c at steps and cubic edges, 3c on corners) generally indicated as  $\text{M}_{\text{Nc}}^{2+}$  and  $\text{O}_{\text{Nc}}^{2-}$  with  $N = 3, 4, 5$ . The reactivity of the surface exposed ions (for instance the basicity of  $\text{O}_{\text{Nc}}^{2-}$ ) is expected to increase with decreasing coordination.

This simple view explains the surface reactivity of alkaline earth oxides (hereafter AEO) in a number of cases. However, some divergences from the illustrated model have been reported in the case of calcium oxide. In particular, several years ago, Cordischi and co-workers<sup>12</sup> observed the formation of surface ozonide anions ( $\text{O}_3^-$ ) by direct adsorption of molecular oxygen onto CaO. This phenomenon (not observed for MgO) was interpreted in terms of the presence of arrays of  $\text{O}^-$  ions at the surface after thermal activation. Some years later Freund et al.<sup>13</sup> explained the activity of bare CaO in the oxidative dimerization of methane observed above 823 K, once again in terms of the presence of  $\text{O}^-$  ions in the solid as suggested by charge distribution analysis experiments. The  $\text{O}^-$  ion, in fact, can be regarded to as a defect electron (hole) associated to an oxide  $\text{O}_{\text{LC}}^{2-}$  ion. Despite the presence and the role of  $\text{O}^-$  invoked by the mentioned papers, no direct observation of this paramagnetic ion was obtained by electron paramagnetic resonance (EPR, the most suited technique to detect small concentrations of paramagnetic species) on thermally activated CaO. The only spectra of  $\text{O}^-$  observed in CaO are those recorded when this species is associated to cation vacancies in the bulk (V-type defects) of the irradiated solid.<sup>14,15</sup> This lack of detectability of  $\text{O}^-$  species in nonirradiated CaO is usually explained<sup>12,13</sup> with the presence in CaO of diamagnetic aggregates of  $\text{O}^-$  anion; however the whole problem remains not yet fully understood.

The purpose of the experimental work reported in the present paper was to investigate the particular reactivity of the CaO surface not observed for MgO and not simply amenable to its higher basicity. This has been done by revisiting the interaction of oxygen with the bare CaO surface and carefully monitoring the early steps of the interaction of the surface with nitric oxide.

In particular, an effort is made to elucidate the nature of highly reactive surface oxygen species which cannot be directly monitored by EPR.

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**Figure 1.** EPR signal of the ozonide  $\text{O}_3^-$  species formed by adsorption of  $\text{O}_2$  at the surface on bare, thoroughly dehydrated, CaO. Spectrum recorded at 77 K. The upper trace is overamplified to show the absence of superoxide species.

## Experimental Section

Since details of the CaO preparation were reported elsewhere<sup>10,11</sup> we will briefly mention the basic points of the procedure. The experiments were carried out using CaO obtained via slow thermal decomposition of commercial high-purity  $\text{CaCO}_3$  (ex- Aldrich). The activation of the sample, to obtain a carbonate- and hydroxyl-free surface, was performed at 1170 K under a residual pressure of  $10^{-5}$  mbar for 1 h. The surface area of the resulting oxide is  $83 \text{ m}^2 \text{ g}^{-1}$ . Traces of  $\text{Mn}^{2+}$  ions in the bulk of CaO produce an EPR signal consisting in the typical manganese sextet centered nearby the free electron  $g$  value. This signal always appears in the EPR spectra of the solid and has been used as widely indicated in the literature as internal standard for  $g$  values calibration. The amount of  $\text{Mn}^{2+}$  in the solid, however, is extremely low ( $9.5 \times 10^{15}$  Mn atoms per g of CaO), and the  $\text{Mn}^{2+}$  sextet intensity is not affected by contacting the sample with the gases employed in this work. Any participation of  $\text{Mn}^{2+}$  to chemical interactions of CaO is therefore ruled out.

Contrastingly the unavoidable presence of Na traces, even in high-purity  $\text{CaCO}_3$ , generates an alteration of stoichiometry of the system (see below). In the starting material the amount of sodium corresponds to  $2.85 \times 10^{18}$  Na atoms per g of CaO.

High-purity  $\text{H}_2$ ,  $\text{O}_2$ , and  $^{14}\text{NO}$  (Matheson) and  $^{15}\text{NO}$  (Icon Service) have been used in all experiments.

X-band EPR spectra were recorded at room temperature and at 77 K on a Bruker EMX spectrometer operating at 100 kHz field modulation. The EPR computer simulations were obtained using a program derived from the program SIM32.<sup>16</sup>

Chemical analysis of the starting material to evidence the concentration of metal ionic impurities was performed by inductively coupled plasma atomic emission spectrometry (ICP-AES). Standard solutions for calibration are prepared in aliquot for sample blanks.

## Results and Discussion

**1. Reactivity with  $\text{O}_2$ : Localization of Holes at the Activated Surface.** An important difference is observed between CaO and MgO when the two fully dehydrated oxides are contacted with  $\text{O}_2$  at room temperature. MgO does not react at all with oxygen whereas CaO does, forming a surface-adsorbed paramagnetic species. Thoroughly dehydrated CaO does not exhibit any EPR signal except for the described sextet of lines due to traces of  $\text{Mn}^{2+}$  ions. When molecular oxygen (30 mbar) is adsorbed on the solid an EPR spectrum is given rise which is reported in Figure 1 and whose spectral parameters are listed in Table 1. On the basis of the  $g$  values derived from computer simulation (Figure 2) the signal is easily identified as a surface-



**Figure 2.** Experimental and computed EPR spectra of the ozonide ion adsorbed on CaO.

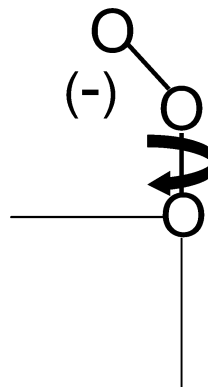
**TABLE 1: Spin-Hamiltonian Parameters of the Paramagnetic Species Described in the Present Paper**

adsorbed species on CaO	Ab, %	$g_{zz}$	$g_{yy}$	$g_{xx}$
ozonide ( $\text{O}_3^-$ )	71	2.0031	2.0189	2.0101
	29	2.0040	2.0178	2.0100
superoxide ( $\text{O}_2^-$ )	100	2.097	2.009	2.007

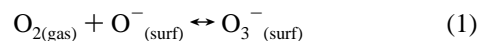
  

adsorbed species on CaO	Ab, %	$g_{\parallel}$	$g_{\perp}$	$(^{14}\text{N})A_{\parallel}, \text{G}$	$(^{14}\text{N})A_{\perp}, \text{G}$
$\text{NO}_3^{2-}$	75	2.0057	2.0055	61.72	41.00
	25	2.0069	2.0059	61.48	38.32

## SCHEME 1



adsorbed ozonide ( $\text{O}_3^-$ ) radical anion. An extremely similar spectrum was already reported by Cordischi and co-workers<sup>12</sup> several years ago, recorded using samples prepared starting from calcium hydroxide. However, in that case, the authors detected, in addition to  $\text{O}_3^-$ , the presence of a consistent amount of adsorbed superoxide anions ( $\text{O}_2^-$ ). This is not observed in our case as shown by amplifying the spectrum in Figure 1 in the region of the  $\text{O}_2^- g_{zz}$  value. The formation of ozonide can be readily explained by postulating the presence at the surface of  $\text{O}^-$  radical ions and their reaction with molecular oxygen.



The  $\text{O}_3^-$  ion exhibits a bent structure (Scheme 1) similar to that observed for the same species (though generated in a different experiment) on MgO.<sup>17</sup> This has been shown by using  $^{17}\text{O}$ -enriched  $\text{O}_2$  in reaction 1 and analyzing the hyperfine structure ( $^{17}\text{O}$  has a nuclear spin  $I = 5/2$ ) of the EPR spectrum. In the resulting spectrum (figure not shown for sake of brevity) the two oxygen atoms belonging to the adsorbed molecule are not magnetically (hence structurally) equivalent. In fact two distinct sextets with different hyperfine coupling constants have been observed.



**Figure 3.** EPR spectrum observed after decomposition of the ozonide ion at 323 K in dynamic vacuum. The perpendicular component of the  $O^-$  species is clearly visible at  $g = 2.075$ . This component progressively disappears by annealing under vacuum in mild conditions (373 K).

The shape of the spectrum in Figure 1 dramatically changes, when the temperature is raised from 77 K to room temperature due to a rotational motion about the  $\sigma$  bond. This causes the averaging of the two extreme elements of the  $g$  tensor confirming the idea of a bent structure of the surface ozonide (Scheme 1).

The amount of surface ozonide, evaluated by spin counting using weak pitch as a reference standard, is about  $1 \times 10^{18}$   $O_3^-$  per gram of calcium oxide.

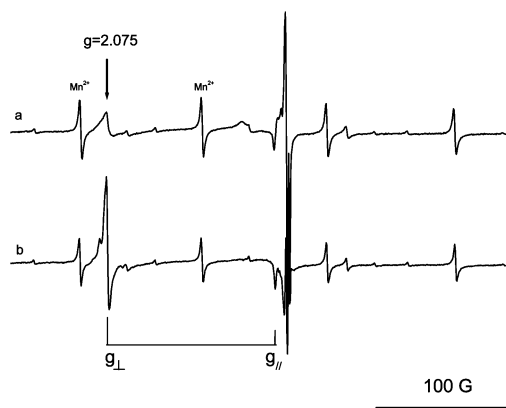
Similar to other cases,<sup>12,13</sup> a question arises from the results reported above since the  $O^-$  ion is a paramagnetic entity and thus, in principle, EPR detectable. However no EPR spectrum is shown by CaO prior the contact with oxygen and we have to preliminarily conclude that the  $O^-$  species in question is EPR silent. Some clue to this dilemma can be obtained by thermal decomposition of surface  $O_3^-$  ions. Gentle annealing of the sample (323 K) under dynamic vacuum leads to decomposition of the ozonide, and two new EPR signals are observed (Figure 3). The first one is due to the well-known superoxide  $O_2^-$  species (nearly axial signal with  $g_{xx} \approx g_{yy} = 2.00$  and  $g_{zz} = 2.10$ , Table 1) while the second consists of a narrow, nearly symmetric line at  $g = 2.075$  not observed in ref 12. A  $g$  value of 2.075 is compatible with the low field component ( $g_{\perp}$ ) of the EPR signal of an  $O^-$  ion.<sup>18</sup> In an asymmetric crystal field, in fact, the p-orbital levels of oxygen are split and one has, in the case for instance of axial symmetry, the following expected  $g$  values<sup>18</sup>

$$g_{zz} = g_{\parallel} \approx g_e$$

$$g_{xx} = g_{yy} = g_{\perp} = g_e + 2\lambda/\Delta E \quad (2)$$

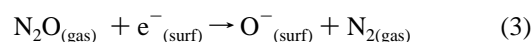
where  $\lambda$  is the spin-orbit coupling constant of oxygen and  $\Delta E$  the splitting between the energy of the  $p_z$  orbital (hosting the unpaired electron) and that of the degenerate  $p_x$  and  $p_y$  orbitals. The line at 2.075 disappears upon contact with  $O_2$  and the typical signal of  $O_3^-$  is restored showing that reaction 1 is reversible. The described decomposition of  $O_3^-$  is, in stoichiometric terms, more complex than a mere formation of  $O^-$  and  $O_2^-$  (which are actually observed by EPR) as in such terms the reaction violates charge balance. The exact mechanism of such reaction, which probably involves the formation of some diamagnetic intermediate, is not, however, essential to the scope of the present paper.

The spectrum of  $O^-$  ions stabilized at the surface of oxides has been already observed in the past, in a few cases including MgO. At the surface of MgO the  $O^-$  ion is generated via



**Figure 4.** EPR spectra observed during irradiation (a) and immediately after irradiation (b) of CaO with UV polychromatic light.

reaction of a surface trapped electron with  $N_2O$  causing electron transfer and nitrous oxide decomposition<sup>19–23</sup>



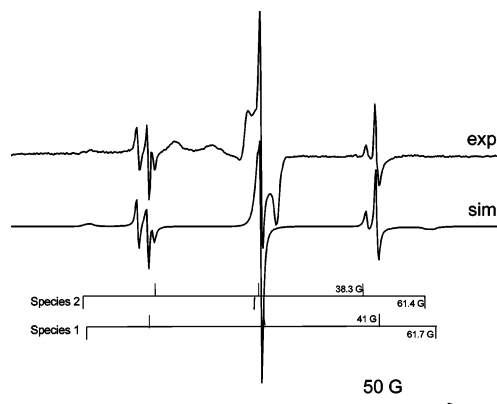
or, alternatively, by irradiation of the solid causing electron-hole separation.<sup>24,25</sup>

By contrast, in the case of calcium oxide the only reported observations of  $O^-$  concerns bulk species stabilized close to cation vacancies ( $V^-$  centers or  $V^0$  centers) having  $g_{\perp} = 2.0697$ .<sup>15</sup> Formation of surface  $O^-$  was never reported before for calcium oxide.

To confirm the assignment of the 2.075 line to  $O^-$  ions, we have recorded the EPR spectrum of a CaO sample under UV irradiation. In such conditions, as shown in the case of MgO,<sup>24,25</sup> charge separation occurs and an electron and a hole are trapped at the surface where they are directly observed during irradiation and, for a limited time, at the end of the irradiation before their recombination. The result of this experiment for CaO is shown in Figure 4 where, beside the signal of the electron at about  $g = 2.00$  a line appears at  $g = 2.075$  which is due to the trapped hole. The line intensity increases immediately after the lamp is turned off. The described experiment unambiguously confirms the assignment to  $O^-$  of the species with a feature at  $g = 2.075$  formed after decomposition of the ozonide (Figure 3). To the best of our knowledge the spectra shown in Figures 3 and 4 correspond to the first observation of the  $O^-$  species on the surface of CaO. Interestingly the  $O^-$  signal in Figure 3 is not stable with temperature increasing and progressively disappears upon heating the system at 343 K under vacuum.

The puzzling conclusion of the series of experiments described above is that the formation of the surface ozonide is amenable to the reaction of  $O_2$  with an  $O^-$  center which is EPR invisible before reaction but which becomes visible after thermal decomposition in very mild conditions of the ozonide adduct. The EPR visible  $O^-$  ion is however unstable as its signal disappears at moderate temperature by thermal annealing.

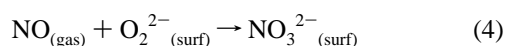
**2. Reactivity with NO at Low Pressure.** In a previous paper from our group<sup>10</sup> concerning the interaction of nitrogen oxides with the CaO surface, a series of narrow EPR lines formed in the early stages of the NO–CaO interaction were observed. The lines disappear upon rising the NO pressure due to the onset of reactions between adsorbed species and the NO molecule. The narrow signal was preliminarily interpreted in terms of the presence of a unique axial species with the two hyperfine elements quite close one to the other ( $A_{\parallel} = 41.8$ ,  $A_{\perp} = 37.3$ ). Successive attempts of reproducing the spectral shape by computer simulation were however unsuccessful and prompted



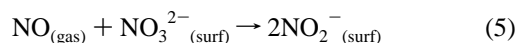
**Figure 5.** Experimental and computer-simulated EPR spectra recorded after adsorption of NO (0.5 mbar) on thoroughly outgassed CaO. In the experimental spectrum some spurious line is observed due to the presence of an initial weak amount of the species which will dominate the spectrum at higher coverage. These lines have not been introduced in the simulation.

us to reexamine the initial assignment also on the basis of new experiments which gave the more resolved spectra here reported. The signal recorded upon adsorption of NO (0.5 mbar) is reported in Figure 5a and has been successfully simulated (two weak lines at the wings of the experimental spectrum are now visible) in terms of two akin species both having axial  $\mathbf{g}$  and  $\mathbf{A}$  tensors with rather high nitrogen hyperfine coupling ( $A_{||} \approx 61$  G,  $A_{\perp} \approx 38\text{--}40$  G, Figure 4b, Table 1). The calculated spectral parameters are in excellent agreement with those expected for a 25-electrons radical ion such as  $\text{NO}_3^{2-}$  and found for this radical when it is isolated in KCl or  $\text{KNO}_3$  matrixes.<sup>26</sup> This tetraatomic radical anion is pyramidal with the 25th electron in an antibonding orbital ( $2a''_2$  if one refers to the planar  $\text{NO}_3^-$  ion) which acquires some  $s$  character and become less antibonding with the progressive bending of the structure.

The formation of the  $\text{NO}_3^{2-}$  radical ions is the result of a net oxidation of NO by the surface and cannot derive, in the experimental conditions of our experiment, from a surface disproportionation of the molecule. To form the observed radical, it is necessary to have at the surface a pair of vicinal  $\text{O}^-$  ions or, more probably, a peroxide group  $\text{O}_2^{2-}$  (vide infra). The reaction can be written as follows



and again indicates an anomaly in the stoichiometry of the solid. The surface  $\text{NO}_3^{2-}$  species is stable in the described conditions but is destroyed by a successive dose of NO at higher pressure (around 30 mbar) which likely leads to the formation of two diamagnetic nitrite groups



An attempt to verify whether the two species here described ( $\text{O}_3^-$  and  $\text{NO}_3^{2-}$ ) form on two independent surface sites was performed adsorbing  $\text{O}_2$  and NO in successive steps. The attempt was however unsuccessful (data not shown for brevity) as NO destroys the surface ozonide forming  $\text{NO}_3^{2-}$  which, in turn, is destroyed by another dose of oxygen. After this second oxygen dose the two species are no longer observed at the surface as they are probably replaced by stable diamagnetic species which permanently occupy the site.

**Anomalies in the Stoichiometric Composition of CaO: Presence and Role of  $\text{O}^-$  and  $\text{O}_2^{2-}$  Ions.** All evidence reported before indicates that the calcium oxide employed in the present

work presents some deviations from the stoichiometry expected for an ionic oxide exclusively composed of  $\text{Me}^{2+}$  and  $\text{O}^{2-}$  ions. The first anomaly consists of the presence of holes in the system which are localized at the surface by adsorption of molecular oxygen. The origin of the holes very likely depends on the presence of impurities in the solid. The second anomaly is the formation of  $\text{NO}_3^{2-}$ , which has to be related to surface peroxide groups or, at least, of a pair of reactive oxygen ions. We will now examine both types of anomalies and discuss their origin.

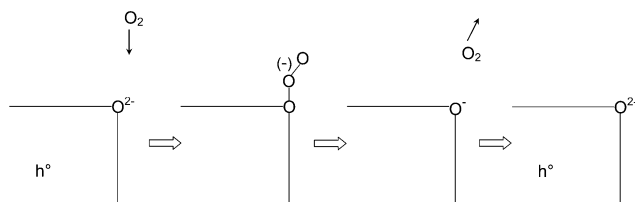
Two types of impurities are known to induce the formation of holes in divalent ionic oxides. The former type consists of monovalent ions such as  $\text{Li}^+$  and  $\text{Na}^+$  whose presence in a cationic site automatically introduce a positive hole into the lattice. It has to be noted that, in this case, the hole formation does not involve the parallel formation of a vacancy in the lattice. In particular a paper from Freund et al.<sup>13</sup> suggests that the activity of undoped CaO in the oxidative dimerization of methane is due to the presence of holes in the system which become catalytically active over 823 K. The authors start from the fact that no  $\text{O}^-$  is observed by EPR at lower temperature to claim that, in such conditions, they are present under the form of “dormant” dimers or peroxide anions  $\text{O}_2^{2-}$  which dissociates at high temperature.

A second phenomenon leading to stoichiometric anomalies in AEO has been described and consists of the dissolution of small amounts of molecular impurities ( $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ) in the solid. The detailed mechanism of these reactions has been described by Kathrein et al.<sup>27</sup> All have in common the formation of cation vacancies and of  $\text{O}^-$  ions or, alternatively, peroxide  $\text{O}_2^{2-}$  groups. With all this in mind we can now try to explain the above-reported data on the surface reactivity of CaO considering a few distinct points.

1. Even though it is not yet totally clear whether the anomalies in CaO surface chemistry have to be ascribed to the presence of chemical impurities or to some intrinsic propensity of this metal oxide, the fact remains that the presence of cationic impurities in CaO seems to be unavoidable even in the case of carefully prepared single crystals. The chemical analysis performed on the starting material employed in the present work indicates, despite the purest calcium carbonate available on the market, the presence of small amounts of monovalent (mainly  $\text{Na}^+$  and  $\text{Li}^+$ ) and divalent ( $\text{Mn}^{2+}$ ) cations (see Experimental Section). Concentration of  $\text{Li}^+$  and  $\text{Mn}^{2+}$  is 1 order of magnitude lower than that of  $\text{Na}^+$ . The presence of  $\text{Na}^+$  to substitute  $\text{Ca}^{2+}$  automatically causes the formation of a hole but not that of cation vacancies. We can thus assume that, whatever their origin, the as prepared calcium oxide contains a small concentration of holes which, in principle, are homogeneously distributed in the solid. The spin counting performed on the ozonide ions (though intrinsically less accurate than the analytical measurements on  $\text{CaCO}_3$ ) gives a value about three times lower than that of the sodium concentration. We can therefore look at the ozonide formation as a surface localization of a fraction of the holes present in the solid.

2. The absence of an EPR spectrum in the case of chemical reactivity apparently due to  $\text{O}^-$  has puzzled several authors<sup>12,18</sup> in the past. One way of explaining this is the formation of peroxy-like species or, alternatively, of other diamagnetic aggregates of oxygen ions. This phenomenon, however, is likely to occur in some instances but is not necessarily required to explain the EPR silence of  $\text{O}^-$ . First of all, a positive hole is in principle mobile and, over a certain temperature, delocalizes. Under such circumstances no EPR of  $\text{O}^-$  is detectable. Second, an  $\text{O}^-$  is a  $2\text{P}_{3/2}$  system and requires EPR observation of a certain





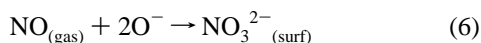
**Figure 6.** Schematic view of a positive hole trapped at the surface of CaO via adsorption of oxygen. The decomposition of the surface ozonide is also shown.

asymmetry of the coordinative environment. In fact in a highly symmetric environment, like the octahedral crystal field of the CaO bulk, the resonance line is broadened beyond detection because of insufficient quenching of the orbital angular momentum and shortening of the spin–lattice relaxation time.<sup>28</sup> Only a net reduction of the symmetry around the oxygen ion localizing the hole allows the observation of the EPR spectrum of  $O^-$ . This occurs in the case of the presence of a cation vacancy in the first coordination sphere of  $O^-$  (like for the  $V^-$  center<sup>29</sup> or of the  $V_{OH}$  center<sup>30</sup> or in the case of localization of the hole on a low coordination ion at the surface. In such a case the splitting ( $\Delta E$ ) of the oxygen p orbitals is large enough to lead to a relatively small  $g$  anisotropy and to a visible spectrum. Something similar is observed in the classic case of silicon-based semiconductors (e.g., boron-doped silicon) where holes are EPR inactive unless a strong mechanical stress is applied to the solid to remove band degeneracy.<sup>31</sup>

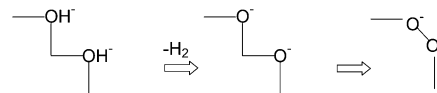
3. The two surface reactions reported in the present paper (eqs 1 and 4) seem to be due to the interaction of  $O_2$  and NO with two distinct surface centers and both lead to a paramagnetic product. In the former case the adsorption of oxygen simply localizes a hole present in the solid which, being relatively mobile, reaches the surface where the interaction with oxygen takes place. The energy developed by reaction 1 is the driving force explaining the migration and the stabilization of the (preexisting) hole at the surface. The phenomenon, remarkably, is reversible. The mechanism of eq 1 is proved by the demolition of the ozonide adduct. In fact the direct decomposition of the ozonide in mild conditions allows the observation of  $O^-$  at the surface as shown by Figure 3. These surface  $O^-$  ions however are unstable in these conditions and a moderate annealing, necessary to overcome a small activation barrier, mobilizes the hole which migrates in the bulk becoming again EPR invisible (Figure 6). The reversible surface localization of charge carriers by the action of adsorbates has been observed in the case of few other solids such as  $TiO_2$ <sup>32</sup> or porous B-doped silicon.<sup>33,34</sup>

The surface site where the holes become localized are most likely at corners of the CaO cubic crystals. The preferential migration of the holes to those sites having the lowest possible coordination has been elegantly shown by Sterrer et al.<sup>24</sup> in the case of photoexcited MgO and is extremely probable also in the present case as CaO has the same structure and morphology of MgO.

4. The reaction of NO leading to the surface  $NO_3^{2-}$  radical anion according to eq 4 is, in principle, compatible with another mechanism not implying the presence of surface peroxides. The same result in fact could be produced by the surface localization of a pair of holes at a suitable site of the surface. In this case the true mechanism should be



However the migration of two holes from the bulk and their simultaneous capture by a single NO molecule seems, at the



**Figure 7.** Schematic view of the formation of surface peroxides on CaO at the double step site or, alternatively, at the reverse corner.

moment, rather unlikely. For this reason we assume reaction 4 as the most likely mechanism for the formation of  $NO_3^{2-}$  surface radical anions. Both mechanisms, however, should be tested by theoretical modeling in order to verify the energies involved in each reactive step. To explain the existence of an  $O_2^{2-}$  group at the surface, we follow the arguments of Kathrein et al.<sup>27</sup> who showed that, especially under geologically relevant conditions, some amount of water can dissolve into the bulk of a binary oxide (MgO, CaO) generating a pair of  $OH^-$  groups and a cation vacancy. The two  $OH^-$  groups facing each other across the cation vacancy eliminate  $H_2$  becoming two  $O^-$  ions which, in turn, gain stabilization forming the chemical bond of a peroxide group within the bulk of the solid. The energy costs needed to compensate the homolytic cleavage of the  $OH^-$  group are provided, according to the scheme, by three distinct contributions, namely,  $H_2$  formation from two H atoms, peroxide formation ( $2O^- \rightarrow O_2^{2-}$ ) and surface relaxation.

The oxide employed in the present work was never submitted to the severe experimental conditions necessary to dissolve non-negligible amounts of water. However, a mechanism such as that described in ref 28 may occur at the surface during the process of surface dehydration at particular sites where the surface morphology reproduces the symmetry present around the bulk cation vacancy. This occurs at a double step of the planar surface or at the reverse corner (RC) site. Both sites exist at the surface of high area alkaline earth oxides and, as shown in the recent past, play an important role in the surface chemistry of these oxides.<sup>35,36</sup> The reaction we propose is schematically described in Figure 7.

It has to be noted that the two residual  $OH^-$  groups at the RC site are in a structurally similar situation of two bulk OH separated by a cation vacancy previously described. With the spin pairing (after  $H_2$  elimination) the two  $O^-$  merge in a single peroxide group undetectable by EPR. This hypothesis explains the systematic formation of tiny amounts of  $NO_3^{2-}$  systematically observed on CaO upon adsorption of small doses of nitric oxide. The fact that the same reaction is never observed on MgO has probably to be ascribed to the higher propensity of calcium to form peroxides with respect to magnesium. The stability of alkaline and alkali earth peroxide is, in fact, known to increase with increasing the cation atomic weight. The possibility of confirming the hypothesis here exposed by a direct observation of surface peroxides (for example by Raman spectroscopy) is severely limited by quantitative factors as the concentration of the paramagnetic  $NO_3^{2-}$  species is very small and its detectability is possible thanks to the extremely high sensitivity of the EPR technique. We rather think that a theoretical simulation of the described process could be attempted in the future to verify the reliability of each step.

## Conclusions

While magnesium oxide, the most investigated alkaline earth oxide, does not react with molecular oxygen and reacts with NO forming (on very few basic sites) an adduct on single  $O^{2-}$  ion (the  $NO_2^{2-}$  ion), the homologous calcium oxide shows a significantly different behavior. It forms in fact surface ozonides upon  $O_2$  adsorption and  $NO_3^{2-}$  anions under low pressures of NO. This different behavior reveals the presence, in CaO, of

anomalies with respect to the current idea about alkaline earth oxides which are usually thought of as formed by  $\text{Me}^{2+}$  and  $\text{O}^{2-}$  ions differing only in terms of coordination degree and Madelung potential. We have identified two types of defects which are as follows:

(i) Holes dispersed in the bulk originated by the presence of  $\text{Na}^+$  ions in the composition of the solid. This anomaly suggests that a better notation for  $\text{CaO}$  should be  $\text{Na}_x\text{Ca}_{1-x}\text{O} (\text{h}^\circ)_x$ . It has to be noted that the preparation of a totally sodium free  $\text{CaO}$  sample seems to be a very difficult task.

(ii) Peroxide groups which form at particular surface sites by pairing of two distinct  $\text{O}^-$ . This process is likely to be unrelated to the presence of impurities but, rather, to a certain propensity of the solid to form such ions at the surface along the dehydration process.

Both defects have been indirectly identified by adsorption of molecules forming surface paramagnetic adducts. It is worth mentioning that the reversible formation of ozonides by oxygen adsorption is particularly interesting and deserves further investigation. This phenomenon can be seen, in fact, as a reversible localization at the surface of a mobile charge carrier (the hole) by an adsorbate (the oxygen molecule). A similar phenomenon has been observed in some cases for semiconductors but is uncommon for insulators.

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## References and Notes

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