Partially Hydroxylated Polycrystalline Ionic Oxides: A New Route toward Electron-Rich Surfaces

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Abstract: Charge traps at the surface of oxide materials play a fundamental role in various chemical processes, such as the activation of supported metal clusters. In this study, combining electron paramagnetic resonance with cluster model DFT calculations, we show that excess electrons at the surface of MgO, CaO, and SrO polycrystalline materials can be generated by preparing weakly hydroxylated surfaces followed by deposition of small amounts of alkali metals. The residual OH groups present on specific sites of the partially dehydroxylated surface act as stable traps for electrons donated by the alkali metal (Na in this case) which forms a Na^+ ion distant from the trapped electron. This process results in the formation of thermally stable $(H^+)(e^-)$ color centers at the surface of the oxide. The procedure could be of interest for the stabilization and activation of supported metal nanoparticles with potential use in catalysis.

1. Introduction

Hydroxyl groups are ubiquitous impurities in wide-gap oxide insulators and there is wide consensus that they play a fundamental role in dictating the chemical and physical properties of oxide surfaces.[1,2] The role of OH groups has been indicated as a crucial factor in determining the photocatalytic properties of TiO_2 surfaces[3] and key to explain electron trapping phenomena at Al^{3+} ions in ZSM-5 zeolites.[4] Surface science studies have demonstrated a remarkable difference in the reactivity of clean and hydroxylated surfaces. For example Kelber et al.[5] observed that Cu growth on a partially hydroxylated α-Al_2O_3 (0001) surface is dominated by two-dimensional islands, while on dehydroxylated surfaces Cu growth is dominated by three-dimensional island formation. It has been proposed that these differences arise from the presence of surface OH groups, which induce an enhanced reactivity of the surface toward metals.[6] This aspect is of crucial importance as metal atoms and clusters deposited on oxides supports are important chemical systems with applications spanning from catalysis to microelectronic devices and anticorrosion protection.[7-9] The aim of this study is to investigate the role played by isolated hydroxyl

groups in stabilizing excess electrons which modify the reactivity of the MgO surface. The excess electrons can be introduced by specific donors such as alkali metal atoms. In previous studies we demonstrated that on a fully dehydroxylated MgO surface alkali metal atoms are bound to oxide anions and stabilized at specific sites, where the alkali metal wavefunction is strongly polarized while the metal remains neutral.[10,11] In this paper we show that the presence of residual hydroxyl groups drastically alters the surface reactivity toward the adsorbed alkali atom leading to spontaneous ionization of the metal with subsequent formation of surface-trapped electrons.

Surface excess electrons are remarkable entities, which lead to specific functionalization of oxide systems and to a corresponding complete change of their chemical (and catalytic) reactivity.[12] At variance with normal polycrystalline MgO, an electron-rich MgO surface is able to activate rather inert molecules such as N_2 with formation of the corresponding radical anion.[13] Electron-rich surfaces, that is, surfaces characterized by the presence of excess electrons stabilized at specific sites, can be used to modify the catalytic activity of supported metal nanoclusters. It has been reported that negatively charged Au clusters are much more active in promoting conversion of CO to CO_2 then their neutral counterparts.[14,15] Charging is

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usually obtained by creating a highly defective surface (e.g., by generation of oxygen vacancies) and by subsequent evaporation of the metal onto the modified substrate.[16] Recently, a completely different procedure to generate charged supported Au species has been proposed, on the basis of the use of ultrathin oxide films on a metal substrate.[17−19] Here electrons tunnel through the thin films leading to negatively charged supported Au clusters with shape and reactivity which differ substantially from that of the corresponding neutral species.[20−22] These few examples well illustrate the potential of chemically modified oxide surfaces also in practical applications.

Surface electron trapping on oxides was first observed by Tench and Nelson in 1968 by exposing MgO to hydrogen.[23] The phenomenon was tentatively attributed to the population of empty sites naturally present on the surface[23] by extending the De Boers model of bulk F center to the surface.[24] A bulk F center consists of two electrons trapped in a three-dimensional anion vacancy. However, work performed in the past decade,[25−29] and recently summarized in a review article,[30] has clearly shown the different nature of these centers. Exposure of MgO[31] or CaO[32] surfaces to hydrogen atoms results in fact in the spontaneous ionization, at temperatures as low as 77 K, of H• with the subsequent formation of excess electrons and extra protons on the surface, as schematically represented in eq 1.

$$H^{\bullet} + -M^{2+}-O^{2-}- \rightarrow -\overset{e^-}{M^{2+}} -\overset{H^+}{O^{2-}}- \qquad (1)$$
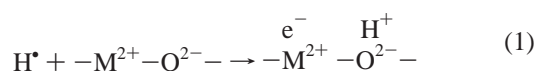
These centers have been named $(H^+)(e^-)$[25] to clearly indicate that they result from the ionization of the H atom, with subsequent stabilization of the electron on low-coordinated cationic sites, and of the proton on surface oxide anions. Reaction 1 leads to surface excess electron color centers, stable up to 373 K, fully characterized by EPR, IR, and UV measurements and theoretical calculations.[25−30]

In this paper we show that the same result can be obtained simply by a controlled dehydroxylation of alkaline-earth oxides followed by evaporation of small amounts of alkali atoms (e.g.,

Na). We will show, based on a combined experimental−theoretical characterization of the resulting centers, that the hydroxyl groups are precursors of electron trapping sites, thus providing a natural and simple way to functionalize an oxide surface. The role of the OH groups is essentially that to "solvate" the excess electron which derives from the ionization of the alkali metal atom. To be thermodynamically favorable, the process requires also that on the surface are present morphological sites like reverse kinks and reverse corners which are required to stabilize the resulting alkali metal cation. In this respect, the present study represents an example of surface defect engineering, where both morphological irregularities of a polycrystalline sample and residual OH groups are used to chemically modify and functionalize an oxide surface.

2. Experimental Section

2.1. Experimental Details. High-surface-area polycrystalline MgO, CaO, and SrO oxides were prepared by slow decomposition of the corresponding hydroxides (MgO) and carbonates (CaO and SrO) in vacuum as described elsewhere.[33] Thermal activation at 1173 K produces virtually hydroxyl free samples,[34,35] which have been investigated in previous studies.[10,11] All three oxides (MgO, CaO, and SrO) display the same NaCl-like structure, high thermal stability, and surface areas of about 200 m^2 g^{-1} (MgO), 70 m^2 g^{-1} (CaO), and 30 m^2 g^{-1} (SrO). In the experiments the weight of the samples was normalized with respect to the surface area.

To explore the role played by isolated residual surface hydroxyls, experiments were performed on samples activated at 1073 K. At this temperature only few OH⁻ groups are left on the surface at low coordinated sites, which are at the limit of infrared spectroscopy detectability.[36]

Sodium metal shots were distilled in vacuum to form a metal mirror in a separate part of the quartz cell used for EPR measurements. The metal was evaporated on the sample in situ by heating the metallic mirror while keeping the powder at nearly room temperature. The amount of metal deposited on the sample was roughly controlled by varying the exposure time of the powder to the metal vapors. To obtain a low level of added metal, the metal evaporation was stopped at the first appearance of a pale blue color of the oxide powder.

EPR spectra were recorded at 298 K and at 77 K on a Bruker EMX spectrometer operating at X-band frequencies and equipped with a cylindrical cavity operating at a 100 kHz field modulation. CW spectra were recorded at 1 mW microwave power and 0.05 mT modulation amplitude. The intensity of the EPR signal was obtained from the absorption curve area by a numerical integration of the data. DPPH (g = 2.0036) and a solid solution of Mn^{2+} in MgO (g = 2.0064) have been used as standards for g-value calibration and quantitative evaluation of the number of centers. The CW-EPR spectra were simulated using the SIM32 program.[37]

2.2. Computational Details. The surface of MgO is represented by a finite nanocluster, containing several thousands of atoms. The central part of the cluster, treated quantum-mechanically (QM), is surrounded by a region of classical ions whose polarizability is described by a shell model (SM).[38] Cations in the SM region at the interface with the QM region are replaced by ions (hereafter indicated as Mg*) on which a semilocal effective pseudopotential (ECP) is centered, to reproduce the Pauli repulsion and avoid the nonphysical polarization of QM

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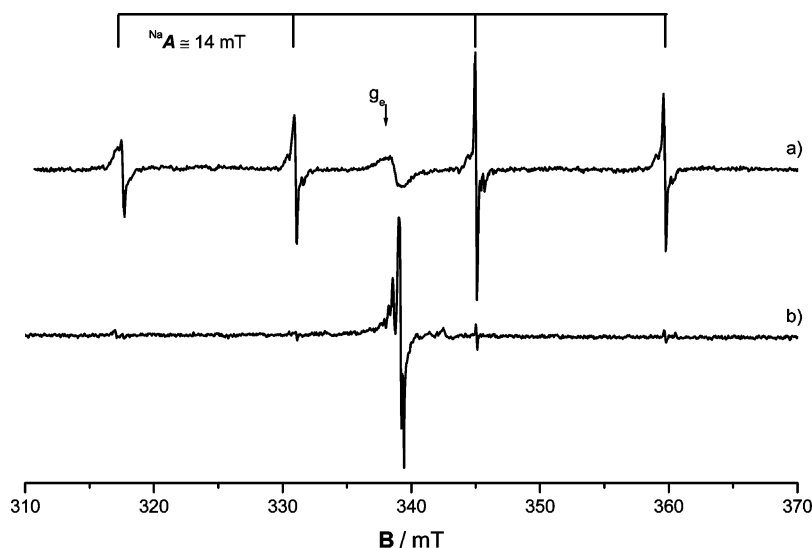(38) Dick, B. G.; Overhauser, A. W. *Phys. Rev.* **1958**, *112*, 90.

Figure 1. EPR spectra of Na atoms adsorbed on (a) fully dehydrated and (b) partially hydroxylated MgO. Both spectra were recorded at 77 K.

interface anions. Region I, QM and SM, is then surrounded by a large array of point charges (PC) to reproduce the long-range electrostatic potential.

This scheme is implemented in the GUESS code[39] interfaced with the Gaussian 03 code,[40] and the total energy of the hybrid system is calculated as a sum of classical and QM contributions. Forces acting on all centers in region I, both QM and classical (cores and shells), can be calculated allowing the simultaneous optimization of their position. All centers in QM region and Mg* interface atoms have been allowed to move during the optimization, while only shells, not cores, have been relaxed in the SM region. Thus, the electronic polarization has been included in a large portion of the surface, while ionic polarization is restricted to a few tens of atoms. The total energy and the electronic structure of the QM cluster are calculated within density functional theory (DFT) using the hybrid B3LYP exchange-correlation functional.[41,42]

A nanocluster made up of $23 \times 23 \times 12$ atoms, cut in different ways to reproduce different types of surface defective sites, has been used; the dimension of region I is $15 \times 15 \times 8$ atoms. Three different QM clusters have been considered to model a step site: $Mg_{18}O_{18}Mg*_{24}$, $Mg_{20}O_{20}Mg*_{27}$, and $Mg_{23}O_{23}Mg*_{30}$. A $Mg_{21}O_{21}Mg*_{28}$ QM cluster has been used to model an anionic reverse corner site. A cationic reverse corner and a kink site have been simulated by $Mg_{19}O_{19}Mg*_{25}$ and $Mg_{16}O_{16}Mg*_{22}$ QM clusters, respectively.

The 6-311+G** basis set has been used for the H atoms; the 6-311+G* basis has been used for Na and the Mg atoms adjacent to the H species. A 6-31G* basis set was adopted for the O atom belonging to OH$^-$ groups and for surface Mg and O atoms directly bound to adsorbed species. All other atoms are treated with a standard 6-31G basis set.

To estimate the spatial distribution of the unpaired electron in paramagnetic centers, atomic spin populations have been evaluated, and plots of iso-surfaces at constant spatial-resolved spin density have been generated. The isotropic hyperfine interaction (Fermi contact term) of the unpaired electron with H, Na, and Mg_{LC}^{2+} cations have been determined.

3. Results and Discussion

3.1. EPR Spectra. The interaction of alkali metal atoms with thoroughly dehydrated high-surface-area MgO leads to deeply

blue colored solids associated with EPR spectra characteristic of isolated monomeric species.[10,11] Figure 1a shows a representative X-band EPR spectrum recorded at 77 K obtained by contacting a fully dehydrated MgO sample, activated at 1173 K, with Na vapors. The spectrum is dominated by a quartet of lines separated by about 14 mT, arising from the hyperfine interaction of the unpaired electron wave function with the sodium nucleus, $I = {}^3/_2$. Similar results were obtained for the deposition of K atoms, and a detailed analysis of the signal can be found in references 10 and 11. At approximately $g = 2$ a small unresolved signal is present in the experimental spectrum which includes contributions from low-atomic-character species ($<1\%$) related to the presence of tiny amounts of surface oxygen vacancies (F centers)[43] together with small metal particles, both of which have been previously studied.[44] Performing the same experiment using a sample dehydrated at 1073 K and exposed to the same amount of Na vapors leads to a blue colored sample characterized by the EPR spectrum shown in Figure 1b. At this temperature a few isolated OH groups are left on the surface which are barely detected by means of IR spectroscopy; it is the role played by these isolated OH groups which will be dealt with in the following. The EPR spectrum of the sample activated at 1073 K displays significant differences with respect to that shown in Figure 1a. The hyperfine quartet due to adsorbed Na atoms is substantially depressed while the intensity of the feature in the $g = 2$ region now clearly dominates the spectrum. This feature is now not only much more intense but also shows clear differences with respect to the completely dehydrated system, Figure 1a, which are best appreciated in Figure 2a , where a magnification of the central portion of the spectrum is reported.

The spectrum is characterized by a powder pattern dominated by an axial feature with $g_{\parallel} = 2.001$ and $g_{\perp} = 1.999$ and characterized by a 0.207 mT splitting of the perpendicular component. From the intensity of the signal a concentration of about 7×10^{15} spins/m^2 is estimated. At lower field a multiplet of lines is present which may be due to Na clusters; this small feature will not be commented upon further. The overall shape and the spin Hamiltonian parameters of the spectrum reported

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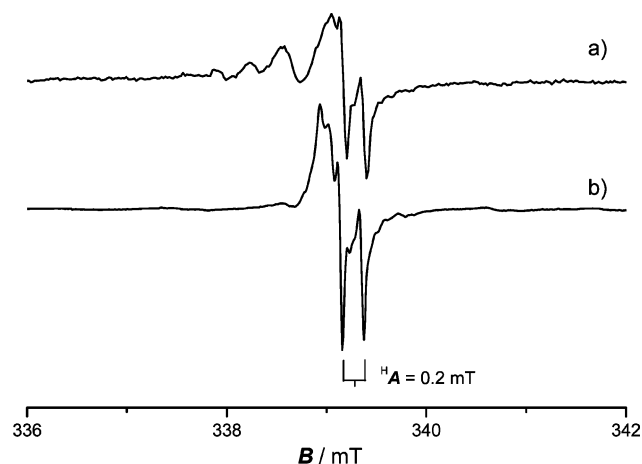
Figure 2. (a) Magnification of the EPR spectrum obtained upon reaction of Na atoms with partially hydroxylated MgO, Figure 1b; (b) Spectrum of $(H^+)(e^-)$ centers generated by reaction of atomic hydrogen with fully dehydrated MgO.
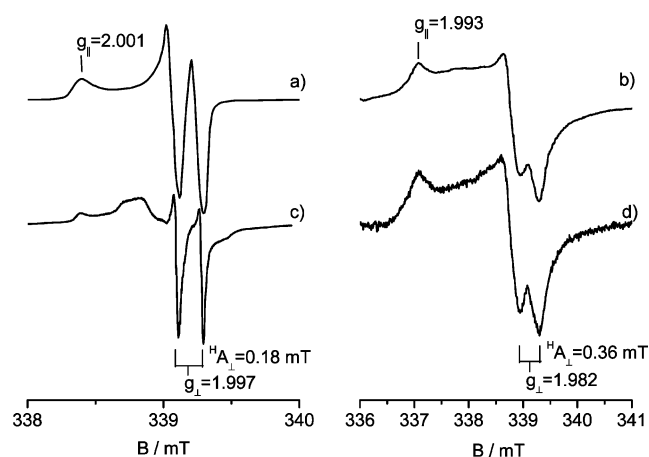

Figure 3. EPR spectra of (a) Na atoms adsorbed on partially hydroxylated CaO; (b) Na atoms adsorbed on partially hydroxylated SrO; (c) $(H^+)(e^-)$ centers on CaO; (d) $(H^+)(e^-)$ on SrO.

in Figure 2a are virtually identical to those derived for the so-called $(H^+)(e^-)$ centers on MgO obtained by reaction of the surface with H atoms.[25−28] To corroborate this assignment a representative spectrum of $(H^+)(e^-)$ centers on MgO is shown in Figure 2b. The analogy is apparent and does not need further comments.

Analogous experiments to those described above have been performed contacting the other members of the alkaline-earth oxides group (CaO and SrO) with Na atoms, Figure 3. Also in this case the oxides were outgassed at 1073 K thus presenting a very low degree of surface hydroxylation, which we assume is comparable for the three oxides. Contrary to what observed in the case of the high temperature activated oxides,[11] the characteristic features of isolated adsorbed atoms are absent in this case and the spectra are dominated by intense axial features with $g_{\parallel} = 2.001$ and $g_{\perp} = 1.997$ for CaO, Figure 3a, and with $g_{\parallel} = 1.993$ and $g_{\perp} = 1.982$ for SrO, Figure 3b, and doublet hyperfine splittings of the perpendicular components of about 0.18 and 0.36 mT for the two oxides, respectively. Comparison of these spectra with those obtained contacting the fully dehydroxylated system with H atoms, Figure 3c,d reveals that the relevant spectral features are identical, thus indicating that the unpaired electron in the two cases experiences the same environment. It is interesting to note that the shift of the parallel
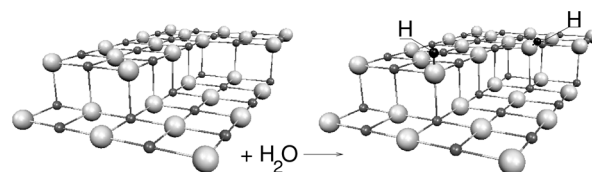

Figure 4. One H_2O molecule has been adsorbed dissociatively on a defective site of the MgO(100) surface. The H^+ species is bound to an O_{3c} anion on a kink, while the OH^- fragment is bound on a cationic reverse corner. In the resulting structure, two hydroxyl groups with similar environment are formed.

g component at higher fields going from MgO to SrO scales linearly with the spin−orbit coupling constant of the metal cations. This fact strongly suggests that the unpaired electron is localized on the M^{2+} oxide's cation nearby a proton, as indicated by the hyperfine coupling in the perpendicular region of the spectrum.

As we mentioned in the introduction, surface morphological features such as steps, corners, or reverse corners are able to promote the dissociation of H atoms stabilizing the two fragments (H^+) and (e^-) in the form of a surface hydroxyl unit and of an excess electron (eq 1).[30]

The experimental results reported so far can then be explained considering the ionization of the Na atom and the subsequent localization of the valence electron nearby a preexisting OH group to form the same $(H^+)(e^-)$ center. This reaction can be schematically written as follows:

$$Na^{\bullet} + -M^{2+} \overset{H^+}{-O^{2-}} - \rightarrow -M^{2+} \overset{e^-}{-O^{2-}} \overset{H^+}{-} + Na^+ \quad (2)$$
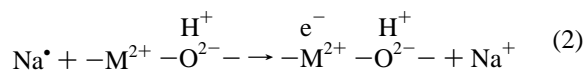
the Na^+ cation being localized sufficiently far away from the paramagnetic center, so that no hyperfine coupling to the ^{23}Na nucleus is detected. This working hypothesis will now be analyzed by means of theoretical calculations for the model system MgO.

3.2. Theoretical Calculations. The aim of the calculations is to investigate the role of residual hydroxyl groups on the MgO surface on the adsorption of Na and the ability of these species to promote the spontaneous ionization of Na. Stated differently, we want to analyze theoretically if OH groups at particular locations of the surface create potential electron traps which can be populated by doping the surface with alkali atoms. A second aspect to consider is the distance between the adsorbed Na^+ ion, formed upon ionization, and the resulting $(H^+)(e^-)$ defect center.

In a model calculation, one H_2O molecule has been adsorbed on low-coordinated sites of the MgO(100) surface, Figure 4 (these are the sites where residual OH groups remain after partial dehydroxylation). The heterolytic dissociation of water formally leads to a proton, H^+, bound to an oxide anion, O^{2-}, and a hydroxyl group, OH^-, bound to a surface cation, Mg^{2+}. This distinction, however, is purely semantic. In fact, in both cases a hydroxyl group is formed whose properties only depend on the location on the surface. If the two "ionic" fragments, H^+ and OH^-, are adsorbed on a three-coordinated corner oxide anion, O_{3c}, and on a cationic reverse corner site, respectively, Figure 4, two OH groups are formed with similar coordination. Not surprisingly, the calculation of the vibrational frequencies of the two OH groups done with a $Mg_{18}O_{18}Mg^*_{23}$ embedded cluster model leads to two nearly identical values for the OH stretching frequencies, 3684 and 3660 cm^{-1}, respectively,
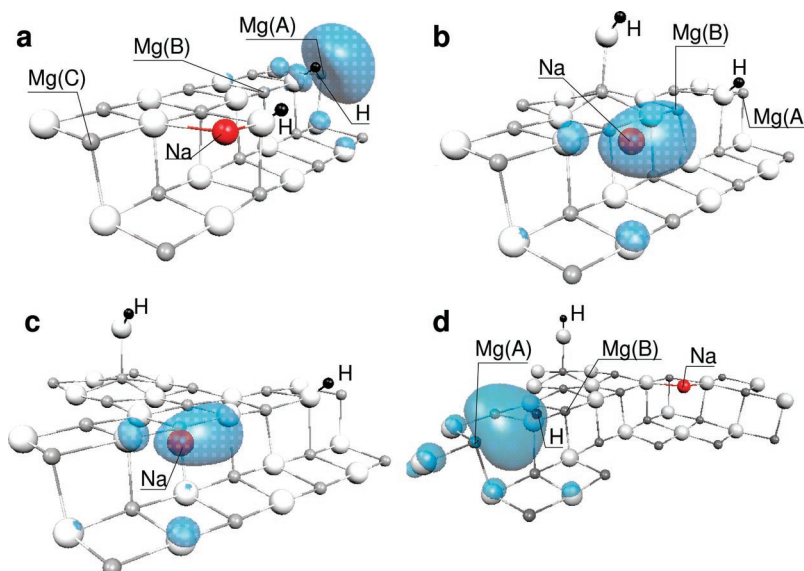
Figure 5. Na atom adsorbed on step sites (a, b, and c) of the MgO(100) surface in the presence of a dissociated water molecule, H$^+$ and OH$^-$. OH$^-$ is coordinated by two Mg^{2+} cations (Mg$_{4c}^{2+}$ and Mg$_{5c}^{2+}$), and by Na (a) or adsorbed on a terrace Mg$_{5c}^{2+}$ cation, as shown in panels b and c, in which Na turns out to be two-coordinated. In panel d the OH$^-$ group is adsorbed on a terrace site, but Na is bound to an anionic reverse corner site where it is three-coordinated. A spin density plot at constant value is shown for each case.

showing the similarity of the two groups (the frequencies have been scaled to take into account anharmonic effects). Notice that these values are close to those reported in a recent study by Chizallet et al.[34] for the residual hydroxyl groups present on the MgO surface after thermal treatment above 600 K. The whole cluster shown in Figure 4 is electrically neutral, resulting from a neutral MgO cluster with one added H$_2$O molecule. The two OH groups differ only for the coordination of the next-neighbors, the rest being practically identical. It is the nature of this kind of hydroxyl groups which is of interest in the present study. In particular, we want to find out if they can effectively contribute to ionize adsorbed alkali atoms and stabilize the resulting free electrons.

Initially, we considered two models where a proton is adsorbed on a four coordinated O$_{4c}^{2-}$ ion at a step site, while the OH$^-$ unit is adsorbed either on a low-coordinated or on a 5-fold coordinated Mg^{2+} cation. In this latter case the situation is not realistic as the OH$^-$ group will tend to migrate to the more stable low-coordinated sites (the OH$^-$ group is quite mobile when adsorbed on the (100) terraces, and in some cases we had to fix its lateral coordinates during geometry optimization).[45] Still, the model is useful since it allows us to have a globally neutral MgO cluster with an adsorbed (dissociated) water molecule where the two resulting fragments, H$^+$ and OH$^-$, are sufficiently distant that their interaction is negligible. Na atoms have then been adsorbed on low-coordinated O$_{LC}^{2-}$ anions on step sites of the hydroxylated surface, Figure 5.

We start by analyzing a monatomic step site (see Figure 5a). Here the H$^+$ and OH$^-$ species are separated by three lattice constants. The OH$^-$ group is in a bridge position over a regular Mg$_{5c}^{2+}$ cation on the lower plane and a Mg$_{4c}^{2+}$ cation on the step, Figure 5a. The Na atom has been initially placed in a position which allows the simultaneous interaction with two lattice anions, O$_{5c}^{2-}$ on the lower plane and O$_{4c}^{2-}$ on the step,
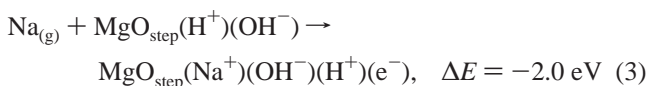
(45) The observation of OH$^-$ group migration from a cationic site to another on the MgO terrace during geometry optimization (0 K) is an indication of the absence of activation barrier for the process.

Table 1. Spin Population and Isotropic Coupling Constants for ^{11}Na, H, and ^{25}Mg Atoms near the (H$^+$)(e$^-$) Species

	step[a]	ARC[b]	CRC[c]	kink
Figure	5a	5d	6a	6b
spin population on Na	0.00	0.00	0.00	0.00
spin population on Mg(A)	1.08	1.15	1.33	0.97
a_{iso}(H), mT	−0.40	−0.40	−0.40	−0.24
a_{iso}(Na), mT	0.01	0.03	−0.01	0.01
a_{iso}(Mg)(A), mT	−2.20	−2.38	−2.93	−5.14
a_{iso}(Mg)(B), mT	−0.25	−0.22	−0.36	−0.08

[a] Only the asymmetric (H$^+$)(e$^-$) configuration on a step site was investigated, with the proton tilted toward one trapping Mg(A). The a_{iso} value for Mg(A) is smaller, in absolute value, than previously reported in ref 25 (3.42 mT). Our tests indicate that this is due to the different model and basis-set used. Here the trapping site is at one side of the QM cluster, thus is less coordinated than in the (H$^+$)(e$^-$) centered model. [b] ARC = anionic reverse corner. [c] CRC = cationic reverse corner.

but also with the OH$^-$ group. During the optimization process, the Na atom loses the 3s valence electron and becomes ionized, while the unpaired electron is transferred to the trap formed by the adsorbed proton, H$^+$, and a Mg$_{4c}^{2+}$ ion at the step. No spin density is left on Na, according to the spin population analysis, Table 1. Also the spin density map, Figure 5a, clearly shows the localization of the unpaired electron near the Mg$_{4c}$ ion next to the H$^+$ species (see Mg(A) in Figure 5a and Table 1). A direct observable consequence of this electron transfer is that the isotropic coupling constant with the ^{23}Na nucleus is practically zero (Table 1). On the contrary, the computed coupling constants with the proton and the ^{25}Mg on the step are those typical of the (H$^+$)(e$^-$) centers produced by direct adsorption of H atoms on the MgO surface (Table 1).[25−30]

The process described above is spontaneous and very exothermic. An energy gain of 2.0 eV is associated to the adsorption of the Na atom on the hydroxylated surface and to the consequent Na ionization and electron transfer:

$$Na_{(g)} + MgO_{step}(H^+)(OH^-) \rightarrow$$
$$MgO_{step}(Na^+)(OH^-)(H^+)(e^-), \quad \Delta E = -2.0 \text{ eV} \quad (3)$$
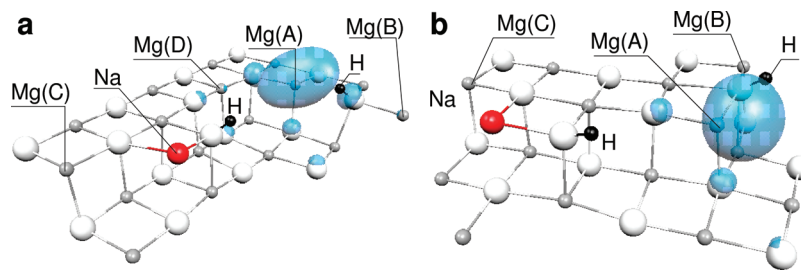
Figure 6. Na atom adsorbed on a step site of the MgO(100) surface in the presence of a dissociated water molecule, H^+ and OH^-. Na is coordinated by three oxygen anions. The unpaired electron is localized in a surface trap $(H^+)(e^-)$ near a cationic reverse corner (a) or a kink (b). A spin density plot at constant value is shown for each case.

This energy gain has a complex origin. It formally involves three processes: the ionization of the Na atom with formation of Na^+, the consequent stabilization of the resulting electron on a specific site of the surface, (e^-), and the electrostatic interactions between the charged fragments. The cost of ionizing the Na atom is quite large in gas-phase ($IP_{Na} = 5.4$ or 5.1 eV in theory and experiment, respectively), but it is strongly reduced when the alkali atom is bound to the surface. In a previous study[43] we have shown that the IP of Na adsorbed on a step or on an anionic reverse corner is 2.6 and 2.3 eV, respectively. On terrace or edge sites it is more than 3 eV. The strong reduction of IP upon adsorption has been observed also for K atoms on the anionic reverse corners of MgO, CaO, and SrO surfaces.[10] On the surface of MgO there are deep electron traps near adsorbed protons (surface OH groups); here the EA can be up to 3 eV or more, depending on the location.[25,26]

This model indicates that the spontaneous ionization of an adsorbed Na atom on a hydroxylated MgO surface is possible, but suggests the essential involvement of both fragments from the water dissociation, the H^+ ion to stabilize the electron and the OH^- group to stabilize the Na^+ cation.

To investigate how important is the direct interaction between Na^+ and the OH^- group resulting from water dissociation, we considered another model where the OH^- unit has been moved away from the step and from the Na adsorption site, so that no interaction can be established. Two cluster models have been used to place the OH^- group at an increasingly large distance from the adsorbed Na atom which is always placed at the step where it interacts with two lattice oxygens, O_{5c}^{2-} and O_{4c}^{2-} (see Figure 5b,c). The H^+ species is adsorbed on a step O_{4c}^{2-} ion as before. We find that in this new model where the OH^- group does not interact with the Na atom, this latter remains neutral and no ionization is observed: the spin density remains localized on Na (Figure 5b,c), and the $(H^+)(e^-)$ pair does not form. The adsorption of the Na atom is still exothermic, by 0.76 eV, but the final configuration is that of an adsorbed neutral Na atom. This result is very important. It indicates that two oxygen anions are not sufficient to stabilize the Na^+ cation. Thus, we may conclude that the population of electron traps at the MgO surface at the expenses of adsorbed alkali metal atoms requires the special condition that the alkali metal is stabilized at a 3-fold coordinated position (these are also the sites where the ionization of the alkali metal is easier).

Once this point is established, one should mention that on the MgO surface similar sites exist also in the absence of adsorbed OH^- groups. A special adsorption site for metal atoms is the anionic reverse corner, where the adsorbed species are strongly stabilized.[10] The anionic reverse corner is a site

characterized by the presence of three oxide anions (two O_{4c}^{2-} and one O_{5c}^{2-}, Figure 5d). To verify the hypothesis that such a site can stabilize a Na^+ ion, we have considered a cluster where a step and an anionic reverse corner are both present. The OH^- fragment has been adsorbed on a terrace Mg_{5c}^{2+} cation, far away from the anionic reverse corner (Figure 5d). The Na atom has been adsorbed on the anionic reverse corner while the H^+ ion has been adsorbed on a step. In this geometrical configuration the Na adsorbate turns out to be ionized, and the unpaired electron is transferred to the trap, forming the $(H^+)(e^-)$ center. This is clearly shown by the spin population and by the values of the hyperfine coupling constants (Table 1). These results show that, to allow the electron transfer and to stabilize the Na^+ cation, very specific sites are required, like for instance the anionic reverse corner, where Na^+ is coordinated by three oxygen anions.

While this condition seems necessary, the number of potential precursors for electron trapping is quite large. Any OH group formed in the vicinity of a low-coordinated Mg^{2+} cation is a good candidate. To prove this, H^+ has been adsorbed on an O_{4c}^{2-} anion on a step site near a cationic reverse corner (Figure 6a), or near a Mg_{3c}^{2+} on a kink site (Figure 6b). In both cases the Na atom has been bound to two surface oxygen anions (one O_{4c}^{2-} and one O_{5c}^{2-}) and to a OH^- group, to guarantee the coordination to three oxygen atoms simultaneously. Both spin population (Table 1) and spin density maps (Figure 6a,b), show the occurrence of the electron transfer and the ionic nature of the Na adsorbate. This is clearly demonstrated also by the isotropic coupling constants with the proton and with ^{25}Mg (Mg A), Table 1.

While the present calculations provide strong support to the observed data, it is still unclear how the electron transfer occurs. This could involve an electron transfer to the conduction band from an adsorbed Na atom followed by electron trapping at a special site, but the process should be thermally activated. The other possibility is that the two centers, Na adsorption site, and proton electron trap are sufficiently close that a weak overlap of the corresponding wave functions is possible. The fact that no hyperfine interaction is measured (or calculated) between the trapped electron and the adsorbed Na atom does not support this second mechanism, unless one assumes that the ionization process is followed by a diffusion of the resulting species which increases their mutual distance.

4. Conclusions

We have shown that by combining a careful preparation of weakly hydroxylated MgO, CaO, and SrO surfaces with exposure to alkali metal vapor, it is possible to prepare electron-

rich oxide surfaces. The residual hydroxyl groups present on the samples act as trapping sites for electrons originating from the ionization of Na atoms and lead to the formation of the same kind of $(H^+)(e^-)$ paramagnetic centers usually obtained by reaction of atomic hydrogen. For a long time these centers have been classified as paramagnetic oxygen vacancies (F^+ centers), and it is only recently that it has been shown unambiguously that their nature is completely different and does not involve the presence of anion vacancies.[30] In this respect, the importance of the present study is to generalize the concept of trapped electrons also to hydroxylated surfaces and to show a new route for the preparation of these materials.

The calculations show that two conditions are necessary to observe the spontaneous ionization of adsorbed alkali atoms and formation of $(H^+)(e^-)$ centers: (1) the OH group must be near a low-coordinated Mg_{LC}^{2+} cation; (2) the Na atom must be adsorbed on a site where it can interact simultaneously with three oxygen atoms. When this occurs, the ionization potential of a neutral Na atom is strongly reduced and the ionization is possible. This can involve either an anionic reverse corner or a step site with an adsorbed OH^- group.

The potential of this study for the functionalization of oxide surfaces is clear. The combined use of theory and experiment allows nowadays the unambiguous identification of the position where the residual hydroxyl groups are formed on a partially hydroxylated surface.[34,35] The population of these sites by electrons provided by suitable donors (e.g., alkali metals but in principle also other electropositive molecular species) offers the opportunity for the generation of thermally stable electron-rich sites on the surface. The subsequent deposition of transition metal atoms (Au in particular) from the gas phase, can lead to two desirable effects: nucleation, growth, and stabilization of metal particles in correspondence of the specific $(H^+)(e^-)$ defects and their chemical activation via electron transfer from the surface electron trap. Preliminary theoretical results from our group indicate that this is a viable process.[46]

Supporting Information Available: Complete ref 40. This material is available free of charge via the Internet at http://pubs.acs.org.

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