Excess Electrons Stabilized on Ionic Oxide Surfaces[†]

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Received June 1, 2006

ABSTRACT

Surface excess electrons are remarkable chemical entities that provide great opportunities for the design of new materials with precisely tuned electronic and magnetic properties. In this Account, we describe the structure and electronic properties of excess electron centers generated at the surface of insulating oxides. We also outline the elementary mechanisms that are at the basis of the generation of excess electrons at solid surfaces, setting a comparison to the general problem of excess electron localization in condensed media. Emphasis is given to morphological aspects relative to the surface-trapping sites as deduced from combined electron paramagnetic resonance and accurate quantum chemical calculations. The remarkable reactivity featured by the so formed "electron-rich" surfaces is illustrated, describing the reduction of simple diatomic molecules that form adsorbed radical anions via direct surface to adsorbate electron transfer.

1. Introduction

The common view of molecular chemistry is that electrons occupy specific orbitals and are spatially localized around atoms or groups of atoms. This neat picture becomes slightly blurred in the case of solvated electrons and excess electrons trapped in solids. These electrons are not associated with any specific atomic or molecular orbital, but on the contrary, the corresponding electron wave function is distributed within a cavity and surrounded by a matrix (either a liquid or a solid). In a sense, excess electrons can be regarded as true fundamental "chemical entities" as elegantly described by F. S. Dainton[1] in his Faraday lecture.

The simplest way of generating solvated electrons dates back to the early days of chemistry and is based on the reaction of alkali metals with liquid ammonia:[2]

$$n\text{NH}_{3(l)} + \text{M}_{(s)} \rightarrow (\text{NH}_3)_n(\text{e}^-)_{(l)} + (\text{NH}_3)_n\text{M}^+_{(l)} \quad (1)$$
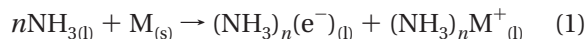
where M is an alkali metal and $(\text{NH}_3)_n(\text{e}^-)$ is a generic representation of the excess (or solvated) electron. This reaction, probably first observed by Sir Humphry Davy in 1807,[3] was explained by Kraus[4] as a result of the dissolution of the metal in the liquid to form M^+ solvated cations [represented as $(\text{NH}_3)_n\text{M}^+$] and solvated electrons, which are responsible for the intense blue coloration of the solution. In a similar way, excess electrons can be generated in the bulk of ionic solids, where they are responsible for a characteristic absorption band in the visible region and, hence, were appropriately named color centers or F centers (abbreviated from the German word for color, *farbe*). By means of a classical solid-state reaction, Weber[5] treated MgO with Mg vapors obtaining a blue-colored sample, where excess electrons where trapped in anion vacancies in the solid. Evaporation of alkali metals within the cavities of certain zeolites was also found to produce excess electron centers,[6] thereby opening up the possibility of designing new materials with unprecedent and intriguing electronic and magnetic properties.[7,8] The possibility of generating well-defined compounds with a high density of excess electrons soon became an exciting, new, and still fluorishing area of research at the crossroads of chemistry, physics, and material science. A relevant example in this sense is the synthesis of a new class of materials known as electrides.[9,10] These are crystalline ionic compounds in which the anions are electrons confined within the complex arrays of cavities provided, in their inorganic form, by all-silica zeolites[11] or by the crystallographic cages of nanoporous main-group oxides, such as $12\text{CaO}\cdot7\text{Al}_2\text{O}_3$.[12]

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If excess electrons can be stabilized within three-dimensional cavities of liquids or solids, can they also be stabilized by a two-dimensional array of ions, such as those on the surface of an ionic oxide? This is an important question because charge localization and transport at oxide surfaces and interfaces are crucial phenomena in several fields of science and technology ranging from photocatalysis to sensors and electronic devices. Surface electron trapping on oxides was first observed by Tench and Nelson in 1968.[13] These surface electrons can be stabilized by strong local potentials of positive and negative ions in particular arrays and in some cases even by single low-coordinated cations. In this way, the surface of the solid can be modified by the addition of electrons (creating an *electron-rich* surface), thereby opening up realistic possibilities to tune the optical, electronic, chemical, and magnetic properties of these materials.

The aim of this Account is to provide a general discussion on the nature of excess electrons localized on ionic oxide surfaces and to discuss some general concepts of the chemical processes occurring in these electron-rich inorganic materials. Because the phenomenon of surface electron trapping is confined to a few peculiar surface locations, particular attention will be devoted to aspects concerned with surface morphology and site-specific mechanisms leading to the formation of trapped electrons. The combined use of spectroscopic techniques [electron paramagnetic resonance (EPR), UV−vis, and IR] and accurate quantum chemical calculations for identification and elucidation of the microscopic aspects of electron trapping will be illustrated with specific reference to alkaline-earth oxides and MgO in particular.

2. Excess Electrons on Nanostructured Alkaline-Earth Oxide Surfaces

Polycrystalline MgO, like the other alkaline-earth oxides, exhibits a NaCl-type structure and a morphology based on cubic crystals with extended (100) planar faces. Both Mg^{+2} and O^{-2} ions at these crystal facets are surrounded by five ions of opposite charge in square pyramidal coordination and are chemically inert. Finely divided MgO materials are built up by assemblies of extremely small interpenetrated cubes with edges of approximate lengths ranging from 4 to 8 nm (Figure 1).

Dependent upon the preparative method, specific surface areas of up to 1000 m^2 g^{-1} can be produced.[14] As a result, the number of low-coordinated ions, primarily located at the edges [four coordinated (4c), corners (3c), and other irregularities, such as steps and kinks, etc.] becomes more abundant. It is mainly at these low-coordinated, highly reactive sites that the formation of surface excess electron centers occurs by chemical doping.

Exposure of MgO[15] or CaO[16] surfaces to hydrogen atoms results 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 2.
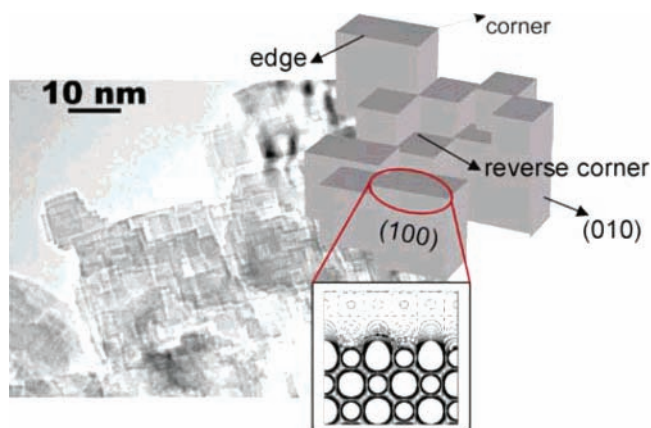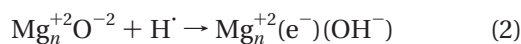
$$Mg_n^{+2}O^{-2} + H^· \rightarrow Mg_n^{+2}(e^-)(OH^-) \qquad (2)$$

FIGURE 1. High-resolution transmission electron microscopy (HR-TEM) micrography of a high-surface-area polycrystalline MgO sample. A schematic model indicating the relevant surface sites discussed in the text is also shown. In the inset, the electrostatic potential in the *xy* plane through the edge is shown.

The electron-trapping site can either be a single low-coordinated cation ($n = 1$) or a small array of surface cations ($n > 1$, *vide infra*), while the proton is stabilized by a single O^{-2} anion in the form of a surface hydroxyl group ($O^{-2} + H^+ \rightarrow OH^-$). This reaction (eq 2), which leads to surface excess electron centers, stable up to 373 K, has many appealing similarities with the reactions responsible for the generation of excess electrons in anhydrous liquid ammonia (eq 1).

The concept of a solid as an ionizing solvent was first proposed by Edwards et al.[3] to describe the interaction of alkali metals with zeolites and provides a robust conceptual framework for the interpretation and rationalization of hydrogen ionization on ionic surfaces. The formation of the resulting excess electrons may be regarded as a dissolution process, whereby hydrogen displays the properties of an alkali metal, undergoing ionization despite its high ionization energy (13.7 eV). The reason for this unusual hydrogen chemistry is due to the strong proton affinity of the very basic O^{-2} surface ions coupled with the energy gain by trapping the electron near low-coordinated Mg^{+2} cations. The intriguing consequence of eq 2 is that by reacting nanostructured polycrystalline alkaline-earth oxides with H atoms we have a way of "dropping" excess electrons on specific surface sites.

3. Unravelling the Nature of Surface Electron-Trapping Sites

A major point of interest concerns the precise description or nature of the surface-trapping sites responsible for eq 2. For many years, these sites were exclusively assigned to surface oxygen vacancies (see also section 4 below); the well-known De Boers model of the *F* center,[17] which was based on an electron trapped in a three-dimensional bulk anion vacancy, was simply extended to a two-dimensional surface equivalent. In this way, the existence of anion vacancies located on the (100) surface of ionic oxides was immediately postulated and largely accepted and unchallenged.[13] However, recent EPR and theoretical evidence
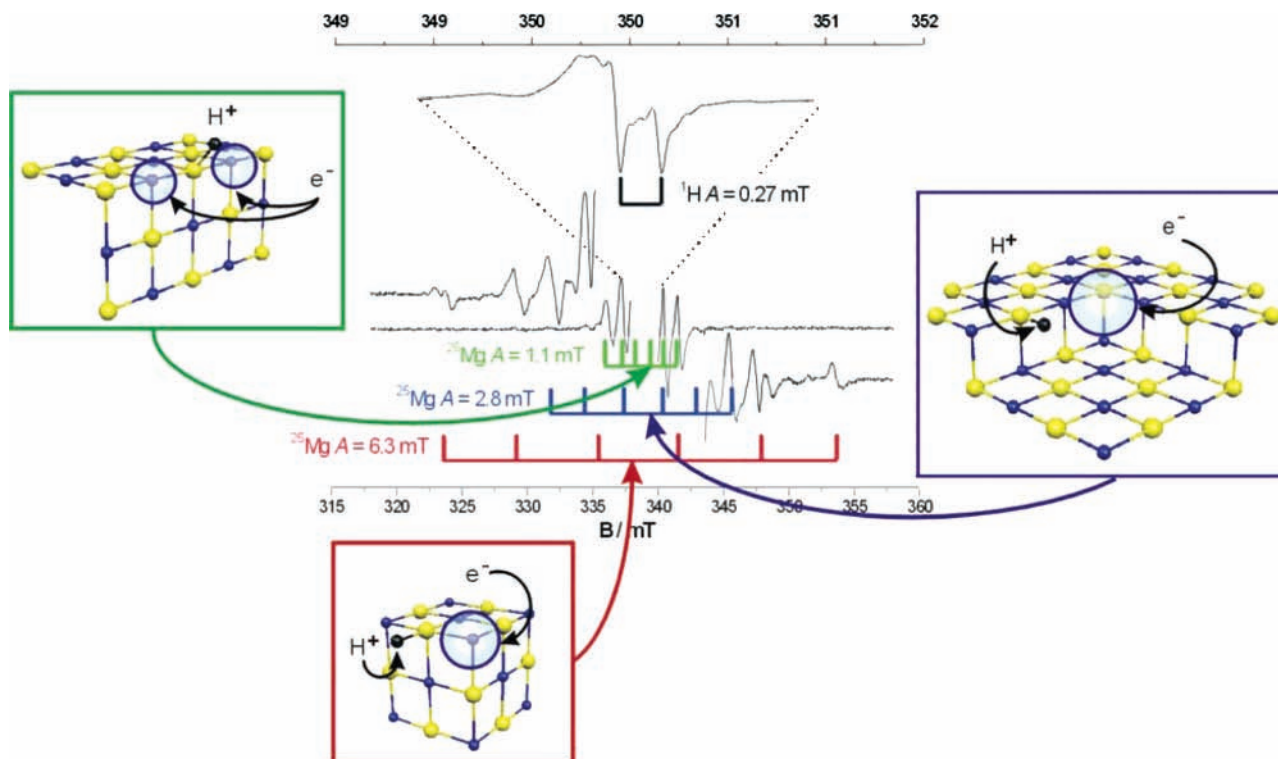
FIGURE 2. EPR spectrum and atomistic models of (H$^+$)(e$^-$) centers on MgO.

from our groups has instigated a completely new debate on the whole idea of oxygen vacancies as electron-trapping sites, and we have shown how other morphological features, commonly found on high-surface-area alkaline-earth oxides, can also trap electrons.

EPR traditionally played a leading role in the study of point defects in materials and specifically excess electron centers in condensed matter.[7] This is true also for surface-trapped electrons. This highly sensitive technique provides an unsurpassed source of information of spin doublet electronic states. In favorable circumstances, the symmetry (point group) of the center can be ascertained and the distribution of the unpaired electron spin density over the nuclei constituting the trapping site can be deduced. Generally, the most informative parameters derived from EPR come from the electron−nuclear (or hyperfine) interaction. Because analysis of the hyperfine coupling tensor (*A*) provides a direct measure of spin density on the nearby nuclei, a realistic chemical and structural description of the surface traps can be achieved.[18] However, to answer the important question on how and where excess electrons are stabilized at surfaces, this information must be complemented with results coming from theoretical modeling.

A selection of particularly representative EPR spectra of excess electron centers on MgO generated by the reaction (eq 2) is reported in Figures 2 and 3.

The EPR spectrum reported in Figure 2 is characterized by a hyperfine doublet pattern arising from the interaction between the trapped electron and a single proton (^{1}H, $I = 1/2$). An accurate investigation of the ^{1}H hyperfine performed by electron−nuclear double resonance (ENDOR) allowed us to detect the hyperfine tensor
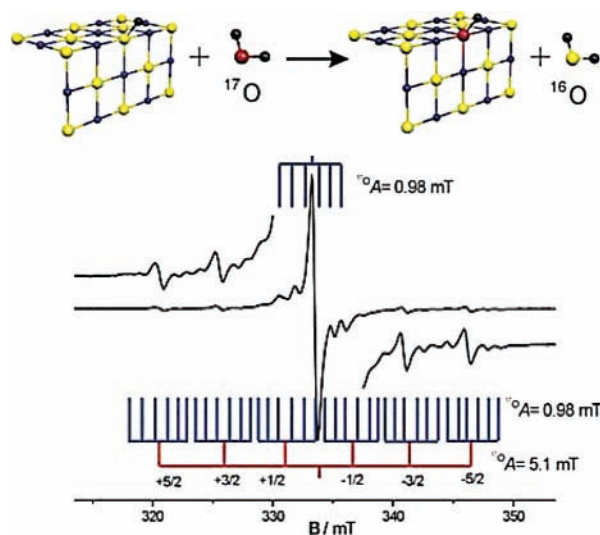

FIGURE 3. EPR spectrum of (H$^+$)(e$^-$) centers localized at the surface of ^{17}O-enriched MgO.

elements ($A_1 = 0.207$ mT, $A_2 = 0.200$ mT, and $A_3 = 0.030$ mT), indicating that the local symmetry of the site is lower than the axial symmetry.[19] The magnitude of these hyperfine couplings clearly indicates a weak electron−proton interaction. In particular, the negligible isotropic component to the hyperfine interaction (i.e., the Fermi contact term) confirms the complete ionization of the H atoms upon contact with the ionic surface.

Fortunately, hyperfine interactions are not restricted to the ^{1}H nucleus. The overlap of the excess electron wave function with the charge clouds of surface ions creates further hyperfine interactions with any surface nucleus possessing a magnetic moment and present in relatively

high abundance, such as ^{25}Mg^{+2} (e.g., $I = {}^{5}/_{2}$ for ^{25}Mg with 10.2% natural abundance). The analysis of the ^{25}Mg hyperfine pattern proved pivotal in solving the long-standing issues surrounding the true nature of the surface excess electron sites. Three distinct ^{25}Mg hyperfine patterns were experimentally observed, with couplings of 1.1, 3.0, and 6.0 mT (evidenced by the colored stick diagram in Figure 2). Detection of the largest hyperfine sextet (6 mT) prompted us to reconsider the commonly held view of the surface electron traps on MgO as based on the classical de Boer model.[20] It is not possible to ascertain *a priori* the complete number of Mg^{+2} ions per trapping site, because the statistical probability of finding more than one ^{25}Mg nucleus within a given surface array is small. As a result, the 1.1 mT hyperfine sextet was previously interpreted as arising from the delocalization of the unpaired electron density over a number of Mg^{+2} cations constituting the surface electron trap. This value is larger than that reported for bulk F^{+} centers in MgO ($\simeq 0.4$ mT)[21] but was explained through consideration of the polarizing effect exerted on the unpaired electron by the proton.[13,18] This effect was reflected in the original nomenclature for these centers, F_{s}^{+}(H), where the subscript s represents surface localization and (H) represents the presence of a proton in the vicinity of the center.[18]

However, the discovery of the new ^{25}Mg hyperfine sextet (6 mT) could not be reconciled with this surface vacancy model. The only reasonable explanation was that the unpaired electron spin density must be localized on a single ^{25}Mg^{+2} cation. Cluster model density-functional theory calculations confirmed this hypothesis and revealed that excess electrons were indeed stabilized by the large electrostatic potential provided by a corner or kink Mg$_{3c}^{+2}$ ion and a nearby proton.[20] Both the experimentally observed EPR parameters and the energetics of the hydrogen reaction were accounted for theoretically. This result required us to formulate an entirely new model of these centers in terms of (H^{+})(e^{-}), electron–proton pairs, bound at morphological surface features such as a corner ion.

The two other ^{25}Mg hyperfine patterns (3.0 and 1.1 mT), observed experimentally, could also be interpreted and explained using the new model. Again, theoretical calculations showed that the 3 mT hyperfine pattern could be reconciled with a (H^{+})(e^{-}) pair localized at the intersection of two steps. It transpires that this morphological feature, also known as a reverse corner, is an important defect on MgO responsible for a number of interesting reactions, from the heterolytic dissociation of H$_2$[22] to the stabilization of alkali metal atoms.[23] Far more problematic was the assignment of the 1.1 mT ^{25}Mg hyperfine pattern, which is also the most intense pattern. The magnitude of this coupling could be equally reproduced, by theoretical calculations, using two drastically different models: the classical surface anion vacancy model, F_{s}^{+}(H) center,[18,24] and the (H^{+})(e^{-}) pairs model localized at surface edges and steps.[22,24] While the energetic and electrostatic considerations clearly favor the second model, the final definitive assignment was only achieved by performing a number of experiments using MgO surface enriched with

^{17}O ($I = {}^{5}/_{2}$). Enrichment was achieved by repeated hydration/dehydration cycles of high-surface-area MgO using H$_2$^{17}O. In this way, the unpaired electron spin density distribution could be monitored over the constituent O^{-2} ions of the surface electron trap.[25] The EPR spectrum of ^{17}O-enriched MgO containing excess electrons is shown in Figure 3.

The spectrum is dominated by two ^{17}O hyperfine sextets arising from the interaction of the unpaired electron with two, magnetically inequivalent, ^{17}O nuclei, which possess different spin densities because of the preferential polarization of the trapped electron toward one of the two nuclei. This polarization is created by the nearby surface OH^{-} group, which has the larger ^{17}O hyperfine coupling, while the smaller coupling belongs to the surface O^{-2} lattice anions. This intuitive assignment was confirmed by theoretical calculations of the ^{17}O hyperfine tensors, which revealed that only the (H^{+})(e^{-}) pairs model, based at surface steps or edges, is consistent with the experimental data, because the ^{17}O hyperfine couplings for the F_{s}^{+}(H) model were far too small.

To summarize, at least three different sites have now been identified on the MgO surface that are able to spontaneously ionize H$^{\cdot}$ atoms and stabilize the resulting products in the form of (H^{+})(e^{-}) pairs, according to eq 2; these sites are illustrated in Figure 2. While EPR spectroscopy was critical in the reassignment of these new surface excess electron-trapping sites, important contributions were also obtained by IR[26] and UV–vis[27] studies. *It should be stressed that (H^{+})(e^{-}) pairs on alkaline-earth oxides are in fact "true" color centers.* Theoretical modeling shows that the (H^{+})(e^{-}) center on MgO (reverse corner) is a deep trap for the electron, which is bound by 3.71 eV and gives rise to two intense electronic transitions in the visible range at 2.07 and 2.39 eV.[22] The same is true for corner sites.[20] This finding provides a new framework for future discussions of electron trapping because discrete morphological features, naturally present on surfaces, have been shown to act as potential wells for electron trapping.

4. Are Oxygen Vacancies Present at the Surface?

In the previous section, a new picture has emerged on the nature of the excess electron-trapping sites on the MgO surface. However, this does not imply that oxygen anion vacancies are irrelevant and absent in the surface chemistry of MgO. In the last 10 years, a great deal of attention has been dedicated to oxygen vacancies at the surface of ionic oxides like MgO and to their role in the chemical and catalytic properties of oxides.[28,29] Oxygen vacancies are thought to be key factors not only in the nucleation, growth, and stabilization of supported metal clusters but also in their chemical activation in catalytic reactions.[30] This intense research activity has generated an accepted understanding and belief within the literature with respect to both the nature and existence of these centers. In this paragraph, we shall discuss what is the situation today in view of the most recent discoveries.

As we mentioned above, the earliest model of the surface anion vacancies on MgO, proposed by Tench in
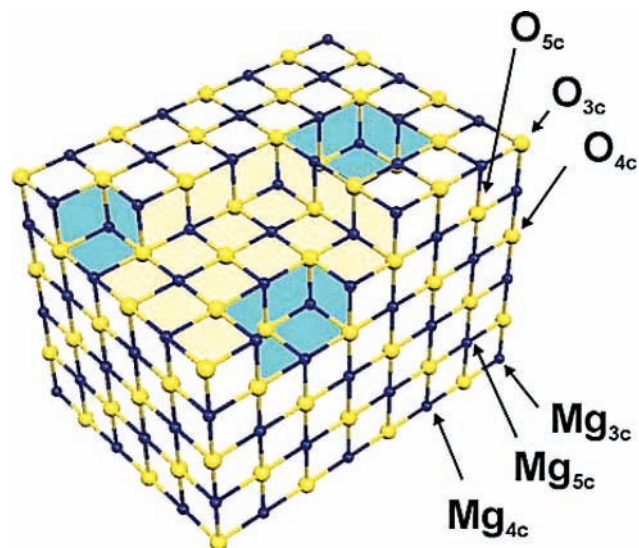
FIGURE 4. Schematic representation of low coordinated sites and anion vacancies with different coordination at the surface of MgO.

the 1960s,[13] is the natural extension of the bulk *F* centers.[17] It consists of a pyramidal hole generated on the (100) surface by removal of an O_{5c}^{-2} ion (Figure 4). This vacancy (labeled F_s^{+2}) can trap one or two electrons, producing surface F_s^+ (paramagnetic) and F_s color centers, respectively. Recently, the model has been refined after it was predicted[18,31] and later proven[32,33] that oxygen vacancies form preferentially at low-coordinated sites such as steps, edges, and corners of the surface (Figure 4). Because low-coordinated sites are quite abundant on polycrystalline powders, the original vacancy model plays only a minor role in electron trapping at the surface of these materials. Atomic force microscopy (AFM) images taken on the surface of MgO single crystals[34] have shown the existence of point defects on the (100) terraces, but their shape is more consistent with the formation of divacancies (pairs of Mg and O vacancies) than of single oxygen vacancies.

A substantial improvement in the knowledge of oxygen vacancies came from the use of thin oxide films epitaxially grown on metal substrates. The nature of these centers on stoichiometric MgO films has been investigated by a number of techniques including EELS (electron energy loss spectroscopy),[35] MIES (metastable impact electron spectroscopy),[36] STM (scanning tunneling microscopy),[37] STS (scanning tunneling spectroscopy), and EPR.[32] All of these measurements have produced spectral features in excellent agreement with theoretical predictions, providing strong evidence for the nature of these centers and confirming their preferential formation on steps and edges. The measurements have also shown that the number of F_s centers in the pristine, as grown stoichiometric films, is very small, below the detection limit of an EPR spectrometer (5×10^{11} centers/cm²).[33] Thus, to be observed, oxygen vacancies must be created either by electron bombardment or by changing the preparation method (and the stoichiometry) of the film.

On the basis of this collective body of work, one must conclude on the one hand that surface anionic vacancies are present on MgO powders subjected to extreme activation conditions (1073 K heat treatment), although their

overall number is far lower than generally thought. On the other hand, the number of these paramagnetic centers on pristine thin films is below the detection limit of EPR. However, they can be created by high-energy treatment of the surface (e.g., electron bombardment of thin films) and used to modify the catalytic properties of a deposited metal nanoparticle, thus opening up an exciting yet largely unexplored area of research.

5. Reactivity of Electron-Rich Surfaces

The surface of MgO decorated by electron−proton pairs is an extremely reactive system. Molecules exposed to the surface are irreversibly reduced, via electron transfer, to the corresponding radical anion. During the reaction, the ionic surface adopts a twin role, acting both as a reducing agent and as a stabilizing medium. While many examples of this reactivity have been studied over the years, here we shall present two general cases of conceptual interest: (a) electron transfer with irreversible formation of a stable adsorbed radical species (the case of O_2) and (b) electron transfer with reversible formation of an adsorbed radical species (the case of N_2).

In the first example, molecular oxygen readily reacts with surface excess electron centers to form the well-known superoxide O_2^- radical ion. O_2^- is stabilized on the surface in proximity to the adsorbed proton (hydroxyl group) of the trapped electron center

$$O_{2(gas)} + (H^+)(e^-)_{surf} \rightarrow (O_2^-)(H^+)_{surf} \qquad (3)$$
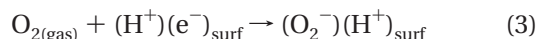
The majority of the surface O_2^- species are adsorbed on 4c Mg^{+2} sites, interacting with the proton of a nearby OH^- group.[38] The structural equivalence and uniform spin densities on the two oxygen atoms at this adsorption site were recently confirmed using $^{17}O_2$.[38] The proposed model was also supported by *ab initio* calculations, which provided additional information on the stabilization of the anion at the edge sites. The magnitude of the calculated ^{17}O hyperfine coupling, particularly the dipolar component, at this site, is in excellent agreement with the EPR observations.[39]

In the second example, molecular nitrogen readily interacts with $(H^+)(e^-)$ centers when physisorbed at temperature lower than 100 K. However, in this case, reversible formation of a N_2^- surface radical occurs following a net one electron transfer from the surface to the π* orbitals of the adsorbed molecule[40]

$$N_{2(gas)} + (H^+)(e^-)_{surf} \rightarrow (N_2^-)(H^+)_{surf} \qquad (4)$$
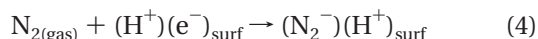
Magnetic and structural equivalencies of the two nitrogen atoms were confirmed by EPR, on the basis of analyses of the $^{15}N_2^-$ and $^{14}N_2^-$ spectra. The set of experimental hyperfine couplings was satisfactorily reproduced by theoretical calculations based on a model of N_2^- stabilized at edge sites.[39] The bond length of the activated N_2^- molecule was found to increase by ~9% in the reduced state. The most intriguing and elegant point concerns the complete reversibility of the process; at lower N_2 pressures or higher temperatures, N_2 is desorbed and
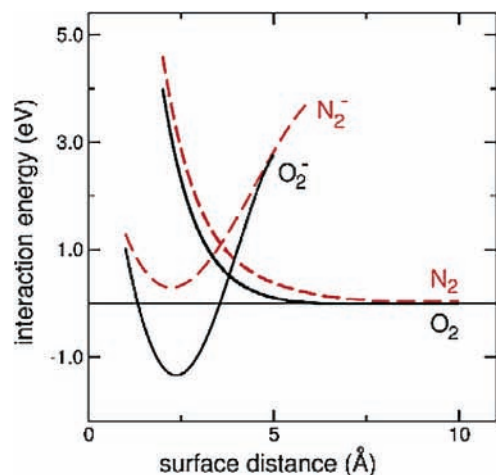
FIGURE 5. Spin-density plot for (a) $(H^+)(e^-)$ centers located at a cationic reverse corner and (b) the complex formed by the interaction with N_2 or O_2 molecules. On the left-hand side, the schematic potential energy curves for the interaction of O_2 (solid curve) and N_2 (red dotted curve) molecules is shown. Negative values indicate bound states.

the electron is released back to the original surface site. The ease of reversibility was explained by quantum chemical calculations, which identified a very small energy barrier between the bound state (electron transfer) compared to the physisorbed state (Figure 5).[40]

At first sight, the reactions involving O_2 and N_2, leading to radical anion formation, are surprising given the low or even negative electron affinity of the two molecules, +0.44 eV for O_2 and -2.0 eV for N_2 (calculated). If the driving force for these reactions was exclusively based on the interplay between the ionization energy of the surface center and the molecular electron affinity, no reaction would occur. However, when electrostatic contributions between the ionic surface and the negative anions are also considered, favorable reaction conditions occur. Once again, only low-coordinated sites of the cubic crystals are capable of providing sufficiently strong stabilization energies. This fact exemplifies and highlights the importance of these low-coordinated surface sites in the chemistry of the MgO surface over and above the rather inert Mg_{5c}^{+2} ions on the planar (100) faces.

6. Summary and Outlook to the Future

A major driving force in the quest for new materials consists of the modification and functionalization of "host" systems to generate new compounds with novel electronic properties. The ability of certain surfaces to dissociate $H^{\cdot}$ atoms leading to $(H^+)(e^-)$ stabilized pairs represents such an example, resulting in the dramatic modifications to both electronic properties and chemical reactivity. In this Account, we have mainly focused on the topological aspects demonstrating that the dominant surface defects capable of stabilizing excess electron and proton pairs are morphological features rather than point defects, as it has been assumed until recently. The observed phenomenon is reminiscent of a number of uncommon reactions, leading to the spontaneous charge separation in atoms, such as the dissolution of metals in liquid ammonia[4] and other polar solvents and the formation of inorganic electrides in zeolites[9] and in porous mixed oxides.[12] The latter system, in particular, closely
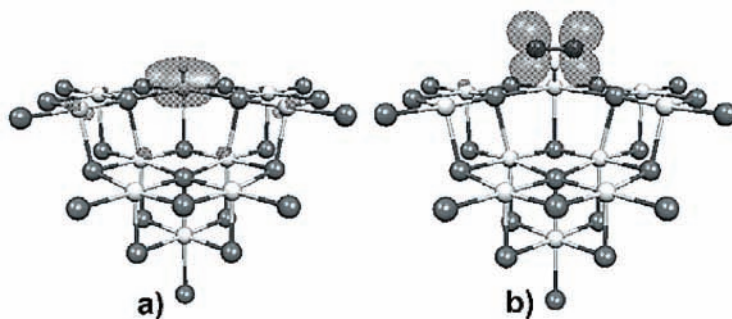
resembles that described here, and its discovery has opened new directions in the field of transparent conductive oxides.

New synthetic methods to prepare these oxides are continuously emerging, allowing for a much greater control over morphological and topological features of powders and films.[41] For example, the possibility to selectively decorate with $(H^+)(e^-)$ pairs surface edges and steps to produce one-dimensional wires of controlled length represents an exciting perspective for the future. Another challenging aspect consists of the chemical modification of the surface to control and manipulate the degree of excess electron localization, for example, by varying the degree of surface hydroxylation. We recently found[42] that when excess electrons are generated at the surface of a hydroxylated surface the unpaired electron wave function is spread over a number of protons of the OH^- groups, which provide patterns for substantial delocalization. These preliminary results could offer a new strategy for designing new materials with targeted magnetic and electronic properties.

The chemical reactivity of these electron-rich surfaces could also offer new avenues for research in heterogeneous catalysis. For example, enhanced catalytic properties were recently observed for selectively charged deposited metal nanoparticles on oxide surfaces. Gold octamers bound to surface F_s centers on MgO thin films were shown to be active in catalyzing the low-temperature oxidation of CO to CO_2.[43] Recently, color centers on a single crystalline oxide surface have been found to act as nucleation centers, substantially affecting the properties of the metal particle as probed by the IR stretching frequency of adsorbed CO molecules.[44] The number of intrinsic surface F centers on alkaline-earth oxides is however too small to be practically useful, and higher concentrations of these defects must be created via electron bombardment, using high-energy radiations or controlling the sample preparation to enhance their abundance. On the contrary, the facile and controlled chemistry involved in the formation of the unusual $(H^+)(e^-)$ surface ion pairs by atomic hydrogen or via UV

irradiation of MgO in molecular hydrogen could potentially provide alternative canditates to achieve metal clusters charging at specific sites and thereby offering unprecedented pathways for the design and synthesis of a new class of supported catalysts.

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