The Color of the MgO Surface—A UV/Vis Diffuse Reflectance Investigation of Electron Traps

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The optical properties of color centers on the surface of MgO nanoparticles were studied by UV/vis reflectance spectroscopy. For color center formation, the MgO nanoparticles were exposed in the presence of hydrogen to polychromatic UV light. Essentially two absorption features at 1.8 and 2.4 eV were observed, with their relative intensities depending on the applied hydrogen pressure during UV irradiation. This is explained by changes in the relative abundance of hydride groups stemming from H_2 chemisorption at different surface defects. The photolysis of irreversibly formed hydride groups results in the low-energy absorption at 1.8 eV, whereas the UV irradiation of a second type of hydride contributes to the appearance of a broad feature around 2.4 eV, which is composed of more than one band. Bleaching of color centers with N_2O and subsequent addition of hydrogen generates atomic hydrogen as exclusive electron source for the MgO surface. In addition to the bands observed before, the appearance of a new band at 3.2 eV indicates that the underlying electron trap is not involved in hydrogen chemisorption reactions, but is capable of H atom oxidation. On the basis of previous infrared spectroscopic findings, a mechanism for the trapping process of hydrogen-derived electrons on the MgO surface is proposed.

Introduction

The physical and chemical properties of insulator interfaces are crucial for a variety of fields, spanning the range from microelectronics[1−3] to heterogeneous catalysis.[4−6] Since equilibrium surfaces are considered as chemically inert, the abundance of defects (either point defects, such as ion vacancies and coordinatively unsaturated ions, or extended defects, such as terrace steps) determines the chemical properties of the surface. For this reason, a tremendous amount of research has focused on their characterization.[7−9] Magnesium oxide is one of the most intensively studied materials because of its purely ionic nature and its simple cubic rock salt structure. Prominent defective surface sites that may act as electron traps are surface color centers or F_S centers, ("s" for surface).[10,11]

In chemistry, F_S centers on MgO have attracted attention because they exhibit reactivity[12] and are involved in the electronic activation of metal clusters[13] when MgO is used as a substrate material. In addition, highly inert molecules such as molecular nitrogen turned out to be activated by these sites at liquid nitrogen temperature.[14] Furthermore, the role of electron traps is of considerable importance in photochemistry because they are intimately related to the fate of photogenerated excitons and their decomposition products, i.e., electrons and electron holes.[15]

On MgO as a divalent oxide, in principle, two types of F_S centers can exist: paramagnetic ones, F_S^+, where an electron-trapping site contains one unpaired electron, or diamagnetic ones, F_S^0, which host two electrons. The discussion of the underlying surface defects of these spectroscopically observable entities started with an early proposal by A. J. Tench, who extended the model of a bulk F center to an anion vacancy located in the (100) surface.[16] In a more recent approach, Giamello et al.[17] put forth the idea that electrons can be trapped in particular regions of the crystal where the ion coordination is significantly lowered compared to (100) terrace sites. Anion vacancies located in edges, steps, and crystallite corners with an enhanced chemical reactivity were considered, and results of a combined spectroscopic and quantum chemical investigation were in good mutual agreement.[17]

In a recent paper by Ricci et al.,[18] theoretical evidence was provided which clearly indicates that the term "paramagnetic surface color center" has to be understood in a more general form: trapping of electrons in step edges and reverse corner sites also gives rise to a broad agreement with existing experimental data. These new structural units no longer belong to the conceptual class of isolated anion vacancies, i.e., point defects, that can be formally obtained by removal of a single oxygen anion from the surface. Even electron trapping at single low-coordinated Mg^{2+} cations was reported after activation of MgO powder with UV laser light in the presence of hydrogen. The main characteristic of these new centers is the strong interaction between the spin of an unpaired electron with a single Mg^{2+} cation, as evidenced by large ^{25}Mg hyperfine coupling constants.[19] Something all of the abovementioned descriptions have in common is that the electron trapping site in question must be related to surface arrays of Mg^{2+} cations with a local deficiency in O^{2-} ions.[19] These entities can be formally subsumed as $(Mg^{2+})_n$ units, where n ranges from 1 to 5, and can incorporate single Mg^{2+} cations, classical anion vacancies, and less regular surface defects.

The abundance of F_S centers on single-crystalline, epitaxially grown MgO films (considered as model surfaces) is very limited. It must be artificially increased by high-temperature treatment

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above 1100 K[20] or electron-stimulated desorption[21] in order to be successfully studied by electron energy-loss spectroscopy. Another approach for their investigation, though related to a much higher complexity, is the use of high surface area powder material which contains a large number of different defect types. As shown recently, MgO nanoparticles which were produced by chemical vapor deposition exhibit surfaces with a surprisingly uniform distribution of spectroscopically very well-defined defects, having specific chemical reactivities.[22]

As for epitaxially grown MgO films, electron-trapping sites on polycrystalline MgO have to be transformed into paramagnetic (e.g., F_S^+, 1 e^-) and diamagnetic (e.g., F_S^0, 2 e^-) centers to facilitate their study by electron paramagnetic resonance spectroscopy[10] and/or by optical spectroscopy in the UV/vis range,[17] respectively. This transformation corresponds to an electronic reduction of the surface and can be achieved by chemical means, such as the ionization of deposited alkali metal atoms[23] or the simultaneous exposure to molecular hydrogen and UV light.[10] The latter technique involves the dissociation and UV-assisted oxidation of hydrogen at essentially three different sets of reactive surface sites.[24]

The purpose of the present UV/vis reflectance study is to investigate the influence of H_2 pressure during surface color center formation in order to elucidate the effect of the underlying chemistry and photochemistry on the optical properties of the polycrystalline MgO surface. It will be shown that, due to their electronic transitions in the energy range between 1.5 and 4 eV, essentially three types of F_S centers can be observed. Their relative abundance clearly depends on the chemical nature of hydrogen species (i.e., chemisorbed hydride groups and atomic hydrogen) that serve as electron donors in the process of surface color center formation.

Experimental Section

All experiments were carried out with MgO powder samples obtained by chemical vapor deposition (CVD) in a flow reactor system.[25] In this preparation procedure, high-purity Mg pieces, supplied by Johnson Matthey GmbH, are used as educt material. The specific surface area of the resulting MgO powder, which consists of cubic nanoparticles with edge lengths between 5 and 8 nm, was determined by BET (LN_2) measurements and is around 400 m^2/g. Before each experiment, the sample was gradually heated to 870 K (10 K/min) and then treated at this temperature with oxygen to burn off organic contaminants originating from the oil of the vacuum pumps used in the flow reactor system. Further annealing to 1173 K under dynamic vacuum ($<10^{-5}$ mbar) was selected to guarantee a totally dehydroxylated surface.[26] This thermal activation process leads to a decrease of the specific surface area, down to 300 m^2/g. Hydrogen (99.999% purity) as a reducing agent was provided by Messer Griesheim. For color center formation, UV activation of MgO powders was carried out with a 300 W Xe lamp (Oriel) equipped with a water filter in order to avoid sample heating by IR irradiation. The incident UV light intensity at the position of the sample surface was approximately 1 W/cm^2, as measured with a thermopile detector (International Light). Typical UV exposure times were between 10 and 30 min.

For UV/vis diffuse reflectance measurements, the MgO powder was placed in a high-vacuum tight quartz cell with optical windows made of Suprasil. Thermal activation as well as adsorption and desorption steps were performed by connecting the cell to a vacuum line that guarantees pressures less than 10^{-5} mbar. The UV spectra were acquired using a Perkin-Elmer Lambda 15 spectrophotometer equipped with an integrating sphere.

The presented spectra show changes in optical absorption before and after color center formation. After Kubelka−Munk transformation of each experimental reflectance curve, the reference spectrum acquired right after previous outgassing at 1170 K was subtracted. Since only changes in the range $4.1 \geq E \geq 1.6$ eV ($300 \leq \lambda \leq 800$ nm) will be discussed, spectral contributions from optical transitions due to the excitation of low-coordinated anions and luminescence effects at energies above 4.1 eV ($\lambda < 300$ nm) are excluded.[15,27] The same is true for color centers in the bulk and subsurface regions, since their optical absorptions are located around 5 eV.[28] Under high-vacuum conditions, the optical absorption patterns measured after the different preparative steps did not change on a time scale of days.

Results and Discussion

1. Photochemistry of H_2 on Polycrystalline Surfaces. In the present study, F_S centers were formed on MgO nanoparticles by sample exposure to molecular hydrogen and UV light. Three fundamentally different experimental procedures were chosen in order to initiate specific reaction channels for the electronic reduction of the surface. Before the presentation of the UV/vis diffuse reflectance spectra, these channels will be briefly outlined below.

Procedure a. The MgO sample is contacted with hydrogen and subsequently evacuated. After removal of any reversible H_2 chemisorption product, UV activation is applied. On the basis of previous IR and EPR spectroscopic studies performed in our laboratory,[24] this treatment implies the occurrence of the surface reaction step represented by eqs 1−4.

In the first step (eq 1), H_2 is split heterolytically and—at room temperature—irreversibly. It is transformed into mainly one type of neighboring hydroxyl and hydride groups:

$$O^{2-}-(Mg^{2+})_n + H_2 \rightarrow O^{2-}H^+-(Mg^{2+})_nH^- \qquad (1)$$

These hydride groups then become effective as electron donors when UV light is applied (eq 2):

$$(Mg^{2+})_nH^- + h\nu_{UV} \rightarrow (Mg^{2+})_n + e^- + H^\bullet \qquad (2)$$

The photolysis of chemisorbed hydride (eq 2) provides, directly (e^-) and indirectly ($H^\bullet \rightarrow H^+ + e^-$), electrons for color center formation (eqs 3 and 4):

$$(Mg^{2+})_n + e^- \rightarrow (Mg^{2+})_n^- \qquad (3)$$

$$(Mg^{2+})_n + O^{2-} + H^\bullet \rightarrow (Mg^{2+})_n^- + O^{2-}H^+ \qquad (4)$$

Paramagnetic $(Mg^{2+})_n^-$ is characterized by EPR and $O^{2-}H^+$ by FTIR spectroscopy.[29] The presence of diamagnetic species may not be excluded.

Procedure b. In the second procedure, MgO samples are exposed to UV light and molecular hydrogen at the same time. Parallel to the reaction channel related to procedure a (eqs 1−4), a second one must now be considered, which is based on a—at room temperature—reversible, heterolytic H_2 splitting process. The resulting hydride groups are nonbridged, i.e., $n = 1$. With this modification, eqs 1−4 also hold for this reaction channel. Furthermore, UV-induced ionization of low-coordinated surface oxygen anions[30] opens up the route to homolytic H_2 splitting[31] according to

$$O_{LC}^{2-} + h\nu \rightarrow O_{LC}^- + e^- \qquad (5)$$

$$O_{LC}^- + H_2 \rightarrow O_{LC}^{2-}H^+ + H^\bullet \qquad (6)$$

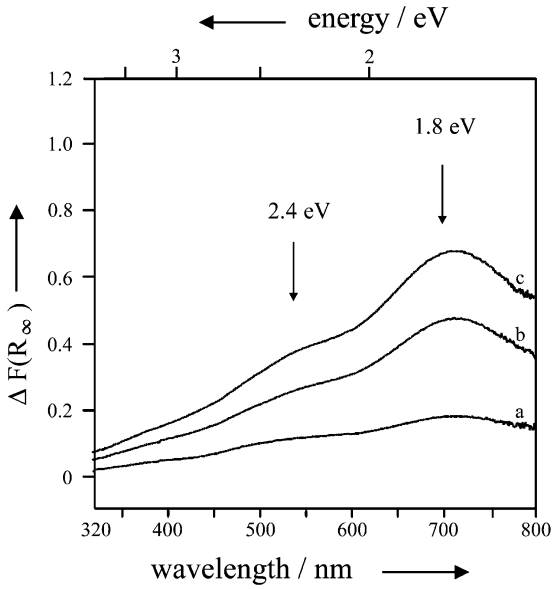


Figure 1. Difference curves between the Kubelka−Munk functions $\Delta F(R_\infty)$ before and after F_S-center formation according to procedure a. The surface color centers were generated by (a) 1-, (b) 5-, and (c) 15-fold iteration of the following sample treatment: exposure to H_2 (20 mbar, 1 min), evacuation, and subsequent UV activation under dynamic vacuum conditions for 5 min at 298 K.

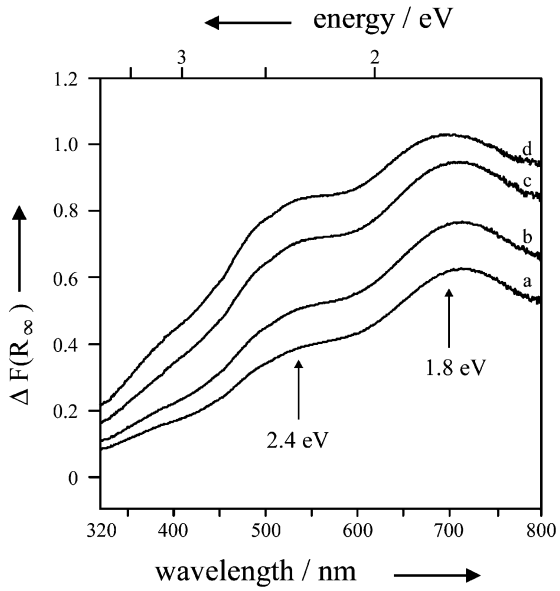


Figure 2. Difference curves between the Kubelka−Munk functions $\Delta F(R_\infty)$ before and after sample activation at (a) 0.1, (b) 1, (c) 10, and (d) 100 mbar H_2 with polychromatic UV light for 10 min at 298 K. Longer UV exposure times in the presence of hydrogen do not alter structure and intensity of the absorption pattern.[32]

and thus provides additional electrons (e^-; $H^\bullet \rightarrow H^+ + e^-$) for color center formation (eqs 3 and 4).

Procedure c. The third procedure is based on existing F_S centers, which were produced by procedure b. These will be—for the sake of brevity—designated color centers of the zeroth generation and are subsequently used as educts for two further, consecutive reaction steps. First, the F_S centers are bleached by N_2O gas admission according to

$$(Mg^{2+})_n^- + N_2O \rightarrow (Mg^{2+})_n{-}O^- + N_2 \qquad (7)$$

At room temperature, N_2 does not interact with surface defects to a significant extent.[14] The resulting paramagnetic O^- sites are used for homolytic H_2 splitting:

$$(Mg^{2+})_n{-}O^- + H_2 \rightarrow (Mg^{2+})_n{-}O^{2-}H^+ + H^\bullet \qquad (8)$$

It should be mentioned that, besides serving as an electron source, a considerable fraction of atomic hydrogen out of eqs 2, 4, and 6 can also desorb into the gas phase without participating in any further surface reaction or by becoming active at sites remote from its formation.

2. UV/Vis Diffuse Reflectance Spectra. For procedure a, the MgO sample is subjected iteratively to the following three-phase treatment: (i) H_2 chemisorption in the dark by sample exposure to 20 mbar H_2 for 60 s, (ii) removal of excess H_2 gas and any reversible H_2 chemisorption product by evacuation, and (iii) UV irradiation under dynamic vacuum conditions for 5 min.

In the UV/vis spectrum, the reduced MgO surface gives rise to one dominating broad band centered around 700 nm (1.8 eV, Figure 1a), attributed to an electronic F_S center excitation. A second excitation occurs around 520 nm (2.4 eV), where a weak shoulder appears. On increasing the number of treatment cycles, the relative ordinate values increase uniformly in the spectral interval between 320 and 800 nm and exhibit moderate saturation behavior (Figure 1b, c). The bandwidths of these absorptions are estimated via band fitting to lie between 0.2 and 0.5 eV. The whole spectral pattern is perfectly bleached

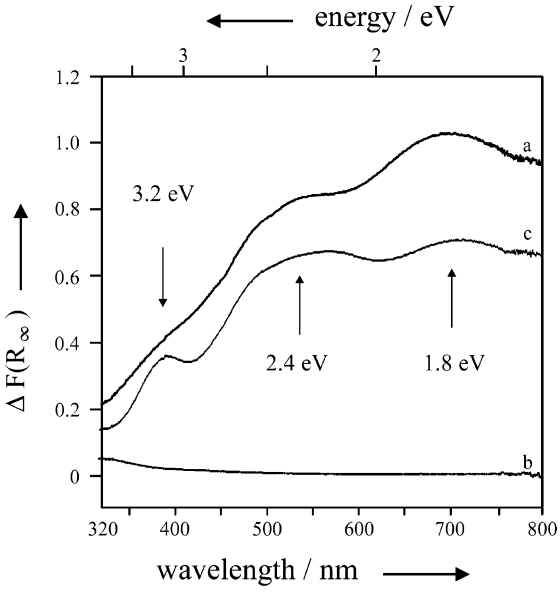


Figure 3. Comparison between F_S centers of the zeroth (a) and the first generation (c): The curve in (a) was obtained after sample activation with polychromatic UV light at 100 mbar H_2 for 10 min. Afterward, the sample was contacted with N_2O and evacuated. The originally blue sample bleaches out (b). Subsequent addition of 1 mbar H_2 leads to new sample coloration, as shown by (c).

after addition of oxidizing agents such as N_2O (see Figure 3b), proving that only surface defects are involved.

According to procedure b, dehydroxylated MgO nanoparticles are exposed to polychromatic UV light and molecular hydrogen (0.1, 1.0, 10, and 100 mbar) at the same time.[32] The contour of the absorption spectra for the lowest H_2 pressure (0.1 mbar, Figure 2a) strongly resembles that observed after multiple treatment cycles of procedure a (Figure 1c): again, two broad and overlapping bands centered around 520 (2.4 eV) and 700 nm (1.8 eV) appear. The intensity ratio is, however, shifted in favor of that at 520 nm (2.4 eV). This trend holds when the H_2 pressure in procedure b is raised. At the same time, both bands exhibit—as in Figure 1—moderate saturation behavior.

TABLE 1: Compilation of Experimental Data for Optical Absorption Energies of F_S Centers in the Bulk and in the Surface

experiment	electronic transitions of F centers (eV)				sample type
this study		3.2	2.1/2.6	1.8	polycryst. CVD
(1) Nelson et al.[16]			2−2.3		polycryst. ex hydroxide
(2) Paganini et al.[17]		3.3	2.4	1.7	polycryst. ex hydroxide
(3) Wu et al.[20]	5.33	3.58		1.15	MgO/Ag(100) films
(4) Kramer et al.[35]	5.5	3.4/2.4	2.8	1.3/1.0	MgO/Ag(1,1,19) films

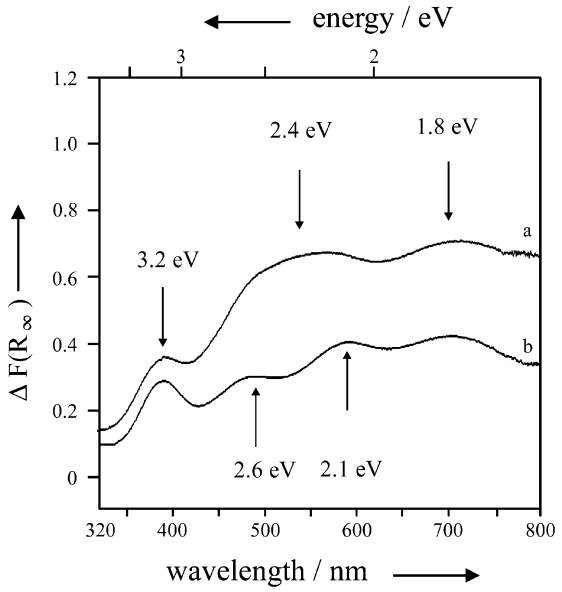


Figure 4. Thermal stability of color centers of the first generation. The difference curves of the Kubelka−Munk functions $\Delta F(R_\infty)$ in (a) and (b) were obtained before and after 5 min of thermal treatment of first generation color centers at 400 K under dynamic vacuum conditions, respectively.

Procedure c. The spectrum in Figure 3a is related to F_S centers of the zeroth generation and was taken after UV activation of MgO nanoparticles in the presence of 100 mbar H_2 for 600 s with subsequent evacuation (see also Figure 2d). As shown in Figure 3b, they are instantaneously bleached upon contacting the sample with N_2O. After another evacuation step and addition of 1 mbar H_2, the sample regains its blue color. The absorption spectrum of the newly formed F_S centers of the first generation (Figure 3c) exhibits distinct differences compared to that of the zeroth generation (Figure 3a). The absorption feature centered at 520 nm (2.4 eV) gains relative intensity compared to that at 700 nm (1.8 eV), and, in addition, a third band at 380 nm (3.2 eV) appears.

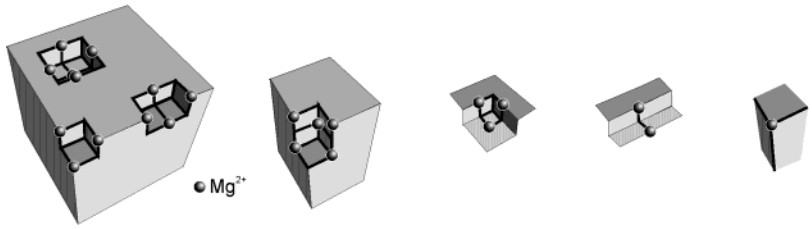
In addition to experiments concerning different mechanisms of generation, preliminary experiments addressing both thermal stability and photostability of surface color centers were carried out. For this purpose, a MgO sample containing color centers of the first generation (procedure c, Figure 4a) was subsequently subjected to either low-energy radiation or thermal treatment under dynamic vacuum conditions. Figure 4b shows the resulting diffuse reflectance UV/vis spectrum after heating the first generation color centers to 400 K for 5 min. Similar results are obtained after exposing the same sample to low-energy quanta of $E < 1.5$ eV ($\lambda > 830$ nm). Besides the photoassisted reduction of the whole absorption pattern between 320 and 800 nm, the spectrum in Figure 4b also reveals that the absorption feature centered at 540 nm (2.4 eV) in Figure 4a is actually composed of two bands at 480 (2.6 eV) and 580 nm (2.1 eV). Furthermore, the depletion process is more effective for color centers exhibiting transition energies in the low-energy region (2.6−1.8 eV) than for those absorbing at 3.2 eV.

3. Proposed Mechanisms. The energies of the bands observed here are listed in Table 1, in comparison with other experimental data, obtained either on powder samples (entries 1 and 2) or on epitaxially grown MgO surfaces after defect generation (entries 3 and 4). There is perfect agreement with the study of Paganini et al.,[17] performed on high surface area MgO, which was produced by the controlled thermal decomposition of magnesium hydroxide. Apparently, after sample annealing above 1100 K, samples of different preparative origin and morphology[22,33] contain sites with identical chemical and spectroscopic properties and, consequently, similar electronic structure on an atomic level.

For MgO as a perfect insulator, it was reported that bulklike electronic properties of MgO thin films develop within the first 2−3 monolayers.[34] Hence, with respect to the electronic structure on the atomic level, thin MgO films are appropriate models for polycrystalline MgO surfaces. An early experimental study on the properties of thermally generated defects on MgO (100) thin films by Wu et al.[20] gave electron energy loss features at 5.3, 3.6, and 1.1 eV (Table 1, entry 3), which were attributed to electronic excitations of bulk F centers, surface F-center aggregates, and surface F centers, respectively. More recently, Kramer et al.[21] have observed a whole set of loss features between 3.4 and 2.0 eV on an epitaxially grown MgO (100) film, which has been subjected to electron bombardment. By comparing the ratio of the intensities of distinct loss features on MgO films grown on a flat (100) and a vicinal Ag (1,1,19) substrate,[35] these authors were able to further refine their results and to give an assignment of the loss peaks to electronic transitions of F centers located at differently coordinated sites on the surface. The loss energies of 2.4 and 3.4 eV were attributed to multiplet transitions[36] of color centers located at a terrace site, and the measured loss energy of 2.8 eV was assigned to the electronic $1s \rightarrow 2p_{x,y}$ transition of a low-coordinated color center at a step site.

The specific loss energies compare well to the UV/vis bands[37] observed in the present study (Table 1) and, thus, nicely relate to the properties of more realistic catalyst materials. A major unknown in our investigation is, however, the charge state of the electron trap. Whether diamagnetic (two electrons) or paramagnetic states (one electron) are present on the surface of MgO nanoparticles, and to what extent, cannot be decided on the basis of absorption experiments alone: theoretical calculations reveal that paramagnetic and diamagnetic centers have similar transition energies,[36] which is not experimentally resolvable due to actual bandwidths between 0.2 and 0.5 eV. However, the coincidence of certain transitions associated with both types of materials is promising and suggests that similar structural defects are involved. Further corroborating studies are needed to ascertain potential connections between defects on polycrystalline and monocrystalline surfaces.

The abundance of color centers on MgO nanoparticles clearly depends on the experimental conditions. After application of procedure a (Figure 1), one dominating color center species absorbing at 1.8 eV is observed. It emerges after the UV-induced oxidation of the hydride group (eq 2) when the released electron replaces H^- in the corner anion vacancy (eq 4).[24] The resulting



	single anion vacancies [36]	anion/cation divacancies [11]	reverse corner [18]	step edge [18]	low coordinated Mg sites [19]
calculated electron affinity in eV	4.5-5.8	0.6-1.1	0.7 *3.1 plus $O^{2-}H^{+}$*		0.6-2.0
calculated electronic transition energy in eV	5C 4C 3C 3 2.4 2.1		*2.0*	*1.8, 2.4*	*2.0, 2.4 plus $O^{2-}H^{+}$*

Figure 5. Models, calculated electron affinities, and electronic transition energies of electron traps on the surface of MgO.

neutral H radical is—unlike the electron (eq 2)—only weakly bound to the MgO surface[18] and, therefore, likely to be mobile on the ionic surface. Thus, it may act as reducing agent for any other—possibly remote—type of $(Mg^{2+})_n$ array acting as an electron trap. The weak shoulder around 2.4 eV (Figure 1) indicates that one of them is particularly favored, because of its abundance or its electron affinity. Taking into account the stoichiometric ratio of 1:1 for the electrons and the surface mobile $H^{\bullet}$ radicals (eq 2), it follows that the surface color centers emerging at the sites of irreversible heterolytic H_2 splitting are the most abundant ones (1.8. eV). The obvious trend of color center formation toward saturation on raising the number of treatment cycles (Figure 1) is intimately related to the saturation effect observed for the irreversible heterolytic H_2 splitting process.[24]

When UV light and molecular hydrogen ($p(H_2) > 10$ mbar, procedure b) act simultaneously on the MgO surface, a larger reservoir of reducing agents is available since, in addition to the irreversible heterolytic splitting (eqs 1−4), both the reversible heterolytic (eqs 1−4) and the UV-induced homolytic H_2 splitting[31] processes (eq 6) become effective. The reversible process—like the irreversible counterpart—provides electrons and H radicals in the stoichiometric ratio. They emerge, however, from the reversible hydride groups located at step edges (see procedure b). Recalling that the electron is likely to stick to the $(Mg^{2+})_n$ array which previously hosted H^-, we assign the resulting color center (according to Figure 2) to the absorption feature centered at 520 nm (2.4 eV). On the other hand, the UV-induced homolytic H_2 splitting process also provides H radicals (eq 6) in addition to electrons (eq 5) which become trapped in an as yet unspecified form close to the site of O^{2-} excitation.[15] The increased supply of mobile H species should further favor the formation of the color center type to which the band at 520 nm (2.4 eV) was attributed. In fact, the relative intensity at 520 nm (2.4 eV) grows faster with the applied H_2 pressure than that at 700 nm (1.8 eV) (Figure 2).

So far, color centers of the so-called zeroth generation have been discussed exclusively. In the first step of procedure c they are bleached by N_2O addition (eq 7). The respective UV absorption bands (Figure 2d and 3a), as well as the EPR signal components,[38,39] vanish completely. The latter ones are replaced by those of surface O^- species[38,39] which are then available for homolytic H_2 splitting, according to eq 8. After all, the color centers of the zeroth generation are replaced by isolated OH groups (eq 8) and surface mobile H radicals (see above). These are available for probing the MgO surface for anion vacancies as electron traps which have not yet been consumed by previous reaction steps (eqs 3, 4, and 7). In fact, Figure 3c shows that the absorption bands at 1.8 and 2.4 eV observed during the procedures a and b reappear, even though they have strongly changed relative intensities. The H radicals formed in the course of homolytic H_2 splitting (eq 8) are likely to be supplied with so much excess energy that they reach $(Mg^{2+})_n$ arrays on the surface of the MgO sample which were previously not accessible in both procedures a and b for H_2 molecules (eq 1) and/or UV quanta (eq 2). Among them are sites where, in principle, irreversible or reversible heterolytic H_2 splitting may occur. Of course, they are likely to act preferentially as local potential minima for the electrons of mobile H radicals and thus to explain the appearance of the same band positions in procedure c on one hand and procedures a and b on the other. The most striking observation is, however, the presence of a third comparatively sharp absorption band at 3.2 eV (380 nm) which is absent in the experiments based on procedures a and b. Quantum chemical calculations[18,19,36] predict the excitation energy of electrons trapped in anion vacancies and O^{2-} anion-deficient $(Mg^{2+})_n$ arrays in general (Figure 5). The value for an ideal surface color center in a perfect (100) plane is in good agreement with the absorption band around 3.2 eV. As there are neither experimental nor theoretical evidences for a heterolytic H_2 splitting at the respective type of $(Mg^{2+})_n$ array, a direct electron transfer from a hydride to the vacancy in a perfect (100) plane appears, therefore, not to be possible. Consequently, the abundance of the corresponding surface color centers in procedures a and b does not reach the detection limit of UV/vis absorption spectroscopy. On the other hand, under the experimental conditions during the formation of first generation color centers, H radicals may dispose of sufficiently high kinetic energy in order to reach single anion vacancies in (100) planes and to be trapped there.

The quantum chemical calculations also show that shallow $(Mg^{2+})_n$ electron traps may be strongly stabilized by closely spaced surface OH groups (Figure 5).[19] These emerge under the experimental conditions described above in both heterolytic cleavage of H_2 and electron transfer from mobile H radicals to $(Mg^{2+})_n$ traps. According to the calculations, the excitation energies at 1.8 and 2.4 eV (Figure 4) are likely to be related to such surface OH-stabilized electron centers. On the other hand, it must be emphasized that the color center absorbing at 3.2 eV is attributed to a non-OH-stabilized color center—in agreement with the fact that heterolytic H_2 splitting and, thus, hydride

formation does not occur at the respective anion vacancy (see above). Relevant support for the tentative assignments given here stems from IR and EPR spectroscopic studies revealing electronic and magnetic coupling, respectively, between closely spaced surface OH groups and surface-trapped electrons on MgO surfaces.[29]

A moderate temperature rise from 300 to 400 K already partially bleaches the absorption bands at 2.4 and 1.8 eV (Figure 4), which are related to sites of heterolytic H_2 splitting. The band at 3.2 eV, on the other hand, survives essentially unaffected. This experiment reveals that the whole absorption pattern between 2.5 and 1.5 eV is made up of more than two types of differently stable electron centers. The influence of the surface OH groups on neighboring trapped electrons may also help in the attempt to understand the comparatively low thermal stability of most of the electron centers absorbing in the spectral interval between 3 and 1.5 eV. In fact, the quantum chemical calculations clearly show a wide variety of surface electron traps, the electron affinity (EA) and the transition energy of which depend on both the structure of the local $(Mg^{2+})_n$ array and the presence of a closely spaced OH group. Figure 5 only contains a limited selection of such surface sites. The thermal energy supplied in the bleaching process is only a fraction of the ionization energy required for the surface species in question. It may, however, suffice to excite a low-energy mode of the OH group involved and thus initiate a reaction channel:

$$O^{2-}H^{+} \cdots \underset{\cup}{\bullet} \xrightarrow{kT} O^{2-} + \cup + H^{\bullet} \qquad (9)$$

However, this hypothesis, though highly speculative, is intimately related to reliable strategies of corroboration: in the course of the bleaching process, specific surface OH groups must definitely disappear, and hydrogen must emerge in the gas phase. The respective experiments are in the process of being prepared in our laboratory.

Conclusions

In the present study, we have shown that, on the surface of polycrystalline MgO, color centers are formed selectively by applying different kinds of formation procedures involving two types of electron donors: hydride ions and H radicals. The former ones are related to hydrogen chemisorption sites on the surface, which are subsequently also the main electron-trapping centers. H radicals, on the other hand, are mobile on the surface and, therefore, able to reach remote electron traps, which are not directly involved in the hydrogen photochemistry on MgO. The transition energies of the color centers are in reasonable agreement with studies on MgO thin films, which is evidence of the morphological uniformity of MgO samples of different origin. Although the assignment of the observed absorption features to optical transitions of specific structural surface entities capable of trapping electrons and their stability is not entirely unambiguous, the results presented here provide some further important insights into the defect chemistry on MgO.

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