

Energy Transfer on the MgO Surface, Monitored by UV-Induced H₂ Chemisorption

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Abstract: Surface anions on edges (4-coordinated = 4C) and on corners (3-coordinated = 3C) of cubic MgO nanoparticles exhibit UV resonance absorptions around 5.5 and 4.6 eV, respectively. After monochromatic excitation of either site the electron paramagnetic resonance (EPR) spectrum exhibits exclusively signal components related to 3-coordinated O⁻ radicals (O_{3C}⁻, electron hole centers), which are perfectly bleached by H₂ addition. The disappearance of the O_{3C}⁻ EPR signal components is paralleled by a depletion of the UV resonance absorption of the 3-coordinated O²⁻ only and the appearance of one single band in the OH stretching region of the IR spectrum. Obviously the sites of UV excitation and subsequent UV induced surface reaction with H₂ are not the same. This may coherently be explained in terms of mobility of the exciton (O_{4C}²⁻)^{*} or – after ionization – of the corresponding electron hole O_{4C}⁻ along the edge where it was created. Finally the mobile state is trapped at a corner site where the O_{3C}H group is formed.

Introduction

Heterogeneous photocatalysis is based on light-induced surface reactions. Relevant model surfaces are provided, e.g., by alkaline earth oxides. Their band gap (>6 eV) is significantly wider than that of semiconductor materials, the realization of photoinduced processes requires far-UV light and would, therefore, be absolutely ineffective from the energetic point of view. The presence of defects, either intrinsic ones (vacancies and/or coordinatively unsaturated surface ions) or extrinsic ones (such as impurity dopants) on the oxide surface may give rise to absorption bands at energies below the vacuum UV (<6 eV or, correspondingly, at wavelengths above 200 nm).^{1,2} Light absorption by these isolated sites can cause electronic transitions into localized and delocalized excited states, which then may initiate photochemical reactions at sites with specific electronic properties and geometry. These need not necessarily be identical with the previously optically excited ones, since considerable energy transfer via excitons, photogenerated electrons, and electron holes may occur.^{3,4} In this study we demonstrate a means to monitor this energy flow on the surface of cubic MgO nanoparticles chemically. This is of major importance in the field of chemistry on oxide surfaces, since a UV induced selective activation of sites may open a new path for the

development and application of alkaline earth oxide based catalyst systems.²

Highly dispersed alkaline earth oxides have optical absorption bands that are not representative of pure single crystals, since their number of surface ions is dramatically increased. With respect to anions in the bulk, surface anions experience a reduced coordination and, correspondingly, the respective Madelung potentials are smaller in value, leading to the absorption of light at energies lower than the band gap.⁵ For MgO, absorption bands of low coordinated surface structures including 4-coordinated oxygen anions in edges at 5.5 eV (225 nm) and 3-coordinated oxygen anions in different types of corners at 4.6 eV (270 nm) (Figure 1) are readily distinguished.^{6–8} The primary event of light absorption can be described by the formation of a surface bound electron–hole pair, a so-called surface exciton. It can relax via emission of light or decompose into a surface-trapped electron and a localized surface hole state (O⁻ radical). These are typical for oxide catalysts with pronounced acidic and basic properties.⁹ The electron and the hole are then disposable for interaction with an electron acceptor (e.g. O₂) or an electron donor (e.g. H₂, CH₄) molecule, respectively, from the gas phase. For instance, in an oxygen atmosphere the electron is trapped by O₂ from the gas phase upon formation of a surface-complexed superoxide anion O₂⁻.^{10,11} In this way the probability of electron–hole recombination related to the phenom-

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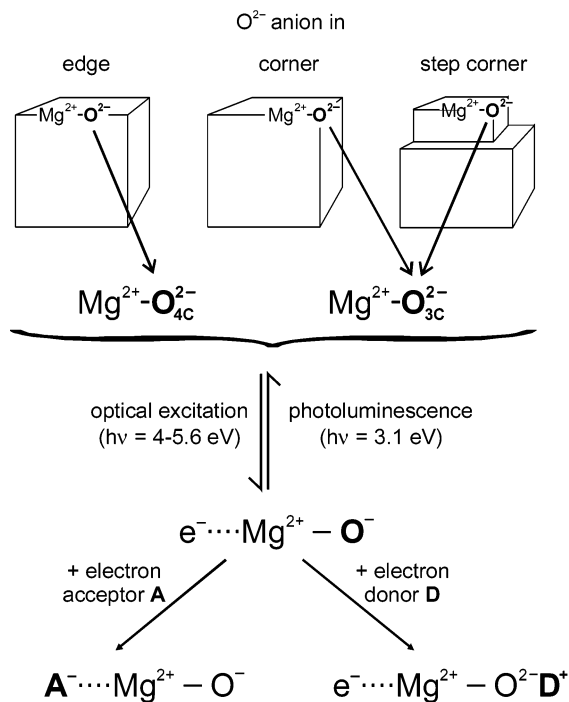


Figure 1. Schematic representation of the optical excitation and consecutive processes of differently coordinated surface oxygen anions on MgO nanoparticles. The step corner shown here is one example for a whole set of irregular 3C O²⁻ anions (next nearest Mg²⁺ neighbors not all 4-coordinated).

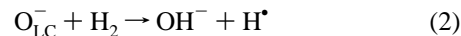
enon of luminescence (Figure 1),^{6,12} is considerably reduced and the total abundance of surface O⁻ species, correspondingly, increased.¹³ At this point, it has to be noted that under vacuum conditions the photogenerated electron can be trapped either by anion vacancies¹⁴—electron affinity > 2 eV—or by other more shallow potential minima on the surface (electron affinity < 2 eV). The latter types of defects have so far not been specified. However, owing to the principle of electroneutrality, they must be there.³ For the sake of simplicity, in Figure 1 all types of electron traps are schematically subsumed by a “e⁻ · · · Mg²⁺ + ” unit.

Localized electron hole states can be observed by electron paramagnetic resonance (EPR). The respective signals contain information about the coordination state and the geometric environment of the underlying surface anion.^{15,16} Therefore, their selective generation^{2,17–19} and subsequent detection by EPR in combination with quantum chemical calculations has become a powerful tool for the investigation of the electronic structure and reactivity of defects on metal oxide surfaces.^{13,20} From a chemical point of view O⁻ centers are surface radicals and play an important role in heterogeneously catalyzed oxidation reactions.^{15,21,22} Therefore, the present investigation aims to

elucidate the interaction between photoexcited low coordinated (LC = 3C or 4C) surface anions (eq 1)



with the simplest electron donor molecule available, namely molecular hydrogen, which is split homolytically at these sites (eq 2)^{11,14}



Three of the participants of the reactive happening represented by eqs 1 and 2 will be monitored by three independent spectroscopic techniques: (a) Electron paramagnetic resonance spectroscopy reveals the presence of surface radicals after optical excitation in the absence of hydrogen (eq 1); (b) IR spectroscopy proves the formation of infrared active hydroxyl groups (eq 2); and (c) diffuse UV reflectance spectroscopy monitors the loss of surface O²⁻ sites transformed into hydroxyl groups (eqs 1 and 2).

Experimental Section

All experiments were carried out with MgO nanoparticles obtained by chemical vapor deposition in a flow system.²³ High purity Mg pieces as educt were supplied by Johnson Matthey GmbH. The specific surface area of the resulting sample material determined by BET (LN₂) measurements is around 400 m²/g. Further details regarding the surface properties of these nanometer-sized particles—their edge length ranges from 5 to 8 nm—are given elsewhere.²³ To guarantee a totally dehydroxylated surface, the sample was gradually annealed at 1173 K under dynamic vacuum (<10⁻⁵ mbar) before each experiment. This leads to a reduction of the specific surface area to 300 m²/g. The rate of temperature increase for the annealing steps was 10 K/min. The gases H₂ (99.999%) and ¹⁶O₂ (99.998%) for adsorption studies were provided by Messer Griesheim. A 300W Xe lamp (Oriel) was applied for UV irradiation. The light beam passed through a water filter in order to avoid sample heating by IR irradiation. All UV excitation experiments on MgO were carried out at room temperature. Wavelength selective excitation of the sample material for IR and EPR studies was attained by passing the light beam through a monochromator system (M160.1, Proscan GmbH), whereas for the UV diffuse reflectance measurements a band filter was applied (237 and 282 nm; fwhm: 40 nm). The spectral output of the monochromator was measured as spectral irradiance (Wm⁻² nm⁻¹) by the aid of a spectroradiometer (Bentham DTM 300). The UV irradiation time amounted to 30 min for IR and UV diffuse reflectance to 60 min for EPR experiments.

The IR, EPR, and UV diffuse reflectance sample cells are connected to appropriate high vacuum pumping racks. They provide vacuum of less than 10⁻⁵ mbar and allow adsorption/desorption experiments with diverse gases. For the IR experiments small quantities of MgO powder (20–30 mg) were pressed into self-supporting pellets. For the EPR and UV diffuse reflectance experiments MgO powder of the MgO sample batch, also used for IR spectroscopy, was filled in an EPR tube or the special quartz cell with Suprasil windows, respectively.

The IR spectra were recorded using a Fourier transform IR spectrometer model IFS 113v (Bruker Optik GmbH). The resolution was 3 cm⁻¹. Three hundred interferogram scans were averaged in order to guarantee a reasonable signal-to-noise ratio. The reference for the absorbance spectra is a MgO sample previously subjected to thermal activation and then cooled to room temperature. The EPR spectra were recorded using a Bruker EMX 10/12 spectrometer system in the

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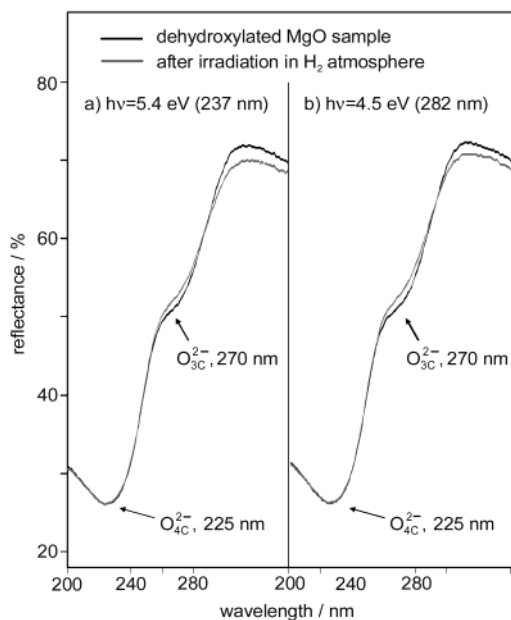


Figure 2. Diffuse UV reflectance spectra of MgO nanoparticles after thermal activation at 1173 in high vacuum (black curves in a and b) and subsequent irradiation at 237 nm (a, gray curve) and 282 nm (b, gray curve) in 1 mbar H₂.

X band. The respective MgO samples were cooled to 77 K in order to avoid line broadening. Ten coadded spectra sufficed to obtain a satisfactory signal-to-noise ratio. The DPPH signal as well as the lines originating from traces of Mn²⁺ in the sample was applied for *g* value calibration. The UV spectra were acquired using a Perkin-Elmer Lambda 15 spectrophotometer equipped with an integrating sphere. BaSO₄ powder was used as a reference. All experiments were carried out in the presence of 5 mbar O₂ to suppress luminescence.

Results and Discussion

The diffuse reflectance spectrum of entirely dehydroxylated MgO nanoparticles is shown in Figure 2 (black curves). In perfect agreement with literature,⁵ it contains two absorption features corresponding to minima in reflectance at 5.5 eV (225 nm) and 4.6 eV (270 nm) to be attributed to the optical excitation of 4- and 3-coordinated surface anions, respectively.^{5,8,24} The same sample was then—in two separate experiments—exposed to 1 mbar H₂ and irradiated by “monochromatic” UV light (fwhm: 40 nm), the center wavelengths of which correspond to the resonance absorptions of 4- and 3-coordinated oxygen anions, respectively (237 and 282 nm, respectively). The intensity of the absorption of 4-coordinated O²⁻ at 5.5 eV (225 nm) is absolutely unchanged in both experiments (Figure 2a and 2b, gray curves). On the other hand, the intensity of the absorption of 3-coordinated O²⁻ is significantly depleted after resonance excitation of both 4- and 3-coordinated O²⁻ (Figure 2a and 2b, gray curves).²⁵

This indicates that a UV induced reaction between O²⁻ and H₂ has—to a significant extent—only occurred at 3-coordinated sites. Obviously the site of excitation and that of reaction with H₂ are not the same. Whether H₂ reacts with an exciton, (O_{LC}²⁻)^{*}, or—after its ionization—with an electron hole, is for the moment an open question.

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(25) The absorption above 300 nm is related to the presence of O₅⁻ species. They originate from a side reaction of O₂ added in order to quench luminescence and do not at all interfere with the present study.

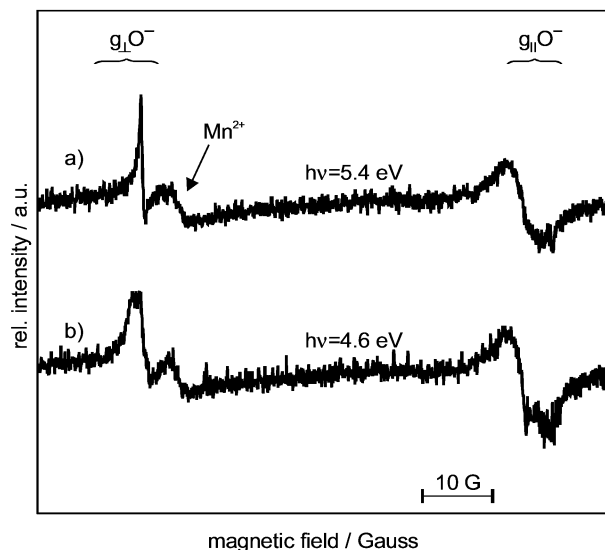
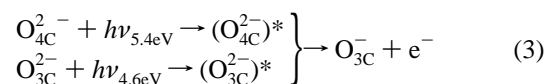


Figure 3. Electron paramagnetic resonance spectra of two different types of electron hole centers trapped at 3-coordinated anions on the surface of MgO nanoparticles: The spectra comprise both *g*_⊥ and *g*_∥ components of the O⁻ radicals and were obtained after optical excitation at 5.4 eV (a) and at 4.6 eV (b), respectively. (The measured EPR spectra are not normalized with respect to the incident photon flux.)

In fact, after monochromatic excitation of MgO nanoparticles at 5.4 eV (230 nm) and 4.6 eV (270 nm), electron paramagnetic resonance spectroscopy proves (Figure 3a and b, respectively) the presence of two types of O⁻ radicals. The puzzling point is that their EPR signal components appear at essentially the same magnetic field position and can only be discriminated on the basis of their different line shapes.¹³

The *g* factors (*g*_⊥ = 2.036 and *g*_∥ = *g*_e = 2.003) clearly indicate that both O⁻ radicals are 3-coordinated



The differences in line shape originate from differences in the coordination state of the next nearest Mg²⁺ neighbors: 5.4 eV excitation provides O_{3C}⁻ species in ideal cube corner position, 4.6 eV excitation mainly those in less regular corner positions (Figure 1).¹³ Both types of O_{3C}⁻ signal components are instantaneously depleted on D₂ or H₂ addition even at 77 K.¹¹ Obviously, the respective O_{3C}⁻ species are extremely reactive. The mechanism of ionization (eq 3) is still unknown. Phonon-assisted electron abstraction from the exciton (O_{LC}²⁻)^{*} would be one explanation. More likely is the absorption of a second photon, which transforms (O_{LC}²⁻)^{*} into O⁻.

The foregoing interpretation is in contrast to findings of Volodin et al.²⁷ who attributed the EPR signal component at *g*_⊥ = 2.036 to an O⁻ center in 4-fold, and a different signal component at *g*_⊥ = 2.042 to an O⁻ center in 3-fold coordination state. We have experimental evidence that the latter species originates from surface ozonide, which is the result of photo-stimulated adsorption of molecular oxygen on specific local surface sites. This process occurs at lower energies than the resonance absorption of 3-coordinated anions.¹³

Summarizing the results of the UV diffuse reflectance and EPR experiments, it has to be emphasized that there is one relaxation channel for the excited O_{4C}²⁻ site, which is related to

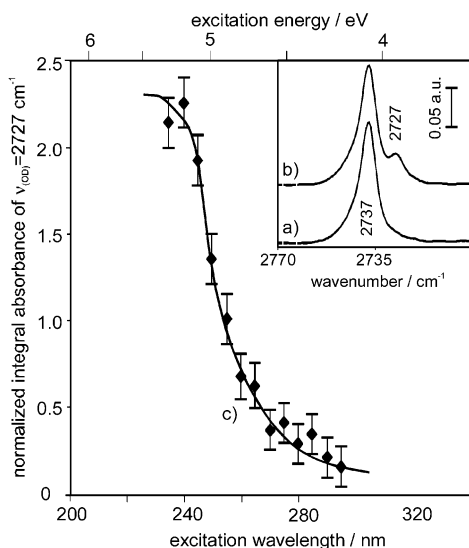


Figure 4. IR spectra (OD stretching region) of MgO nanoparticles after addition of 1 mbar D₂ (a) in the dark and (b) under UV irradiation (265 nm). (c) Representation of the relative yield of OD₂₇₂₇ resulting from UV induced homolytic D₂ splitting. The integral IR absorbance values are normalized with respect to the UV photon flux.

a transfer of either the exciton or its ionized form—the electron hole—from a 4- to a 3-coordinated site. Irrespective of whether the excitons or the holes are mobile, the EPR spectrum exclusively reveals the presence of 3-coordinated holes, which are bleached instantaneously by H₂ or D₂ addition.

The inherent changes in the OH stretching region of the IR spectrum then permit us to reliably probe the consumption of electron holes on the MgO surface. Only recently, one single OH stretching band at 3698 cm⁻¹ was unambiguously attributed to UV-induced H₂ chemisorption, i.e., homolytic H₂ splitting.²⁶ It is relatively sharp and exempt from any significant interaction with other groups in the surface environment.²⁶ Spectral congestion may, under the given experimental conditions, only arise to a controllable extent from the OH band at 3712 cm⁻¹ attributed to heterolytic H₂ splitting in the dark, which involves very specific 4-coordinated O²⁻ sites.^{27,28} Of course, this process also occurs during UV irradiation. It does not, however, at all interfere in the present study because the abundance of the respective 4-coordinated sites compared to the total number of excitable 4-coordinated sites is negligibly small.²⁷

From the foregoing discussion, it is clear that bleaching of electron holes by H₂ plays a crucial role in the assessment of excitation and subsequent relaxation processes related to LC O²⁻ anions on MgO surfaces. Therefore, the band at 3698 cm⁻¹ and its dependence on the wavelength of the exciting irradiation was studied with extreme care. First of all, H₂ as surface probe was replaced by D₂: the resulting OD stretching band (Figure 4b) is located at 2727 cm⁻¹ (instead of 3698 cm⁻¹ for OH) and thus appears in a spectral interval of considerably higher signal-to-noise ratio. The D₂ chemisorption in the dark (Figure 4, parts a and b) then gives rise to an absorption at 2737 cm⁻¹ (instead of 3712 cm⁻¹ for OH). Second, the monochromasy of the exciting UV light was improved by the use of a monochromator

(bandwidth: 5 nm) in front of the 300 W Xe lamp. This imposed, however, a limitation of the photon flux and consequently led to an upper energy limit of the spectral range available for the excitation at 5.4 eV (230 nm). The effective flux of the exciting UV photons was used later on in order to normalize the abundance of the photoproducts (surface OD groups absorbing around 2727 cm⁻¹).

Both the position and the shape of the IR band at 2727 cm⁻¹ do not at all depend (a) on the D₂ pressure in the interval between 1 and 100 mbar and (b) on the photon energy of the exciting UV light in the interval between 5.4 and 4.0 eV (230 and 310 nm, respectively). Thus, only one simple type of photoproduct, namely a 3-coordinated surface OD group at 2727 cm⁻¹, is detected. This means that the different local environments of the two 3-coordinated O⁻ species (Figure 1) as educts clearly discriminated by EPR spectroscopy (Figure 3) are, after the transformation in 3-coordinated OD groups, no longer seen by IR spectroscopy (Figure 4). It also means that 4-coordinated excitons do not react with D₂ or H₂, since a corresponding isolated OD (OH) group at 2741 cm⁻¹ (3718 cm⁻¹)²⁶ does not appear in the IR spectrum.

Different from the position and the shape of the band, its normalized (see above) integral absorbance characteristically depends on the energy/wavelength of the exciting UV photons. It decreases monotonically from 5.4 to 4.0 eV (Figure 4c) and clearly reflects the decay of the absorbance coefficient related to the electronic excitation of 4-coordinated surface O²⁻ anions (edge sites) within this energy/wavelength interval (Figure 2). It has to be admitted, however, that the excitation of 3-coordinated surface O²⁻ anions (both types of corner sites, Figure 1) may, even though with a much lower efficiency, contribute to the abundance of 3-coordinated OD groups absorbing at 2727 cm⁻¹ (hardly recognizable from the experimental data around 4.6 eV in Figure 4c).²⁹

Still there is an unattended open question: Why is the reaction channel involving the 4-coordinated oxygen anions as educts so much more efficient than that involving the 3-coordinated oxygen anions? There is a relevant argument for the expectation of the contrary since the 4C channel (5.4 eV) ends up with the appearance of holes exclusively in the 3C position of ideal cube corners,¹³ whereas UV excitation at 4.6 eV comprises all types of 3-coordinated sites (Figure 1). However, the product of the probabilities of excitation of 4C sites exciton transfer to 3C and ionization obviously appears to be significantly larger than that of excitation and ionization of 3C sites.

The intriguing fact that after excitation at 5.4 eV, all spectroscopic techniques applied—UV diffuse reflectance, EPR, and IR transmission spectroscopy—evidence the sites of excitation and reaction with D₂(H₂) to be different from each other, necessarily imply the mobility of either excitons or electron holes in 4-coordinated surface sites.³ Previously, photoluminescence studies suggested that the deactivation of excitons does not necessarily occur at the original location of optical excitation.^{6,12} The excited state can hop to sites of the same or lower coordination. However, the lower the initial coordination the less likely the process will occur. Recent theoretical calculations

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corroborate this interpretation showing that relaxed excitons are strongly localized at 3-coordinated and delocalized at 4-coordinated sites.³ Delocalization of an excited electronic state, on the other hand, means that the reactivity at the site of excitation is reduced. This is in perfect agreement with the absence of a corresponding absorption of a 4-coordinated OD(OH) group in the IR spectrum after irradiation with 5.4 eV photons. Similar calculations as those mentioned above support the assumption that electron holes formed on 4-coordinated O²⁻ sites are mobile, whereas hole states emerging after electronic excitation in corner positions are localized precisely there.³

Conclusions

In the present study, the phenomenon of energy transfer between 4- and 3-coordinated surface oxygen anions on insulating metal oxides such as MgO is evidenced via site selective homolytic splitting of molecular hydrogen. A conclusive answer to the question of why the excited 4-coordinated oxygen anions (or the 4C hole states) do not react with D₂ or H₂ may not be given on the basis of the experimental data available. Detailed photoluminescence and quantum chemical studies are likely to contribute to the decision whether this is due to thermodynamic reasons or to an extremely short time scale for the transfer of the excitons or electron holes to an ideal cube corner position.

O⁻ anions on metal oxide surfaces are likely to catalyze partial oxidation reactions of small hydrocarbons.^{15,21,22} These radical species are expected to emerge at reaction temperatures

between 600 and 800 °C and to be responsible for the H radical abstraction as initial activation step. As shown in the present paper, the O⁻ production on MgO surfaces is also feasible by properly selected optical excitation thus enabling molecular hydrogen to be split homolytically at room temperature. Therefore, partial oxidation reactions are likely to benefit also considerably from the photoinduced production of O⁻ species on MgO, which should subsequently initiate the homolytic splitting of C–H bonds at comparatively low temperatures. This appears to be a new approach to site-selective oxidative photocatalysis. Its efficiency should not only be checked for MgO, but rather also for other types of metal oxides and binary mixtures thereof, e.g., MgO surface-doped by CaO.^{9,30,31}

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