

H₂ chemisorption and consecutive UV stimulated surface reactions on nanostructured MgO

Oliver Diwald, Peter Hofmann and Erich Knözinger*

Institut für Physikalische Chemie, Technische Universität Wien, Getreidemarkt 9, A-1060 Wien, Austria. E-mail: knoezing@fbch.tuwien.ac.at

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MgO nanoparticles obtained by chemical vapour deposition (CVD) were exposed to H₂ and subsequently to UV irradiation and/or molecular oxygen at room temperature. A combined IR/EPR study reveals the role of low coordinated surface sites and anion vacancies in the diverse reaction steps. The hydride groups emerging from the initial H₂ chemisorption processes (heterolytic splitting) play an active role in the consecutive reactions. They provide the electrons which are required for the UV induced formation of surface colour centres and for the production of superoxide anions (redox reaction). Both the colour centres and the superoxide anions are EPR active. The hydroxy groups resulting from H₂ chemisorption do not actively participate in the consecutive reactions. Together with the OH groups formed in the course of colour centre formation they rather play the role of an observer. They undergo specific electronic interactions with both the colour centre and the superoxide anion which are IR inactive (or IR inaccessible) surface species. They may, however, be observed by IR spectroscopy *via* the specifically influenced OH stretching vibrations. This proves the intimate interplay between IR and EPR spectroscopy as applied to the surface processes under investigation. As a result, two paths were found for the three consecutive surface reaction steps: H₂ chemisorption, colour centre formation and superoxide anion formation. In the first one a single, well defined surface area element is involved, namely a low coordinated ion pair, the cation of which is a constituent of an anion vacancy. In the second path a diffusion controlled intermediate step has to be adopted in which the electron required for the colour centre is transported by an H atom travelling from a hydride group to a remote anion vacancy. In either case there is clear experimental evidence that the finally resulting superoxide anions are complexed by the colour centre cations.

Introduction

It is generally accepted that equilibrium (100) surfaces of MgO which are made up of '5'-coordinated anions and cations are essentially non-reactive.^{1,2} The surface reactivity of MgO necessarily implies the presence of surface imperfections, *i.e.*, low coordinated sites^{3,4} as well as surface vacancies.^{5,6} Therefore, chemical vapour deposition (CVD) is particularly well suited to create reactive surface centres on MgO. The extreme non-equilibrium conditions during solid formation permit the production of nanostructured MgO particles with quantitatively and qualitatively enhanced surface reactivity.⁷ On the other hand, the resulting material exhibits a comparatively high thermal stability which guarantees a specific surface area (BET) of more than 300 m² g⁻¹ after thermal treatment at 1173 K.⁷ This is in agreement with the mean particle diameter of 5 nm obtained *via* the Scherrer formula from the line width of X-ray reflections and with a mean edge length of the cubic MgO particles observed by transmission electron microscopy.⁸

To characterize the surface of nanostructured MgO obtained by CVD, the chemisorption of H₂ has extensively been studied by FTIR spectroscopy in our laboratories in the past. In addition to a heterolytic H₂ splitting, giving rise to surface OH and MgH probes, two homolytic mechanisms were postulated which would require the presence of anion and cation radical states on the surface. The admission of O₂ undoubtedly reduces the surface concentration of metal hydride created by H₂ chemisorption.^{9–11} At the same time

new characteristic surface OH groups appear. Comparable studies with EPR spectroscopy were performed on MgO originating from the thermal decomposition of hydroxide (ex hydroxide) or carbonate precipitated from solutions.^{12–14} The authors interpreted the results in terms of surface redox reactions between O₂ and MgH, leading to the superoxide anion O₂⁻ complexed by surface cations.^{12–15}

Under appropriate conditions the UV irradiation of MgO in a H₂ atmosphere gives rise to an electron transfer from hydride groups to surface anion defects. The resulting surface colour centres are either diamagnetic (two paired electrons, F_s⁰) or paramagnetic (one unpaired electron, F_s⁺). The latter ones have been characterized by EPR and ENDOR spectroscopy in combination with quantum chemical calculations.^{16–18} Low coordinated surface elements were suggested as the preferred location of these surface point defects. They obviously react with O₂ since the MgO sample loses the typical blue colour after O₂ admission. The resulting superoxide anion species exhibit EPR signals which provide site selective information related to coordinating surface cations. Thus, in addition to the hydride groups, which are observed in the IR spectrum *via* the respective stretching vibration, the superoxide anion turns out to be a second efficient surface cation probe.^{19–21}

Transmission electron microscopy on our CVD MgO after thermal treatment at 1173 K clearly exhibits an exclusively cubic morphology.⁸ In the absence of atomic resolution there may still be a huge site variety on the apparent (100) surface planes of the nanoparticles. Only recently a simple model of a

truncated Madelung surface potential that incorporates exclusively next nearest neighbour interactions was, however, successfully applied to characterize the surface sites on the MgO surface.²² This means that in fact the relevant surface defects on CVD MgO [as compared with '5'-coordinate centres in infinitely extended (100) planes] are '3'- and '4'-coordinated cations and anions as well as anion and cation vacancies in planes, on edges and on corners.

The aim of the present paper is to exploit this apparently simple situation in a combined FTIR/EPR study. It should shed light on the mechanism of the following site sensitive surface reactions: (1) colour centre formation starting with different metal hydrides as educts and (2) surface superoxide anion formation from both surface colour centres and from surface hydride groups.

Experimental

All experiments were carried out with the same type of MgO obtained by CVD in a flow system.²³ As starting material, high purity Mg pieces supplied by Johnson Matthey were used. The specific surface area of the resulting MgO material determined by BET measurements is around 400 m² g⁻¹. To get a totally dehydroxylated surface the sample was annealed at 1173 K under dynamic vacuum (<10⁻⁵ mbar) before each experiment. This leads to a reduction of the specific surface area to 320 m² g⁻¹. The rate of temperature increase for these annealing steps was 10 K min⁻¹. All samples were treated at 870 K with oxygen to burn off organic contaminants originating from the oil of the vacuum pumps used in the flow system. The gases H₂ (99.999%) and ¹⁶O₂ (99.998%) for adsorption studies were provided by Messer Griesheim. A 300 W Xe lamp (Oriel) was applied for UV irradiation. The light beam passes a water filter to avoid sample heating originating from IR irradiation. The exposure time of the MgO samples to UV light at room temperature was 10 min in all experiments. For both spectroscopic techniques the cell with the sample was connected to an appropriate high vacuum pumping rack. It allows thermal activation of the sample at less than 10⁻⁵ mbar and adsorption and desorption experiments with diverse gases.

For the IR experiments, small quantities of MgO powder (20–30 mg) were pressed into pellets of around 50 mg cm⁻². The pressure applied was less than 10 bar and did not initiate any change of the specific surface area. The IR spectra were recorded using a Fourier-transform IR spectrometer model IFS 113v (Bruker Optik). The resolution was 3 cm⁻¹; 300 interferogram scans were averaged to guarantee a reasonable signal-to-noise ratio. The reference for the absorbance spectra was a MgO sample previously subjected to thermal activation and then cooled down to room temperature.

For the EPR measurements a Bruker EMX 10/12 spectrometer system in the X band was applied. The colour centre signals were obtained at room temperature in one scan, whereas the O₂⁻ spectra required a reduction of the temperature to 77 K to improve resolution. In this case 10 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 were applied for *g* value calibration. Double integration of the individual EPR signals provided rough estimates of the respective number of spins.

Results

In previous FTIR studies in our own laboratory¹¹ different reaction channels for the chemisorption of H₂ on nanostructured MgO had been observed. The heterolytic splitting of H₂, giving rise to an OH stretching band at 3462 cm⁻¹ and a MgH stretching band at 1325 cm⁻¹, was confirmed [Fig. 1(c)]. This is an equilibrium process which leads to significant

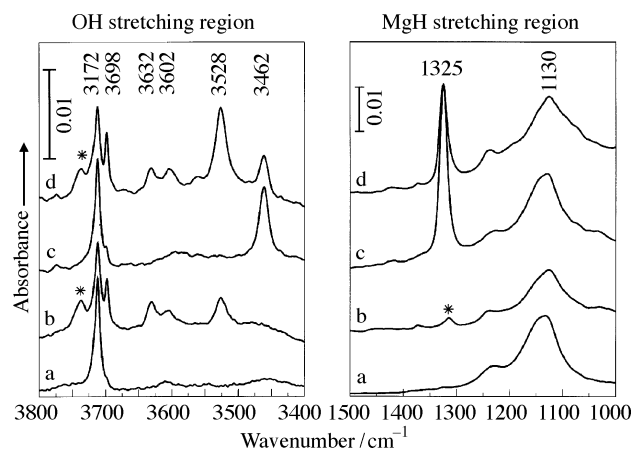
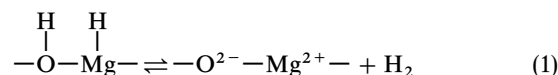


Fig. 1 IR study of H₂ chemisorption and UV induced colour centre formation on MgO in the presence of H₂: (a) 1 mbar; (b) 1 mbar, after UV irradiation under 1 mbar; (c) 100 mbar; (d) 100 mbar, after UV irradiation under 100 mbar. (* Designates impurity induced bands originating from surface reactions of traces of H₂O and CO₂.)

band intensities at room temperature and 100 mbar H₂ pressure. The value of the OH stretching frequency clearly indicates the presence of hydrogen bonded OH groups. On the other hand, the band width is unusually small for H bonded OH groups, reflecting the rigidity of the MgO surface framework in which the proton donor and the proton acceptor are incorporated. At 1 mbar H₂ both bands have essentially vanished from the spectrum. Under these conditions a sharp band at 3712 cm⁻¹ [$\nu(\text{OH})$] and a broad one at about 1130 cm⁻¹ [$\nu(\text{MgH})$] [Fig. 1(a)] remain. The intensities of both depend only slightly on the H₂ pressure between 1 and 100 mbar [Fig. 1(c)]. They have previously been attributed to the products of two different homolytic H₂ splitting mechanisms.¹¹ The respective reaction centres (*i.e.*, O⁻ and Mg⁺) should exhibit paramagnetic properties. In fact, recent EPR studies of the thermally activated MgO samples did not provide any evidence for this. In addition, detailed IR studies clearly show that continuous pumping on the sample at room temperature after H₂ chemisorption initiates a linearly correlated intensity decrease of the two bands at 3712 and 1130 cm⁻¹ (Fig. 2) indicating the desorption reaction given in eqn. (1) as a likely mechanism.



Consequently the reverse reaction—heterolytic H₂ splitting—should explain the appearance of the bands at 3712 and 1130 cm⁻¹. Thus, there are two different reactive centres on the surface of the nanostructured MgO material, confirming the findings of Coluccia *et al.*²⁴ for ex hydroxide material. They give rise to two different surface complexes ($\nu(\text{OH}) = 3712$ cm⁻¹, $\nu(\text{MgH}) = 1130$ cm⁻¹ and $\nu(\text{OH}) = 3462$ cm⁻¹, $\nu(\text{MgH}) = 1325$ cm⁻¹) which will be referred to in this paper as surface complex I (“irreversible”) and II (“reversible”), respectively. In a slower secondary reaction—slower with respect to H₂ chemisorption—a small fraction of the MgH groups of the surface complex II (1325 cm⁻¹) lose the hydrogen in favour of the formation of an isolated OH group which exhibits a band at 3698 cm⁻¹ [Fig. 1(c)]. The thermal desorption process of chemisorption complex I at room temperature is considerably reinforced by UV irradiation ($\lambda > 200$ nm, Fig. 2).

In the presence of H₂ gas, UV irradiation of the MgO sample initiates additional changes in the IR spectrum [Figs. 1(b) and 1(d)]. The band at 3698 cm⁻¹ grows out and three new bands at 3632, 3602 and 3528 cm⁻¹ appear. The band positions of the latter three exclude their assignment to free isolated OH groups and suggest that H bond like interactions are effective [Figs. 1(b) and 1(d)] as in the case of the feature at

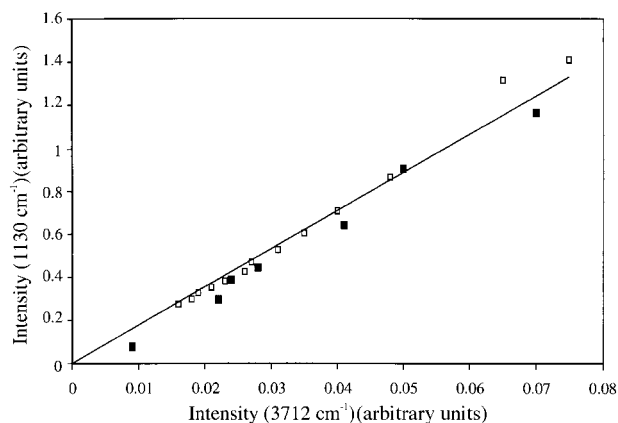
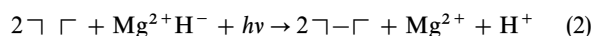


Fig. 2 Correlation of the integral intensities of the bands at 3712 and 1130 cm^{-1} (Fig. 1) after pumping in the dark (\square) and under UV irradiation (\blacksquare).

3462 cm^{-1} [see above, Fig. 1(c)]. UV irradiation ($\lambda > 200 \text{ nm}$) under a hydrogen pressure of 100 mbar gives rise to a loss of intensity for all those bands which are related to the two types of heterolytic H_2 splitting [3462 and 1325 cm^{-1} /3712 and 1130 cm^{-1} , Fig. 1(d)]. In the corresponding experiment at 1 mbar H_2 [Fig. 1(b)] a similar trend is observed for complex I only, since complex II is not present under the given experimental conditions. The three features at 3632, 3602 and—in particular—3528 cm^{-1} exhibit significantly altered relative intensities compared with the 100 mbar experiment [Fig. 1(d)]. A more detailed examination of the broad band at 1130 cm^{-1} reveals that it consists of two subbands. The addition of O_2 [Fig. 4(b) and 4(c) below] and UV irradiation initiate a preferential depletion of the higher frequency feature with its centre at 1145 cm^{-1} as compared with the low frequency component (1125–1130 cm^{-1}). This finding probably corresponds to the recent observation of Giamello *et al.*¹⁶ that the deuteride band at 820 cm^{-1} of an ex hydroxide sample is slightly shifted to lower frequencies after UV irradiation in the presence of D_2 .

A general feature of the IR spectra of nanostructured MgO exposed to UV irradiation in the presence of H_2 is a continuous absorption background which augments from small to large wavenumbers (not seen in Fig. 1 because of the limited spectral intervals) and finally extends into the visible region: the MgO sample undergoes a colour change from white to blue. Obviously the simultaneous exposition to H_2 gas and UV light does not only alter the vibrational, but also the electronic properties of the oxide surface. The respective electron excitation is related to the presence of surface colour centres,^{5,16–18,25} which were formed by the reaction of surface anion vacancies with electrons provided by MgH groups:



Under the experimental conditions applied in the IR experiments presented in Fig. 1(b) and 1(d) (1 and 100 mbar H_2 , respectively, UV) the nanostructured MgO exhibits EPR signals which have to be attributed to surface colour centres $\text{F}_s^+(\text{H})$,^{5,16–18} Obviously the signal intensity related to these $\text{F}_s^+(\text{H})$ centres increases when the H_2 pressure is raised from 1 to 100 mbar, indicating that the number of spins is augmented by a factor 3 to 5 (Fig. 3). There is, however, no major change in the shape of the signal. The colour centre formation occurs parallel to the consumption of hydride groups observed by IR spectroscopy. Evidently the two “hydride families” (1325 cm^{-1} and at 1145/1125 cm^{-1}) contribute in a qualitatively similar form, but to a quantitatively different extent to colour centre formation. The structure of the signal indicates that there is a dipolar magnetic interaction between

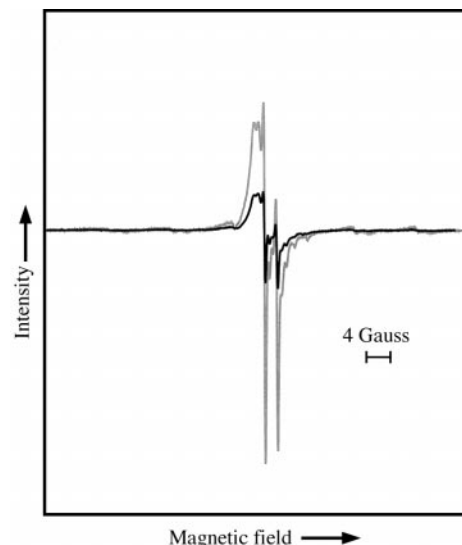


Fig. 3 EPR spectra of the $\text{F}_s^+(\text{H})$ centres created by irradiation of MgO in the presence of 1 mbar H_2 (dark curve) and 100 mbar H_2 (light curve).

the electron spin density of the colour centre and the nuclear moment of a nearby hydroxy proton.^{5,16–18} This gives rise to the so-called superhyperfine splitting of the axially symmetric colour centre signal. The proximity of a proton and a surface colour centre should be reflected by the frequency of the respective surface OH group. In fact, the previously mentioned OH stretching bands at 3632, 3602 and 3528 cm^{-1} [Fig. 1(b) and 1(d)] exhibit positions considerably below those of isolated surface OH groups ($> 3712 \text{ cm}^{-1}$). Both types of spectral features related to the interaction between colour centre electron and the OH proton—the H bond affected IR bands between 3632 and 3528 cm^{-1} and the superhyperfine splitting of the colour centre EPR signal—are not altered by the application of vacuum to the MgO sample.

As has previously been shown the different surface hydride groups sensitively react with molecular oxygen.^{9–11,14,16,26} To facilitate the situation, the less stable (“reversible”) surface species (1325 cm^{-1}) is completely removed by the application of vacuum [Fig. 4(a) and 4(b)]. The subsequent admission of 20 mbar O_2 mainly reduces the intensity at 1145 cm^{-1} [Fig. 4(c)]. The loss of hydride band intensity is accompanied by the appearance of a broad and unspecific OH absorption pattern between 3650 and 3450 cm^{-1} which has to be attributed to surface OH groups with hydrogen bonds between

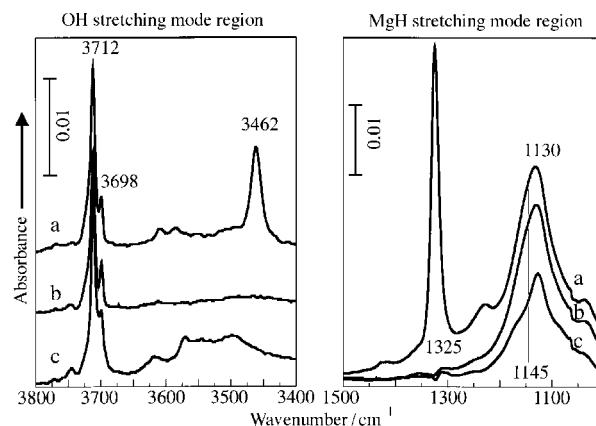


Fig. 4 IR study of the interaction of O_2 with H_2 chemisorption complex I on MgO: (a) admission of 100 mbar H_2 , (b) subsequent evacuation and (c) admission of 20 mbar.

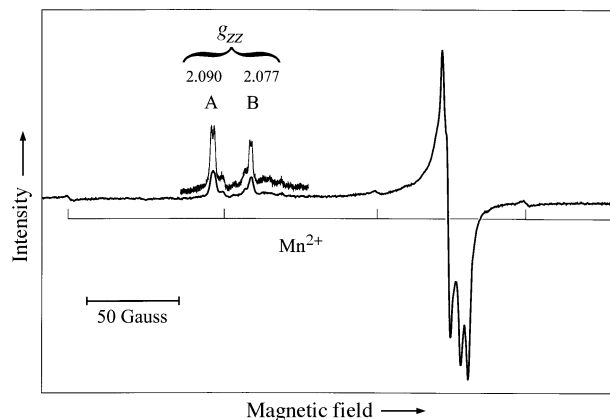
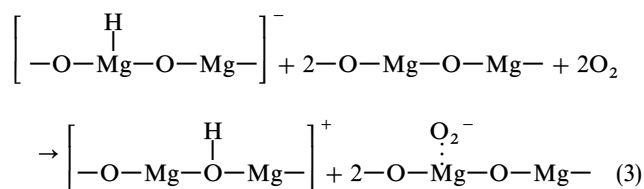


Fig. 5 EPR study of the interaction of O_2 with H_2 chemisorption complex I on MgO (corresponds to curve c in Fig. 4). The high field region of the spectrum was additionally recorded with a lower modulation amplitude to improve the resolution.

them [Fig. 4(c)]. These observations were consistently interpreted in terms of an oxidation of the respective surface MgH hydrogen.^{9,10,14,15} The oxidizing agent O_2 is reduced at the same time to the superoxide anion O_2^- which is then complexed by surface cations [eqn. (3)].²⁰



As O_2^- is paramagnetic its formation may be evidenced by EPR studies (Fig. 5). The respective EPR spectrum consists of three principal values of the g matrix, reflecting the orthorhombic symmetry of the spin centre. While the values for g_{xx} and g_{yy} components do not sensitively depend on the coordination state of the complexing cation, the value of the g_{zz} component is strongly influenced by the local crystal field around the respective surface cation,²⁷ and is described by eqn. (4).

$$g_{zz} = g_e + \frac{2\lambda_c}{\Delta} \quad (4)$$

The energy separation Δ between the two π_g orbitals of the oxygen molecule ion is induced by the electric field of the cation (lifting of degeneracy). The terms λ_c and g_e stand for the spin-orbit coupling constant and the free spin value, respectively. The z direction for this spin system is conventionally taken as parallel to the interatomic axis.

Under the conditions of the IR experiment presented in Fig. 4, essentially two species with differing g_{zz} values (Fig. 5, Table 1) were observed which have to be attributed to O_2^- species complexed by two differently coordinated surface cations. In both cases a discrete dipolar interaction of the spin centre with a nearby proton occurs. It gives rise to a splitting of all g component lines into doublets (Table 1). The principal values

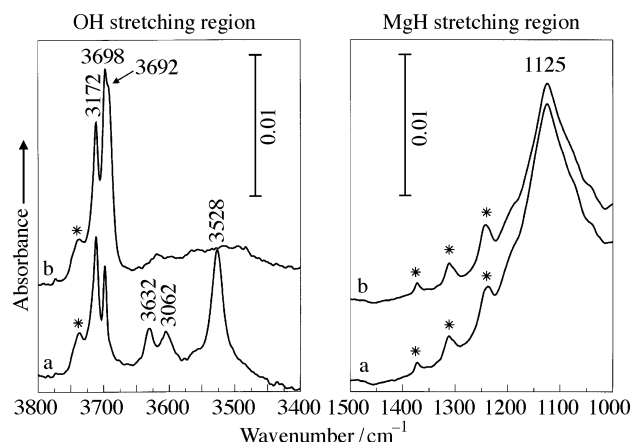
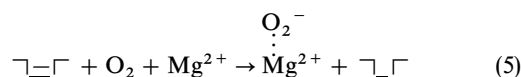


Fig. 6 FTIR study of the bleaching process of surface colour centres on MgO (produced by UV irradiation in the presence of 100 mbar H_2) with O_2 (a) MgO + 100 mbar H_2 + UV, then evacuation; (b) as (a) and then 20 mbar O_2 . (* Designates impurity induced bands originating from surface reactions of traces of H_2O and CO_2 .)

of the superhyperfine parameter matrix of one of the species observed (designated B) are in good agreement with literature data.²⁸

Another well-known reaction that provides superoxide anions on MgO surfaces²⁹ is based on the electron transfer from surface colour centres to molecular oxygen ("bleaching" of colour centres):



This process was monitored by FTIR spectroscopy on a nanostructured MgO sample (Fig. 6). The initial state of the surface [Fig. 6(a)] resulted from UV irradiation of the MgO sample in the presence of 100 mbar H_2 and subsequent evacuation. The admission of O_2 [Fig. 6(b)] removes the three relatively sharp OH bands related to the colour centre formation and replaces them by a broad and unspecific absorption in the same spectral interval. Its contour strongly resembles the one observed during the reaction of surface hydride groups with O_2 [Fig. 4(c)]. Obviously the formation of an effective network of H bonded surface OH groups took place after the access of O_2 . In addition, at 3692 cm^{-1} a new surface OH band appears which indicates a weak interaction of previously free (non H bonded) surface OH groups with a surface complexed O_2^- .¹¹ The stretching vibration of the complexed O_2^- species has so far not been seen in the IR. It is expected to be weakly IR active if at all. The EPR spectrum unambiguously evidences the presence of several O_2^- species on the surface (Fig. 7). Two types of major abundance have g_{zz} values of 2.077 and 2.090. The comparison with those in Fig. 5 and Table 1 shows that the same O_2^- surface species (same g and same a value matrices) are created in the two completely different reactions (O_2 "bleaching" of colour centres and reaction of oxygen with hydrides). Furthermore two considerably weaker components with g_{zz} values at 2.083 and 2.064 are observed [Fig. 7(b)].

The H_2 pressure during the process of colour centre formation has a dramatic influence on the relative intensities of the two relevant g_{zz} components (Fig. 7) observed after the

Table 1 Principal values of the g matrix and the superhyperfine coupling matrix for superoxide anion species designated as A and B

Species	g_{xx}	a_{xx}/Gauss	g_{yy}	a_{yy}/Gauss	g_{zz}	a_{zz}/Gauss
A	2.0019	5.10	2.0085	2.97	2.0901	1.40
B	2.0017	3.76	2.0086	2.06	2.0769	1.10

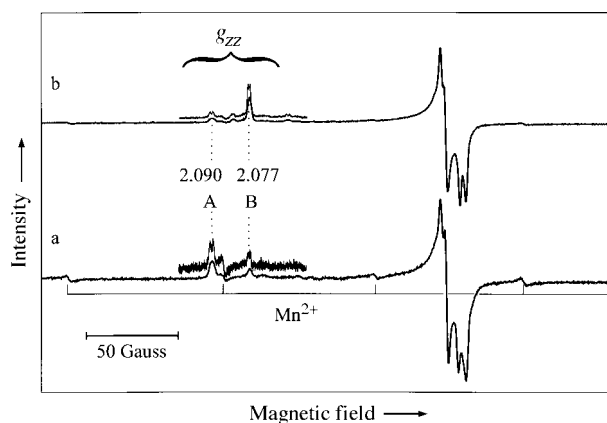


Fig. 7 EPR study of the bleaching process described in Fig. 6 for (a) 1 mbar H_2 , (b) 100 mbar H_2 during the preceding colour centre formation. The ordinate scale of curve b is compressed by a factor of 0.2 compared to that of curve a. In either case the high field region of the spectrum was additionally recorded with a lower modulation amplitude to improve the resolution.

“bleaching” with O_2 : for 1 mbar H_2 the component at 2.090 (superoxide species type A, Table 1) exhibits higher intensity and for 100 mbar H_2 the component at 2.077 (superoxide species B, Table 1) is clearly dominant (Fig. 7). A saturation as for species A has not been observed.

The process of surface colour centre “bleaching” may also be monitored by a series of fascinating IR experiments which are presented in Fig. 8 in the form of difference spectra (absorbance spectrum after addition of O_2 minus absorbance spectrum before O_2 addition). The parameter is the H_2 pressure, which is varied from 0.5 to 100 mbar H_2 . There are clear correlations between the intensity variations of the negative OH stretching bands (3632, 3602 and 3528 cm^{-1}) attributed to OH groups “H bonded” to the colour centre electrons and the intensity variations of the positive OH bands (3702 and 3692 cm^{-1}) attributed to originally free OH groups which are weakly interacting with the O_2^- species attached to cations (see also Fig. 6). Obviously, before and after colour centre “bleaching” there are two sets of surface OH populations, one approaching saturation already at 1 mbar H_2 or even less (3632 and 3602 cm^{-1} /3702 cm^{-1}) and another one which still grows at 100 mbar H_2 and more (3528 cm^{-1} /3692 cm^{-1}).

Discussion

Heterolytic H_2 splitting

The IR spectra in Fig. 1 clearly show that H_2 chemisorption at room temperature occurs essentially in two strongly differing reaction channels, I and II. Both provide, exclusively, pairs of isolated surface OH and MgH groups as the product of heterolytic H_2 splitting. The desorption of the chemisorption complexes of type II at room temperature occurs instantaneously. The correlation between the integrated absorbance values of the OH and MgH groups of type II during a com-

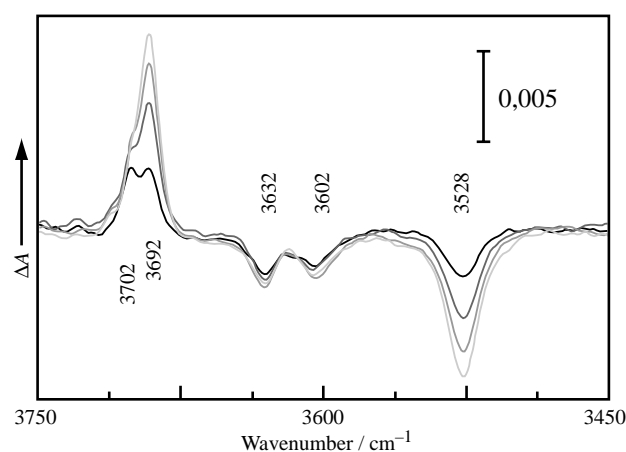


Fig. 8 IR difference spectra obtained by subtracting the trace recorded before colour centre bleaching by O_2 from those recorded afterwards. The H_2 pressure during colour centre formation varies from 0.5 (black curve) to 100 mbar (light curve) (0.5, 10, 50 and 100 mbar H_2).

plete adsorption–desorption cycle (1–100 mbar) was reliably demonstrated.¹¹ Obviously this reaction is a fully “reversible” 1 : 1 process with respect to the products [eqn. (1)]. On the other hand, below 1 mbar H_2 the desorption of the respective surface complexes at room temperature requires hours and, therefore, the chemisorption complex type I is designated here as “irreversible”. Thus, to recognize a correlation between the respective product bands or not, only the desorption mode may be exploited with a justifiable experimental effort. The result (Fig. 2) is, however, indisputable: on applying a vacuum to the MgO sample previously exposed to more than 1 mbar H_2 the bands at 3712 and 1130 cm^{-1} lose intensity very slowly (time scale of hours), but at the same rate. Thus, the depletion of the two surface products of type I, and—most likely—also their formation, appears to be a 1 : 1 process as in the case of chemisorption type II [eqn. (1)].

In Table 2 the IR spectroscopic properties of the surface complexes emerging from H_2 chemisorption as well as the most important process characteristics are presented. Obviously, at room temperature, the surface complexes of type I are considerably more stable (“irreversible”) than those of type II (“reversible”). Their surface concentration is, however, limited. At a H_2 pressure of 1 mbar, saturation of the surface with type I already becomes effective. Under these conditions the surface complexes of chemisorption type II are not yet detectable. On the other hand a saturation effect has never been observed for type II. Even at 500 mbar H_2 the respective absorbance values still grow with H_2 pressure. An estimation of the relative concentrations of the two types of surface complexes from the integrated absorbance values is not possible since the absorbance coefficients of the vibrational transitions for MgH and OH are not known and are most likely (OH!) strongly dependent on the local surface structure.

Table 2 Heterolytic H_2 chemisorption on nanostructured MgO at room temperature

Type of H_2 chemisorption	Surface products	Band positions/ cm^{-1}	Process characteristics
I	isolated free OH	$\nu(OH) = 3712$	saturation for $p(H_2) = 1$ mbar irreversible
I	bridged MgH	$\nu(MgH) = 1130$	saturation for $p(H_2) = 1$ mbar irreversible
II	isolated “H bonded” OH	$\nu(OH) = 3462$	no saturation reversible
II	isolated MgH	$\nu(MgH) = 1325$	no saturation reversible

According to the IR spectroscopic data (Figs. 1 and 2) at room temperature, exclusively heterolytic H_2 splitting may occur. Parallel or consecutive radical reactions appear to be unlikely under the experimental conditions applied since EPR spectroscopy does not provide any evidence for the presence of significant amounts of paramagnetic surface species in the course of the reaction.

Surface colour centre formation

UV irradiation of MgO exposed to H_2 gas gives rise to the formation of surface colour centres which are EPR active if they contain an unpaired electron. An analysis of the signal provides two important messages. (a) There is one type of surface colour centre that contributes predominantly to the signal observed. (b) A superhyperfine coupling of the axially symmetric $F_s^+(H)$ signal^{5,16–18} indicates that there is a dipolar magnetic interaction between the colour centre electron and one proton of a nearby OH group. Only recently, the electronic interaction between the surface colour centre and the OH group was evidenced by IR spectroscopy *via* the OH stretching frequency which is shifted to values typical for H bonded OH groups.¹⁶

The EPR signal obtained in the present investigation on CVD MgO (Fig. 3) exhibits essentially the same characteristics as the one related to ex hydroxide sample.^{5,16–18} On increasing the H_2 pressure during UV irradiation from 1 to 100 mbar, the number of paramagnetic centres is raised by a factor of about 3–5. This result has to be looked at more closely under the auspices of the H_2 pressure dependence of the H_2 chemisorption which was monitored by IR spectroscopy (Table 2). At 1 mbar, only surface complex I exhibits saturation (Fig. 1, compare curves a, for 1 mbar, and c, for 100 mbar). If the MgO sample exposed to 100 mbar H_2 is subjected to rapid evacuation the IR spectrum is nearly identical to the one recorded in the presence of 1 mbar: chemisorption complex I (“irreversible”) is essentially unaffected while complex II (“reversible”) vanishes instantaneously. After UV irradiation of the evacuated sample both the IR and the EPR spectra (not shown here) are identical to the respective traces in Fig. 1 (curve b) and Fig. 3, which were obtained after UV irradiation in the presence of 1 mbar H_2 . This clearly evidences that the reducing agent in the process of colour centre formation is the MgH group.

The UV irradiation reduces the intensity of the MgH band at 1130 cm^{-1} significantly. What happens with the respective hydrogen? The intensity loss of the MgH band at 1130 cm^{-1} (“irreversible” chemisorption complex I) is accompanied by the appearance of the three OH stretching bands at 3632, 3602 and 3528 cm^{-1} . Their positions reveal that these OH groups are subjected to a significant electronic interaction, comparable to that in H bonds. On the other hand they are perfectly isolated from each other. Otherwise the H_2 pressure dependence in this spectral interval should be markedly different from that in Fig. 8. From an analysis of the EPR signal (Fig. 3) we know that there is one and only one OH group in the immediate environment of the surface colour centre. As there is a second OH group emerging in the course of colour centre formation [eqn. (2)], at this stage the assignment of the three bands at 3632, 3602 and 3528 cm^{-1} is not possible. It will be given below.

On raising the H_2 pressure applied during the UV irradiation from 1 to 100 mbar one and the same EPR colour centre signal gains intensity (Fig. 3). In the IR spectrum two out of the three “new” OH bands (3632 and 3602 cm^{-1}) undergo only minor intensity changes, the third one, at 3528 cm^{-1} , exhibits a considerable intensity increase [Fig. 1(b) and 1(d), Fig. 8]. This nicely relates to the process properties of chemisorption type I and II (Table 2). Type I is saturation limited already at 1 mbar H_2 and, therefore, provides a saturation

limited number of the OH groups absorbing at 3632 and 3602 cm^{-1} . Type II is not saturation limited and, therefore, at higher H_2 pressures there is a correspondingly higher contribution of OH groups absorbing at 3528 cm^{-1} . None of the three OH bands exhibits an intensity decrease in the course of UV activation. A consumption of paramagnetic surface colour centres $F_s^+(H)$ in favour of the formation of the diamagnetic ones, $F_s^0(H)$, may, therefore, be excluded under the experimental conditions applied.

If the interaction between the surface colour centre and differently spaced or oriented OH groups may be discriminated by IR spectroscopy, one would expect this to be possible also by EPR spectroscopy. Obviously the magnetic interaction reflected by the superhyperfine coupling is considerably less sensitive to variations of spatial parameters than the electronic interactions between an OH proton and a surface colour centre electron (“hydrogen bonding”!). The EPR spectrum exhibits one set of superhyperfine coupling constants.

For the sake of completeness further UV induced phenomena observed on CVD MgO should be briefly mentioned here although they do not interfere with the general line of argument followed in this paper.

(a) The UV induced reverse reaction of chemisorption type I [$\nu(OH) = 3712\text{ cm}^{-1}$, $\nu(MgH) = 1130\text{ cm}^{-1}$] is much more efficient than the competing surface colour centre formation. This is shown in Fig. 2, where the linear correlation in the UV induced depletion of the respective OH and MgH bands in the vacuum is presented.

(b) There are, so far, unspecified oxygen anion sites on MgO surfaces which at room temperature and, in the dark, are considerably less reactive with H_2 . One of these is likely to be associated with the OH stretching band at 3698 cm^{-1} . It appears during UV irradiation and might be related to short-lived O^- radicals which homolytically split H_2 .³⁰

Reactions of O_2 with surface hydride groups and surface colour centres

It has previously been reported that both surface hydride groups^{9–11,15,16} and surface colour centres,^{29,31} on highly dispersed MgO react with molecular oxygen. In agreement with the structure of the previous section, a detailed discussion of hydride consumption and colour centre bleaching will be presented here with particular attention being paid to the dependence of these processes on the H_2 pressure applied during hydride and colour centre formation.

The reaction of the “irreversibly” formed MgH groups (chemisorption type I) with O_2 according to eqn. (3) is unambiguously evidenced by IR (Fig. 4) and EPR spectroscopy (Fig. 5). The IR band at 1130 cm^{-1} , representing the respective surface hydride groups as educts, loses intensity after admission of O_2 (Fig. 4). It obviously consists of two constituents, at 1145 and 1125 cm^{-1} , which are depleted by O_2 to a different extent. On the same time scale the growth of the EPR spectrum originating from superoxide anions complexed by surface cations as products is observed (Fig. 5). Thus, under the given experimental conditions, stated in the legend of Fig. 4 (curve b and c), there are, exclusively, MgH groups related to chemisorption type I that act as electron donor in eqn. (3). The relative abundance of the resulting superoxide anion species A and B (Table 1) obtained by simulation exhibits a ratio of 2 : 1.

The EPR spectra obtained after the reaction of hydride groups related to chemisorption type I (“irreversible”) with O_2 (Fig. 5) are essentially identical to those obtained after the reaction of surface colour centres with O_2 (Fig. 7, curve a), provided the H_2 pressure during colour centre formation [eqn. (2), Fig. 3] did not exceed 1 mbar. Thus, the two EPR spectra [Fig. 5 and 7(a)] describe two completely different reactions that start from the same educt, namely the hydride

groups related to chemisorption type I, and end up with the same products, namely the superoxide anions complexed by differently coordinated surface cations. This suggests that for both reaction types the cations incorporated in the educts and products are constituents of the anion vacancy framework which is required for surface colour centre formation [eqn. (2)]. The suggestion that anion vacancies and MgO surface sites which are reactive with respect to H_2 splitting are “*not two worlds apart*” was brought forward only recently.¹⁶

The OH groups involved as one of the products in the redox reaction described above [eqn. (2)] are subject to diverse interactions on the surface. There is a dipolar magnetic coupling between the unpaired O_2^- electron and the proton of a so far unspecified nearby OH group emerging either from H_2 chemisorption [eqn. (1)] or from the redox reaction [eqn. (2)]. The resulting sets of superhyperfine coupling constants for the two different superoxide anion complexes (Table 1, Fig. 5) are also different. The evidence for the electronic interaction between the superoxide anion and an isolated nearby OH group is provided by the IR difference spectrum (Fig. 8). The two sharp bands at 3702 and 3692 cm^{-1} have to be attributed to the OH groups interacting with type A and B (Table 1), respectively. The broad and unspecific background [Fig. 4(c)] between 3650 and 3400 cm^{-1} originates from H bonding between neighbouring OH groups.

An independent study of the redox reaction in which the hydride of chemisorption complex II acts as electron donor is not possible. The availability of a significant amount of surface hydride groups, giving rise to the MgH band at 1325 cm^{-1} , necessarily implies the presence of H_2 at a pressure considerably above 1 mbar. If the MgO surface is exposed simultaneously to H_2 and O_2 more complicated surface reactions occur which do not contribute to the envisaged issue of this paper. They will be the subject of a future investigation.

As pointed out previously the two types of hydride groups contribute qualitatively in the same form to surface colour centre formation. There are, however, quantitative differences. At 100 mbar H_2 considerably more surface colour centres originate (Fig. 3) from the “reversible” hydride groups [$\nu(MgH) = 1325\text{ cm}^{-1}$ in Fig. 1] than from the “irreversible” ones [$\nu(MgH) = 1130\text{ cm}^{-1}$]. Consequently, the total yield of superoxide anions formed after bleaching this larger quantity

of colour centres is also considerably higher. The ratio for the relative abundance of the two species A and B (Table 1) is now reversed as compared with the 1 mbar H_2 experiment (Fig. 7). The species B is, by nearly an order of magnitude, more abundant than species A, which exhibits essentially the same intensity as in the 1 mbar H_2 experiment.

The consumption of surface colour centres by O_2 and the simultaneously occurring formation of complexed superoxide anions may—even though indirectly—be monitored also by IR spectroscopy (Fig. 8). The difference spectra with the H_2 pressure during colour centre formation as parameter clearly show the correlation between the colour centre consumption and superoxide anion formation (Fig. 8). The saturation criterion permits one to identify two different reaction paths: the two types of OH groups subjected to strong H bonds of different strength with surface colour centres (3632/3602 cm^{-1} and 3528 cm^{-1}) are transformed in the course of two independent reactions into OH groups that interact with superoxide anion type A [$\nu(OH) = 3702\text{ cm}^{-1}$] and superoxide anion type B [$\nu(OH) = 3692\text{ cm}^{-1}$]. The two product bands (3702 and 3692 cm^{-1}) exhibit positions which are very close to isolated free-OH groups produced in the course of chemisorption type I.

From H_2 chemisorption to superoxide anion formation

As mentioned previously (see Introduction) only a few types of reactive surface sites are expected on CVD MgO which was subjected to an appropriate thermal treatment. Obviously, type I is available only in a limited quantity and gives rise to the irreversible heterolytic splitting of H_2 (IR: 1130 and 3712 cm^{-1}). It is related to saturation phenomena which are repeatedly observed while we travel along the chemical path which starts with chemisorption of H_2 on MgO, passes through subsequent surface colour centre formation and finally ends up with the formation of superoxide anions (Fig. 9). As soon as the H_2 pressure is sufficiently high to permit the surface reaction centres II (IR: 3462 and 1325 cm^{-1}) to enter the reactive game, the respective IR and EPR signals grow—under the given experimental conditions—unlimitedly. At 100 mbar H_2 type II is much more abundant than type I. This follows from the respective contributions of the two types of

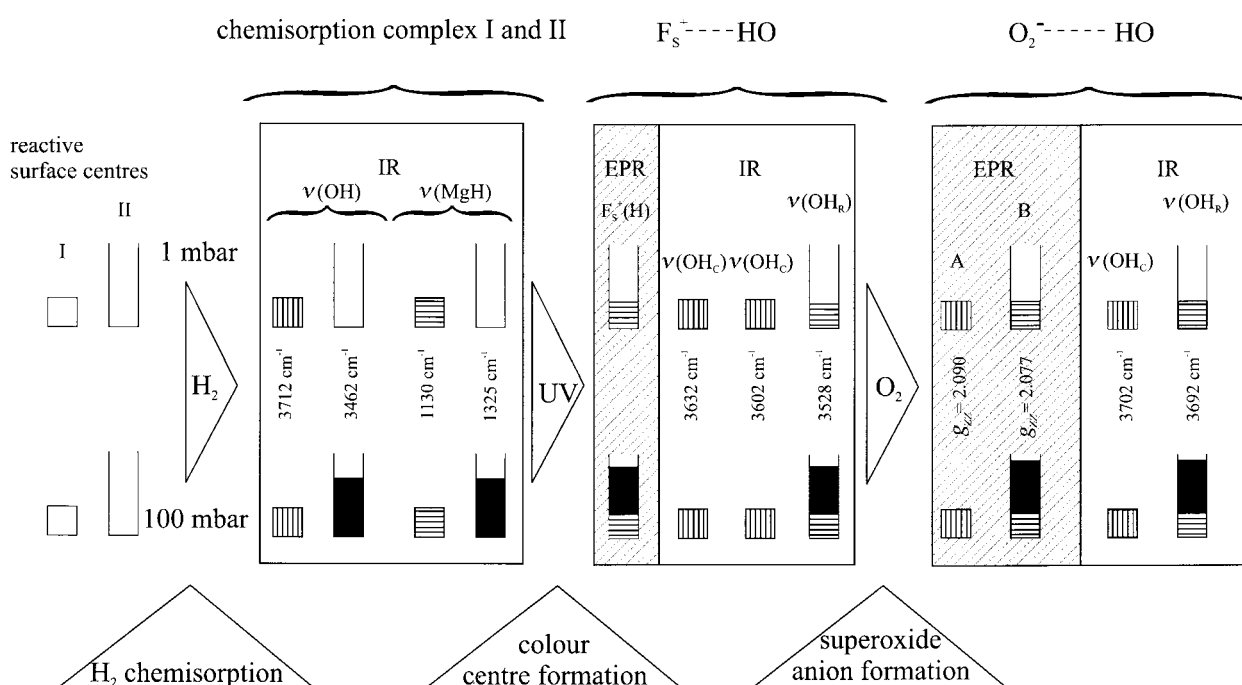


Fig. 9 Schematic representation of the consecutive changes in the IR and EPR spectra by H_2 admission to MgO, UV irradiation and O_2 admission.

hydrides to the colour centre formation as mentioned in relation to Fig. 3. On travelling from left to right in Fig. 9 saturation phenomena do not appear in the reaction steps which involve species of type II. Conversely, all products in the reaction scheme of Fig. 9 which are exclusively related to the surface reaction centre I are clearly saturation limited (compare the bar diagrams for 1 and 100 mbar H_2). This is true for (i) the OH_C group (index C for chemisorption) absorbing at 3712 cm^{-1} (vertical hatching) and the MgH group absorbing at 1130 cm^{-1} (horizontal hatching) belonging to chemisorption type I; and (ii) the OH_C group interacting with the colour centre absorbing at 3632 and 3602 cm^{-1} . The superoxide anion complex A with $g_{zz} = 2.090$; (iii) the OH_C group which interacts with the superoxide anion A and absorbs at 3702 cm^{-1} .

In principle, there is no experimental evidence favouring a specific structure of the anion vacancy involved in surface colour centre formation. Anion vacancies in (100) planes are certainly not stable enough to survive a thermal treatment of CVD MgO at 1173 K . Thus, in the simple surface model applied (see Introduction) anion vacancies on edges and corners should remain in any discussion. Our EPR data do not, so far, allow us to discriminate such species. It shows, however, that there are two distinguishable superoxide anion/surface cation complexes (A and B) which have to be located within the geometry of surface anion vacancies since they are formed there in the UV induced process and in the dark reaction. At this point we speculate that the two different superoxide anion surface complexes could be related to two different surface anion vacancies. The two different sets of superhyperfine coupling constants (Table 1) induced by nearby hydroxy protons would support this assumption. The presence of two different types of colour centres has also been claimed on the basis of a combined EPR/ENDOR study on high temperature activated MgO.¹⁸

The IR data on the hydroxy groups available from Fig. 8 provide even more conclusive evidence: there are two OH groups which are weakly interacting with superoxide anions. They give rise to a band related to the saturation effect (3702 cm^{-1}) and another one which grows without limit with the H_2 pressure applied during the preceding colour centre formation (3692 cm^{-1}). Therefore, the history of these OH groups may be traced back to the two H_2 chemisorption complexes I and II (Fig. 9). The saturation effect observed for the bands at 3632 and 3602 cm^{-1} may then be interpreted in the following way: one of the two types of anion vacancies is limited in number and chemisorption type I occurs precisely there, *i.e.*, the respective cation is a constituent of this vacancy. The OH group resulting from chemisorption type I—after colour centre formation—directly interacts with the colour centre electron. The chemisorption type II occurs more or less remote from any anion vacancy. In the opposite case the original OH stretching band at 3462 cm^{-1} should reappear on destroying the colour centre by O_2^- formation. Therefore, the respective OH group cannot interact with the electron of any type of colour centre. However, the hydride group of chemisorption type II certainly receives sufficient energy in the course of UV irradiation that it may provide an H atom to a remote anion vacancy which thus transforms into a colour centre, strongly interacting with the newly formed and closely spaced OH_R group (3528 cm^{-1} , index R for redox reaction). If the second type of surface colour centre is sufficiently abundant the described process may go on as long as hydride groups are available on the surface (no saturation in the present case). This is evidenced by the intensities of (i) the EPR signals of the colour centres (Fig. 3); (ii) the OH_R band at 3528 cm^{-1} (Fig. 8); (iii) the superoxide anion signal for complex B with $g_{zz} = 2.077$ (Figs. 5 and 7); and (iv) the band related to the OH_R group which interacts with the superoxide anion B and absorbs at 3692 cm^{-1} (Fig. 8).

Conclusions

The H_2 chemisorption and the UV induced consecutive surface reactions on MgO involve both low coordinated ion pairs and anion vacancies, respectively, but still they have been dealt with in the past as if the corresponding two sets of surface area elements did not exhibit an intersection (Fig. 10 upper half). Only recently have Giamello *et al.* suggested the opposite approach as being more adequate.¹⁶

In fact, the present investigation unambiguously evidenced that the intersection (hatched area in Fig. 10, lower half) may not be neglected. On the contrary, it is related to a very specific surface chemistry which incorporates low coordinated cation sites as constituents of the anion vacancy geometry. They are clearly multifunctional and give rise to hydride formation in the course of heterolytic H_2 splitting, colour centre formation and complexation of superoxide anions in one and the same surface area element. Obviously there is a considerably larger quantity of surface hydride groups emerging from H_2 chemisorption, which occurs more or less remote from surface anion vacancies (non-hatched area of the left circle in Fig. 10, lower half). They are, however, not excluded from the colour centre formation. Evidently UV activation provides sufficient energy to transfer an electron of the hydride group to a not too distant anion vacancy. The remaining uncharged H atom is then likely to diffuse to a remote anion vacancy and to leave a second electron there. The proton forms an adjacent OH group. This process of colour centre formation appears to be the dominant one. Both surface colour centres and hydride groups incorporated into anion vacancies (shaded area in Fig. 10) may react with O_2 to form O_2^- anions. They are complexed exclusively by cationic constituents of the anion vacancies, *i.e.*, they are complexed where they are formed.

The fascination of the present study is intimately related to the unbroken chain of IR and/or EPR spectroscopic evidences on the reaction path from the H_2 chemisorption to the formation of surface colour centres and superoxide anion surface complexes. In the course of these reactions OH groups, originating from chemisorption (C) and redox reactions (R), play an important role as observer. Their electronic interaction with the colour centre electron and with the superoxide anion is seen by IR spectroscopy (Figs. 1, 4 and 8), whereas their magnetic interaction is reflected by superhyperfine splitting in the EPR spectra (Figs. 3, 5 and 7).

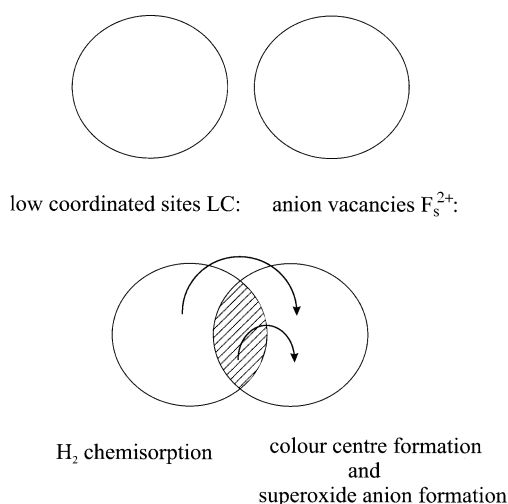


Fig. 10 Schematic representation of surface defects on MgO particles. The hatched area indicates the presence of low coordinated sites incorporated in anion vacancies and their characteristic reactive properties. The arrows visualize the possibility of reactive interplay even between remote partners.

The whole study was enormously facilitated by the comparatively high surface concentrations of low coordinated sites and anion vacancies guaranteed by CVD which we applied to the production of MgO nanoparticles. From preliminary investigations we know that these sites are also likely to be involved in the chemisorption of CH₄ and consecutive reactions in the presence of O₂ and appropriately selected UV quanta. This opens up interesting prospects for the application of nanostructured MgO in the oxidative coupling of methane (OCM) and methane activation in general.

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References

- 1 E. A. Colbourn and W. C. Mackrodt, *Surf. Sci.*, 1982, **117**, 571.
- 2 A. L. Shluger, J. D. Gale and C. R. A. Catlow, *J. Phys. Chem.*, 1992, **96**, 10389.
- 3 E. Garrone, A. Zechina and F. S. Stone, *Philos. Mag. B*, 1980, **42**, 683.
- 4 S. Coluccia and A. J. Tench, in *Proceedings of the 7th International Congress on Catalysis*, Tokyo, 1980, ed. T. Seyama and K. Tanabe, Kodansha, Tokyo, 1981, Part B, 1154.
- 5 A. J. Tench and R. L. Nelson, *J. Colloid Interface Sci.*, 1968, **26**, 364.
- 6 M. C. Wu, C. M. Truong, K. Coulter and D. W. Goodman, *J. Am. Chem. Soc.*, 1992, **114**, 7565.
- 7 S. Benfer, P. Hofman and E. Knözinger, *J. Mol. Struct.* 1997, **410–411**, 115.
- 8 M. Giersig, P. Hofmann and E. Knözinger, unpublished results.
- 9 S. Coluccia, F. Boccuzzi, G. Ghiotti and C. Morterra, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 2111.
- 10 T. Ito, M. Yoshioka and T. Tokuda, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 2277.
- 11 E. Knözinger, K. H. Jacob and P. Hofmann, *J. Chem. Soc., Faraday Trans. 1*, 1993, **89**, 1101.
- 12 V. Indovina and D. Cordischi, *Chem. Phys. Lett.*, 1976, **43**, 485.
- 13 D. Cordischi, V. Indovina and M. Occhiuzzi, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 456.
- 14 E. Giamello, P. Ugliengo and E. Garrone, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 1373.
- 15 E. Garrone, E. Giamello, M. Ferraris and G. Spoto, *J. Chem. Soc., Faraday Trans. 1*, 1992, **88**, 333.
- 16 E. Giamello, M. C. Paganini, M. Chiesa, S. Coluccia, G. Martra, D. Murphy and G. Pacchioni, *Surf. Sci.*, in the press.
- 17 E. Giamello, M. C. Paganini, D. M. Murphy, A. M. Ferrari and G. Pacchioni, *J. Phys. Chem.*, 1997, **101**, 971.
- 18 D. M. Murphy, R. D. Farley, I. J. Purnell, C. C. Rowlands, A. R. Yacob, M. C. Paganini and E. Giamello, *J. Phys. Chem. B*, in the press.
- 19 E. G. Derouane and V. Indovina, *Chem. Phys. Lett.*, 1972, **14**, 455.
- 20 M. Che and A. J. Tench, *Adv. Catal.*, 1983, **32**, 1.
- 21 E. Giamello, D. Murphy, E. Garrone and A. Zecchina, *Spectrochim. Acta, Part A*, 1993, **49**, 1323.
- 22 A. G. Pelmenschikov, G. Morosi, A. Gamba and S. Coluccia, *J. Phys. Chem. B*, 1998, **102**, 2226.
- 23 E. Knözinger, K.-H. Jacob, S. Singh and P. Hofmann, *Surf. Sci.*, 1993, **290**, 388.
- 24 S. Coluccia, F. Boccuzzi, G. Ghiotti and C. Mirra, *Z. Phys. Chem. Neue Folge*, 1980, **121**, 141.
- 25 A. J. Tench and R. L. Nelson, *Trans. Faraday Soc.*, 1967, **63**, 2254.
- 26 E. Giamello, D. Murphy and M. C. Paganini, *Colloids Surf. A*, 1996, **115**, 157.
- 27 W. Kanzig and M. H. Cohen, *Phys. Rev. Lett.*, 1959, **3**, 509.
- 28 E. Giamello, E. Garrone, P. Ugliengo, M. Che and A. J. Tench, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 3987.
- 29 J. H. Lunsford and J. P. Jayne, *J. Phys. Chem.*, 1965, **69**, 2182.
- 30 T. Ito, A. Kawanami, K. Toi, T. Shirakawa and T. Tokuda, *J. Phys. Chem.*, 1988, **92**, 3910.
- 31 R. L. Nelson and A. J. Tench, *J. Chem. Phys.*, 1964, **40**, 2736.

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