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Catalytic properties of F-centres at the magnesium oxide surface: hydrogen abstraction from methane

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Abstract

Surface defects on MgO are known to be involved, as active sites, in the catalytic abstraction of hydrogen from methane. The energetics for the formation at the (001) surface of some of these defects, as well as their electronic structure and reactivity, are explored. In particular, F-centres (anion vacancies with two electrons trapped), Li^+/F^+ couples (a vacancy with one electron coupled to a substitutional Li ion) and the step (where cations and anions are four-fold coordinated) are examined. This study is complementary to a previous investigation, where the activity of Li^+/O^- ionic couples has been considered. In all the cases examined the reaction results to be endothermic at 0 K and F-centres are less reactive than the O^- sites in the doped substrate.

Keywords: Methane; Magnesium oxide; Hydrogen abstraction

1. Introduction

The partial oxidation of methane for the synthesis of higher order hydrocarbons is known to be catalyzed by metal oxides [1,2]. The abundance of methane in natural gas makes the synthesis very appealing for industrial exploitation, but the implementation of reliable and profitable industrial processes still requires a deeper understanding of the mechanisms of the reaction.

There are many experimental evidences that the heterogeneously catalyzed reaction proceeds through a free radical mechanism at the surface of oxides, such as MgO, CaO, Sm_2O_3 [3–9], and there are indications that the rate determining step is the hydrogen abstraction from methane by the surface [10]. The methyl radicals so generated then combine to form different polymerization products [2–4,6,9,11,12], depending on the experimental conditions under which the reaction is driven. The whole mechanism of the reaction is very complicated. There is a variety of catalysts prepared with different methods that can be used in different environments and many intermediate species are formed, that cannot always be easily detected.

MgO has been the subject of several studies [2–19], since it shows good catalytic properties either after some special treatment at high temperature or when doped with alkaline metals, like lithium. It has been suggested [4,16,18,19]

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that defective sites like vacancies, electrons trapped therein, electron holes, low-coordinated ions at steps and corners are responsible for the abstraction of hydrogen.

In a previous study [20] we considered the catalytic activity of the Li-doped (001) surface of MgO and examined the possibility that a Li^+/O^- couple is formed at the surface and methane is adsorbed upon it. The interpretation proposed by many researchers [3–6,13] is that the very reactive O^- radical at the surface binds hydrogen and methyl is released, but the energetics of the reaction is still a matter of discussion and results obtained with different theoretical methods are in partial disagreement [21–26]. Calculations by Anchell et al. [26] on small isolated clusters, simulating different coordination surface sites, indicate that the reaction is exothermic (between -30 and -40 kcal/mol) at the UHF level, while it is endothermic (8.5 kcal/mol) for Børve and Petterson [24], at the same level of theory, with better defined clusters embedded in a Madelung potential. Only with approximations beyond UHF the latter authors find it moderately exothermic (between -4 and -11 kcal/mol). From our calculations [20] (UHF plus a posteriori electron correlation correction) it resulted that at 0 K the energy balance of this step of the reaction is approximately zero and relaxation effects, that are nearly ignored in the cluster calculations, are very important. The activation energy barrier was found to be about 18 kcal/mol from our calculations, whereas it is between 4 and 8 kcal/mol according to Børve and Petterson [24] with better electron correlation treatments, so that it may be supposed that the reaction proceeds spontaneously, following this mechanism, at high temperatures.

In the present paper we begin to consider other defects that are supposed to be present at the surface of MgO and, in particular, we concentrate on the possible role of surface anion vacancies in the reaction. Anion vacancies (F-centres) are also expected to be present in Li-doped MgO at appreciable concentration, as for stoichiometric requirements, in absence of oxidizing agents, they are thought to be a by-product of the solution of Li_2CO_3 or Li_2O in MgO, for compensating the excess of Li cations [27,28]. To investigate if F-centres can explain the catalytic activity observed on defective pure MgO surfaces or be competitive with the Li^+/O^- couples of Li-doped MgO in driving the reaction of dehydrogenation of methane, two kinds of neutral defects have been examined: F_s-centres (a surface vacancy with two electrons), for they are known to be more stable than charged F_s^+ and F_s^{2+} [29], and F_s^+-centres (one electron in the vacancy) coupled with Li ions in the substrate. Then, the importance of low-coordinated sites in the catalytic process is discussed, with reference to some preliminary results obtained for adsorption of hydrogen on four-fold coordinated sites at steps.

2. The method

The method used in this study is the self-consistent-field periodic Hartree–Fock (HF) [30], expressed in the basis of the atomic orbitals, as developed in the CRYSTAL program [31]. This method has the advantage that long-range interactions and the Madelung field are correctly described and that relaxation in the catalyst after the formation of a defect can be accurately determined. Open-shell configuration systems are treated in the Unrestricted Hartree–Fock approximation (UHF).

Geometry optimizations are performed at this level of approximation. However, as correlation effects are expected to be important [24], the SCF defect formation (E_d) and adsorption (E_a) energies, calculated at the equilibrium geometry, are corrected a posteriori through a numerical integration over the unit cell of a density functional applied to the HF charge density, as proposed by Perdew [32]. This scheme has been shown to be very effective in correcting the HF energies [33–36].

In our model the surface is simulated by a

thin infinite slab. In previous studies [37] it has been shown that this represents a good approximation of the (001) surface of MgO, where relaxation and rumpling are negligible. The lattice parameter used is the same as was determined for the bulk (421 pm) [34,38]. Defects are modeled within a supercell scheme, that has proved to be suitable for the treatment of neutral defects [39].

For the substrate the same ionic basis set as adopted in previous calculations on MgO [38] and Li_2O [40] has been used: 9, 9 and 5 atomic orbitals for Mg, O and Li, respectively, grouped in one s- and two sp-type (Mg and O) or two s- and one p-type (Li) shells and corresponding to 8–61 (Mg), 8–51 (O) and 6–1 (Li) contractions of Gaussian type functions. Standard 6–31* basis sets [41] were used for hydrogen and carbon (p polarization functions on H and d on C). The energy of dehydrogenation of methane in the gas phase obtained with this basis set and including the correlation correction is 115.5 kcal/mol and compares well with the experimental value of 0 K (112 kcal/mol [42]).

3. Results and discussion

3.1. The surface F-centre

An F_s-centre can be represented as the result of the removal of an oxygen atom from the surface of MgO and the formation energy can be formally defined as

$$E_d = E([MgO]F_s) - E([MgO]) + E(O^{at}) \quad (1)$$

the three terms referring to the total energy of the F_s-centre system, the corresponding perfect slab and the removed oxygen atom at an infinite distance from the surface, respectively.

For the description of the electron pair in the vacancy the same basis set of oxygen was used, but the exponent α_F changes from 0.21 to 0.07 $bohr^{-2}$, with a stabilization of the system as large as 83 kcal/mol, due to the decreased repulsion between the two electrons. The functions are best centred 15 pm below the corresponding perfect lattice site. No other functions were included into the basis set, as it was checked that the addition of shells with higher angular quantum number in the cavity or of a diffuse sp-function out of the surface plane give only a negligible energy gain.

Table 1
Hartree–Fock formation energy E_d (kcal/mol) of a neutral F-centre at the (001) surface of MgO with no relaxation, as a function of the thickness of the p-layer slabs and of the defect surface density (D)

p	D	E_d
2	1/4	171.9
3	1/4	172.8
4	1/4	172.7
5	1/4	172.7
6	1/4	172.7
7	1/4	172.7
4	1/8	172.7
4	1/16	172.5

In all the calculations four-layer slabs were used, which allow us to model all the defects considered in the present study and discuss relaxation effects. In Table 1 the dependence of E_d on the thickness of the slab and on the density of the F_s-centres D (D = number of defects/number of surface oxygen sites) is explored. The rapid convergence of E_d with thickness confirms that even a three-layer slab would be a feasible choice. As regards D, the value of E_d obtained with a supercell containing only 4 MgO units per layer can be considered as nearly converged. This implies that the interaction between defects at $D = 1/4$ is already negligible.

As is to be expected in the case of a localized defect determining a short-ranged perturbation, relaxation involves only the ions around the vacancy and the displacements from the corresponding perfect lattice positions are small and do not contribute much to the stabilization of the system. The largest relaxation observed is that of the nearest-neighboring Mg ions at the surface, which move slightly outwards from the vacancy, with an energy gain of just 2 kcal/mol. The next nearest O ions at the surface move

downwards, but this corresponds only to a 0.1 kcal/mol stabilization; similarly, the Mg^{2+} below the vacancy moves down with a 0.2 kcal/mol decrease in energy. If relaxation is taken into account, E_d becomes 170.2 kcal/mol. After a posteriori correction for electron correlation [32], E_d increases to 194.1 kcal/mol.

Our HF value compares well with the result obtained by Ferrari and Pacchioni [29], at the HF level, with clusters embedded in an array of point charges (between 166 and 177 kcal/mol, depending on the cluster used). This good agreement is not surprising, as it has been demonstrated [43] that MgO is fairly well described by relatively small clusters after immersion in the correct potential. E_d obtained by Kantorovich et al. [44] in DFT calculations is 225 kcal/mol, i.e. 31 kcal/mol higher than the energy calculated here after correction for electron correlation. A similar discrepancy is observed in the calculation of the formation energy of an F-centre in the bulk (212.8 kcal/mol against Kantorovich's 243.2 kcal/mol). The pattern of relaxation around F_s is the same in all the calculations considered, but in [29] it is slightly more important, as it accounts for 7–9 kcal/mol, while in [44] the relaxation energy is less than 1 kcal/mol, which is closer to the value we obtain.

The fast decay of the defect–defect interaction and the little importance of relaxation support the picture of a well localized defect. Fig. 1 shows that the two electrons are in fact localized in the vacancy and bound, but they are much more diffuse than the valence electrons of the O^{2-} ions and extend further out of the surface. The ions around the vacancy suffer little distortion. Correspondingly, Mulliken population analysis attributes 2.35 electrons to the F_s-centre. The amount of charge in excess is due to the overlap with the surrounding ions.

The localization of the F_s-centre is also confirmed by the appearance of defect states in the gap, as can be seen in a comparison between the density of states (DOS) for the MgO surface before and after the formation of the vacancy (Fig. 2). One peak (centred at −4.35 eV), due to s-type orbitals of the electron pair lies in the lower part of the gap. A second complex peak appears in the upper part of the gap, that is mainly due to the p-type orbitals of the F_s-centre electron pair. States associated with the F_s-centre are also present in the highest valence band (between −15.4 and −10 eV), which is dominated by oxygen p-states. This latter band is narrower by nearly 1 eV than in the perfect surface, as the top of the band is lowered.

The appearance of energy levels in the gap indicates the enhanced reactivity of the defective surface, as the electrons in the F_s-centres

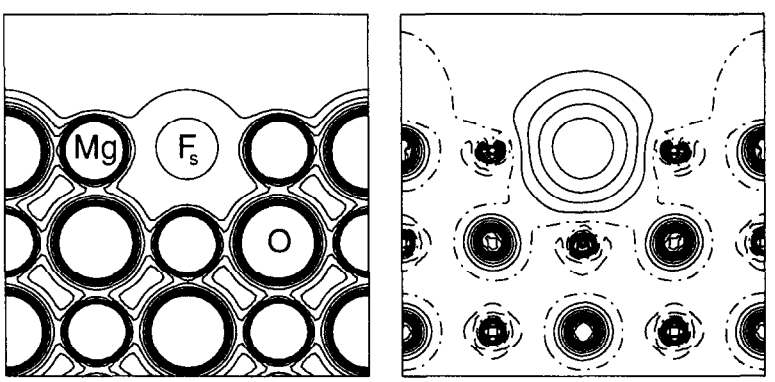

Fig. 1. Total (left) and difference (right) electron density maps of an F-centre on the (001) surface layer of MgO. The difference is calculated with respect to the superposition of the isolated spherical ions. The separation between contiguous curves corresponds to 0.01 e/bohr^3 in the total charge density and 0.005 e/bohr^3 in the difference map. Continuous, dashed and dot-dashed lines denote positive, negative and zero values, respectively.

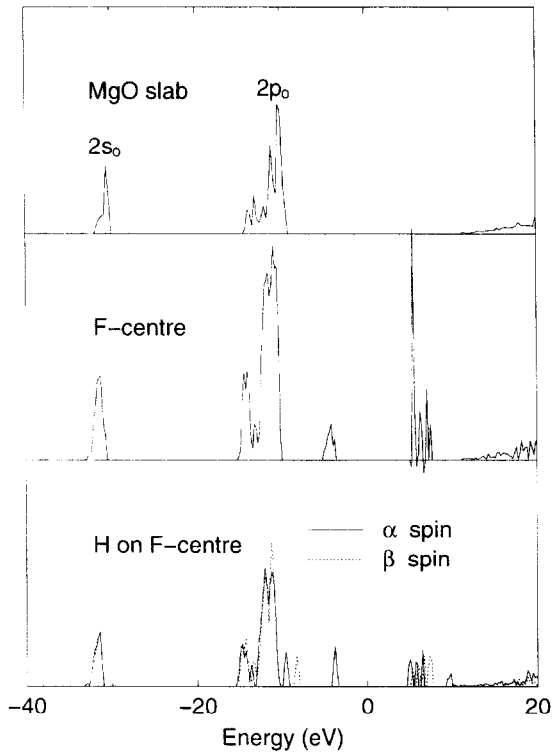

Fig. 2. Total density of states (DOS) for the valence (negative energies) and first conduction (positive energies) bands of a (001) MgO slab. The DOS for the perfect surface (top panel) and an F-centre at the surface before (middle panel) and after (bottom panel) adsorption of hydrogen on top are reported. Arbitrary units for DOS. Intensities of the peaks in the gap are multiplied by a factor 5.

are obviously less bound than the other electrons in the substrate. We tested the reactivity of F_s with respect to the adsorption of H upon it, so as to determine whether this may be an active site in the dehydrogenation of methane.

The optimized α_F exponent of the sp shell centred at the vacancy site is in this case 0.087. The exponents of the outer shells of hydrogen were also optimized ($\alpha = 0.145$ for the s-orbital and $\alpha = 0.9$ for the p-shell), but the corresponding gain in energy is only 0.2 kcal/mol. The hydrogen atom is adsorbed on F_s at a distance of 130.6 pm from the surface plane. The adsorption energy E_a, formally calculated with respect to the non-interacting sub-systems ([MgO]F_s and atomic hydrogen) and corrected for correlation, is −41.3 kcal/mol and the very little modification in the relaxation of the ions around the defect after adsorption has no effect on the energy. When a hydrogen atom is adsorbed on an F_s-centre, a fraction of one of the two electrons in the vacancy is transferred onto H (Fig. 3c), H becomes negatively charged and acquires a partial hydride character. The rest of the surface remains unperturbed. H states mix with the F_s-centre states (Fig. 2) and the three electrons populate the corresponding energy levels. The lowest α-electron peak is found at −9.7 eV, close to the top of the band of O p-states, and that of the β-electron follows at −8.5 eV, while the unpaired electron gives the sharp peak in the gap at −3.8 eV. This peak is narrower than the corresponding peak before adsorption, indicating that the adsorption of H contributes to a better localization of that state. The spin density map (Fig. 3b) shows that the unpaired electron is about 70% localized in the vacancy and 30% on H. Thus, the electron charge transfer only involves H and the F_s-centre and the interaction with the surface is essentially electrostatic through the attraction between the negatively charged H and the cations.

3.2. The substitutional Li-anion vacancy couple

In this section the properties and reactivity of a surface anion vacancy coupling with a Li ion in Li-doped MgO are analyzed. In our model this is formally obtained by substituting one MgO unit with a Li atom, the whole system remaining neutral. Hence, a formal definition of the energy required for the formation of this coupled defect can be formulated as

$$E_d = E([\mathrm{MgO}]\mathrm{Li}^+/F_s^+) - E([\mathrm{MgO}]) + E(\mathrm{O}^{at}) + E(\mathrm{Mg}^{at}) - E(\mathrm{Li}^{at}), \quad (2)$$

the five terms referring to the total energy of the defective system, the corresponding perfect slab and the isolated O, Mg, Li atoms, respectively. The following geometry has been considered: Li substitutes a Mg ion in the sub-surface layer and the oxygen atom upon it is removed from the

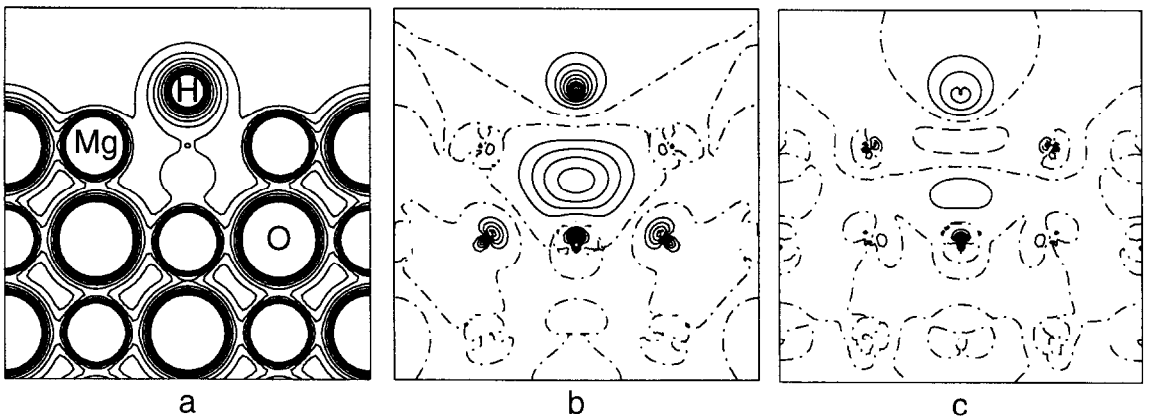

Fig. 3. Total electron (a), spin (b) and difference (c) density maps of the adsorption of hydrogen on an F-centre at the (001) surface of MgO. The difference is calculated with respect to the independent isolated hydrogen atom and the substrate before adsorption. Scales and symbols as in Fig. 1.

surface (Fig. 4). The Li atom ionizes and the unpaired electron localizes in the vacancy, generating an F_s^+-centre.

Also in this case the basis set for the electron in the vacancy was optimized: the best value of α_F is 0.08 bohr^{-2}. D is a more delicate parameter for this system, as convergence on E_d is not as rapidly reached as with uncoupled F_s-centres. In absence of relaxation Hartree–Fock E_d changes from 334.2 to 331.3 and 330.8 kcal/mol at $D = 1/4$, $1/8$ and $1/16$, respectively. The value at $D = 1/16$ can be considered as nearly converged. Relaxation around Li^+/F_s^+ is more important than in the case of the isolated F_s. Li moves 32.4 pm under the lattice plane and all the ions move apart from Li^+/F_s^+ in approximately the same way, as they do in the case when Li couples with a surface O [20]. The energy gain for relaxation is 20.7 kcal/mol (it is 52.4 kcal/mol for the formation of Li^+/O^-), 65% of which is due to the nearest-neighboring surface Mg ions penetrating below the surface plane. When relaxation energy and electron correlation corrections are taken into account, E_d becomes 338.9 kcal/mol.

As happens for the simple F_s-centre, the perturbation is very short-ranged and the unpaired electron is fully localized in the vacancy, but the barycentre of the charge distribution is

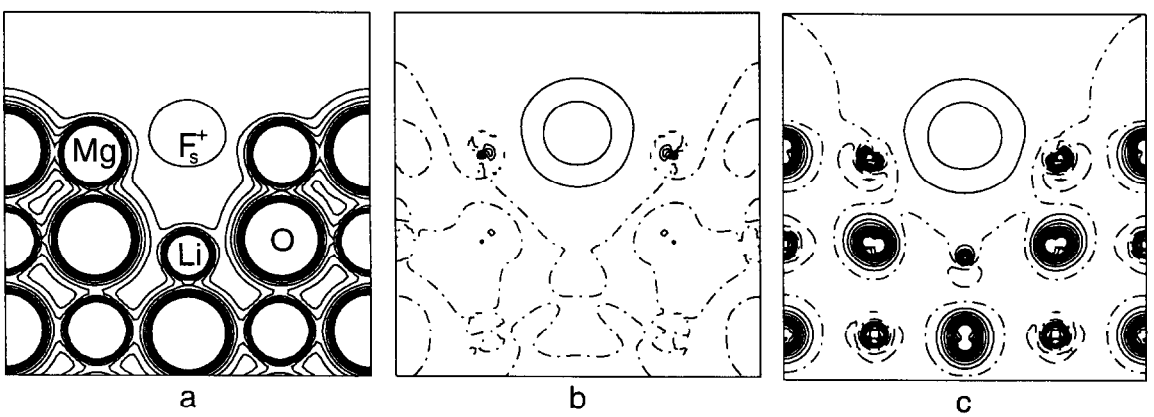

Fig. 4. Total electron (a), spin (b) and difference (c) density maps of a Li^+/F_s^+ coupled defect in a (001) slab of MgO. The difference is calculated with respect to the superposition of the isolated spherical ions. Scales and symbols as in Fig. 1.

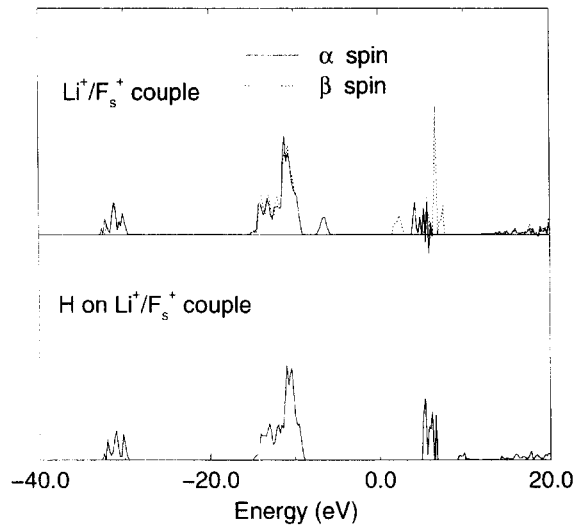

Fig. 5. Total density of states (DOS) for a Li^+/F_s^+ coupled defect in a (001) slab of MgO before (top panel) and after (bottom panel) adsorption of hydrogen on top. Units and scales as in Fig. 2.

shifted out of the surface plane (Fig. 4). The main feature observed in the distribution of the electron energy levels (Fig. 5) is that the α-band associated with the Fe_s^+-centre in the gap is lower in energy by about 4 eV than the corresponding peak for the uncoupled F_s-centre in Fig. 2.

H is adsorbed onto the defective site at a shorter distance from the surface (64 pm) than on the simple F_s-centre. The optimized α_F is 0.117 $bohr^{-2}$. After adsorption the relaxed ions show a little tendency to move back to the perfect lattice positions, that corresponds to a small stabilization of the system of 1.4 kcal/mol. The adsorption energy E_a of H on $[MgO]Li^+/F_s^+$, calculated with respect to the non-interacting sub-systems, is −94.1 kcal/mol (correlation correction included), more than twice the E_a of the F_s-centre system (−41.3 kcal/mol), but less than in the case of adsorption on Li^+/O^- (−115.3 kcal/mol). Unlike the uncoupled F_s-centre system, the transfer of the electron from the vacancy to H to form H^- is complete (Fig. 6) and, consequently, the electrostatic interaction between H^- and the surface is stronger. The formation of hydride is essentially the only modification observed in the electronic structure after adsorption. It is obtained through the coupling of the electron of F_s^+ with the electron of H. The two electrons populate the level of H falling inside the O p-bands (Fig. 5), whereas the other levels associated with the vacancy are located in the upper part of the gap.

3.3. The step

Following the suggestion by Kantorovich et al., the same four-layer (103) slab, as defined in [44], has been chosen to model a step at a (001) surface of MgO (Fig. 7), where the step is one

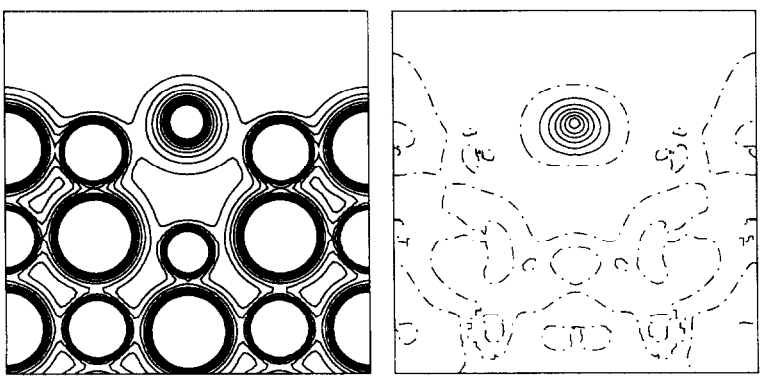

Fig. 6. Total (left) and difference (right) electron density maps of the adsorption of Hydrogen on a Li^+/F_s^+ coupled defect in a (001) slab of MgO. The difference is calculated with respect to the independent isolated hydrogen atom and the substrate before adsorption. Scales and symbols as in Fig. 1.

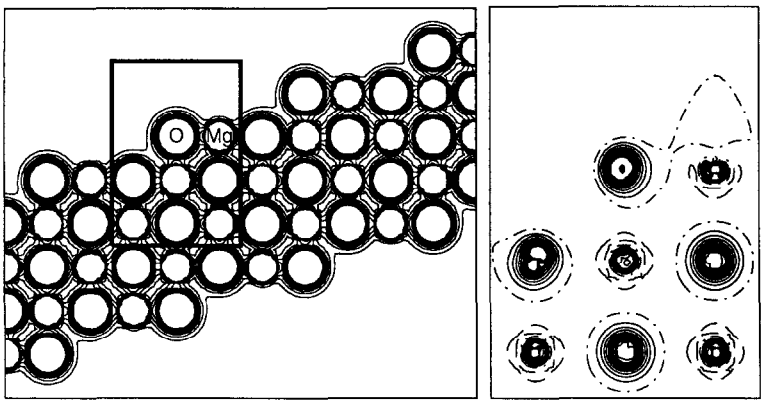

Fig. 7. Total (left) and difference (right) electron density maps of a step at the (001) surface of MgO. The difference is calculated in the area of the small rectangle with respect to the superposition of the isolated spherical ions. Section parallel to the (010) plane. Symbols as in Fig. 1.

inter-ionic distance (d) high, $3d$ wide and the edge has infinite length. In a supercell $4d$ large along the edge there are 52 atoms. With this geometry the periodicity of the slab is preserved, but symmetry is lowered to only two operations and calculations are computationally demanding, although they can be run on average size workstations. For this reason we did not perform a full geometry optimization, but concentrated on verifying the hypothesis that H may be adsorbed at the step. The electron charge density map of Fig. 7 shows that the electronic structure of MgO is not significantly deformed after the formation of a step and the ions of the edge do not differ much from the other ions in the slab on the flat surface. Thus, it is not to be expected that the stepped surface exhibits a very different behavior from that of the flat perfect surface and, in fact, the interaction curve of hydrogen with an edged O is repulsive and decays asymptotically to zero.

The formation of an F-centre at the step has also been considered. The preferred site is on the top edge of the step and E_d is 169.7 kcal/mol, including the correlation correction, but neglecting relaxation. Then, the formation of an F-centre is easier at a four-fold coordinated site by nearly 30 kcal/mol than at a five-fold coordinated site on the flat surface (E_d = 196.3 kcal/mol for the unrelaxed system), as the Madelung potential is obviously weaker. However, the reactivity to hydrogen is not enhanced by the reduced coordination. Although the electron transfer from the vacancy to H is slightly easier in this case, the interaction of H with the surface is weaker and H tends to move closer to the Mg behind the vacancy to maximize the attraction. The adsorption energy is −32.5 kcal/mol (E_a = −41.3 kcal/mol for F_s on the (001) flat surface).

3.4. The reaction

It has been proposed [3–6,13] that the abstraction of hydrogen from methane, the rate determining step of the reaction of dehydrogenation, when catalyzed by Li-doped MgO, follows a radical mechanism of the type

$$[MgO]X\cdot + CH_4 \rightarrow [MgO]XH + \cdot CH_3 \quad (3)$$

with X = LiO, i.e. hydrogen is abstracted by an O^- radical of a Li^+/O^- couple formed at the surface of MgO. The energy of the reaction E_r is then defined as

$$E_r = E([MgO]XH) + E(\cdot CH_3) - E([MgO]X\cdot) - E(CH_4) \quad (4)$$

In a previous paper on the reactivity of the Li^+/O^- couple [20] E_r(X = LiO) was calculated to be very weakly exothermic (−0.2

Table 2
Calculated energy E_r (kcal/mol) for the reaction of oxidation of methane on a F_s-centre and on a Li^+/F_s^+ coupled-defect ($D = 1/16$). The Hartree–Fock energies (E^{HF}) are corrected for electron correlation effects (E^{corr}) with an a posteriori integration of the HF density, using Perdew's density functional [32]

System	E^{HF}	E^{corr}	$E^{HF+corr}$
$[MgO]F_s$	−10982997.5	−31368.0	−11014365.5
$[MgO]F_s$–H	−10983340.3	−31379.3	−11014719.6
CH_4	−25226.9	−200.9	−25427.8
CH_3	−24827.1	−173.4	−25000.5
E_r	57.0	16.2	73.2
$[MgO]Li^+/F_s^+$	−10862391.0	−31105.7	−10893496.7
$[MgO]Li^+/F_s^+$–H	−10862776.6	−31126.4	−10893903.0
CH_4	−25226.9	−200.9	−25427.8
CH_3	−24827.1	−173.4	−25000.5
E_r	14.2	6.8	21.0

kcal/mol). We are now able to check whether the reaction may take place at other defective sites, such as the surface F-centre and Li^+/F_s^+ couple described in the preceding sections, and following the same mechanism. It has been shown that hydrogen is bound to the surface by the two defects and in this process there is a transfer of an electron (or part of it) from the vacancy to hydrogen. However, the gain in energy due to the adsorption is too small to promote the homolytic cleavage of one C–H bond of CH_4 (115.5 kcal/mol, as calculated with the same basis set [20]). From Table 2 it results that in both cases the reaction is endothermic, as $E_r(X = F_s) = 73.2$ kcal/mol and $E_r(X = Li\ F_s^+) = 21.0$ kcal/mol. In particular the two electrons of the F_s-centre are much less reactive than the unpaired electron present in the other two cases considered and reducing the coordination from five to four, as for an F-centre at a step, does not increase reactivity.

4. Conclusions

Neutral anion vacancies, like F-centres coupled at Li impurities, that are known to be present on the (001) surface of pretreated MgO, have been shown to be reactive species that can adsorb atomic hydrogen, but the adsorption energy is not sufficient to promote the dehydrogenation of methane, for which the radical Li^+/O^- sites are more likely preferred. This picture is not expected to change when uncoupled F_s^+ are considered. Some preliminary calculations seem to indicate that these sites are similar to the coupled Li^+/F_s^+ defects. A rough estimate of HF E_r, obtained with no geometry optimization, gave a value of 16.7 kcal/mol, that is close to the E_r obtained for the coupled defect (14.2 kcal/mol). It has also been shown that, as regards surface sites with lower coordination, reactivity is not increased at four-fold coordinated F-centres, as formed at steps. Further investigation will concern three-coordinated sites at corners, that in previous theoretical calculations [25] are indicated to have high hydrogen affinity.

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