Exothermic Mechanism for the Abstraction of Hydrogen from Methane on Li-Doped MgO

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ABSTRACT: Despite its importance, it is still not known by which mechanism Lidoped MgO catalyzes the oxidative coupling of methane to ethane. Nevertheless, it is commonly assumed that the mechanism goes through catalytic H abstraction from methane via a Li^+O^- surface defect. In this paper we use first-principles density functional theory calculations to show that the reaction is significantly more exothermic when the Li^+O^- defect is situated on a step edge instead of on the flat surface. We find that the reaction on the step is exothermic by 0.25 eV, whereas it is endothermic by 0.3 eV on the flat surface. The presence of the Li dopant in the step edge is crucial for the exothermicity of the reaction. These findings suggest that surface steps which include lithium defects could be responsible for the catalytic behavior of Li/MgO. Following the binding of hydrogen to the Li⁺O⁻ defect on the step edge the methyl radical can either depart to the gas phase or bind to an adjacent step-edge oxygen atom, increasing the exothermicity of the overall process to 0.8 eV. Activation energies of 0.2 eV for the first pathway and 0.5–0.8 eV for the second were calculated.



I. INTRODUCTION

The conversion of natural gas, mainly methane, into a more easily transported higher alkane liquid is of great economical interest. The current industrially viable conversion process, using a synthesis gas, is expensive and energy-consuming; therefore, it is necessary to develop alternative methods. One such process, which has attracted a lot of theoretical and experimental interest, is the direct oxidative coupling of methane (OCM) via Li-doped MgO. Two components are necessary for the coupling of methane: an oxidizing agent to make the process exothermic and a catalyst in order to obtain reasonable yields of C_2 hydrocarbons rather than waste products such as CO or CO₂. It has been discovered some time ago that the use of high-temperature Li-doped MgO as the OCM catalyst produces a significant fraction of C2 hydrocarbons.¹ Lunsford and co-workers^{2,3} proposed that the higher alkanes are formed from methane in a two-step process: First methane is activated by breaking the methane C-H bond at the [Li⁺O⁻] surface defect resulting in the formation of a methyl radical. Next the methyl radicals bond in the gas phase to create a C-C bond and form ethane.^{4,5} The overall reaction is given by

$$CH_4 + [MgO]Li^+O^- \rightarrow CH_3^{\bullet} + [MgO]Li^+(OH)^-$$
(1)

$$CH_3^{\bullet} + CH_3^{\bullet} \to C_2H_6 \tag{1b}$$

Here, the key step is hydrogen abstraction by the surface O⁻ species at the first stage (eq 1), while the second stage (eq 1b) occurs in the gas phase. While it is clear that Li-doped MgO acts as a good oxidative coupling catalyst and that the C–H bond-breaking occurs at the surface, it is still unclear exactly where and how this process takes place. Previous studies (see, e.g., refs 5 and 6) have raised the possibility that methane

molecules can be dehydrogenated via a surface O^- entity. The surface O^- species can be generated from a surface oxygen atom adjacent to a Li substitutional defect. When MgO is doped with Li, the dopant Li ion with a charge of +1 replaces a Mg atom with a +2 charge resulting in the formation of an unpaired electron hole which can localize on one or more of the neighboring oxygen atoms. It is thought that the adjacent substitutional Li⁺ ion stabilizes the surface O^- species, and that the methane molecules are dehydrogenated via the resulting [Li⁺O⁻] surface-defect.

Many theoretical studies (see Table 1) have calculated the reaction energy of eq 1 assuming that the $[Li^+O^-]$ surfacedefect is located on a flat MgO surface. They found reaction energies ranging from the mildly exothermic to the mildly endothermic as shown in Table 1.

As can be seen, the estimate for the reaction energy, and even whether it is positive or negative, depends on the level of theory and specific model employed for the calculation. The more elaborate electronic structure methods such as HF+CASSCF and HF+MP4 have been employed on small embedded clusters, whereas the calculations performed on structures with enough atoms to realistically represent the Li/MgO surface use the somewhat less rigorous DFT methods. All the estimates for reaction energy, whether positive or negative, are small and centered on zero. Unfortunately, there are no experimental values for the reaction energy available for comparison. As for activation energies of eq 1, these have been estimated theoretically under the assumption stated above of a flat Li/MgO surface, yielding estimates ranging⁶ from 0.05

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Table 1. Comparison of the Reaction Energies Calculated in Previous Theoretical Studies for Hydrogen Abstraction from Methane on Flat Li/MgO (100) Surfaces^{*a*}

method of calculation	reference	reaction energy (eV)
HF+CASSCF, small cluster + Madelung potential	Børve and Pettersson ⁷	-0.46
HF-MP4, embedded cluster	Ackermann et al. ⁸	-0.41
DFT-B97–1 hybrid, QM/MM embedded cluster (Li in surface layer)	Catlow et al. ⁹	-0.39
DFT-BLYP	Ackermann et al. ⁸	-0.35
HF+CCI+Q, small cluster + Madelung potential	Børve and Pettersson ⁷	-0.04
HF+postcorrection for correlation.	Orlando et al. ¹⁰	0.01
DFT-GGA	Dash and Gillan ¹¹	0.25
HF, small cluster + Madelung potential	Børve and Pettersson ⁷	0.37
DFT-GGA	Nolan and Watson ¹²	0.37
DFT-GGA+U	Nolan and Watson ¹²	0.54
DFT-GGA+U (Li in surface layer)	Scanlon et al. ¹³	0.55
a In all cases Li is in a subsurface layer except where noted.		

to 1.2 eV. Experimentally, the activation energies for the consumption of methane and formation of gas phase methyl radicals or C_2 hydrocarbons over Li-doped MgO range from 0.88 eV¹⁴ to 2.4 eV². Some of the calculated activation energies fall within this range but the uncertainty concerning the reaction exothermicity remains.

An alternative active site for hydrogen abstraction has been proposed^{15,16} in which the reaction takes place not at a $[Li^+O^-]$ surface defect but at a surface oxygen vacancy (F-center) whose formation is promoted by the lithium dopants. However, both Orlando et al.¹⁶ and Dash and Gillan¹¹ have found, using DFT methods, that the hydrogen abstraction energy from methane via a F-center is endothermic by 1 eV and therefore is unlikely to be the active site for hydrogen abstraction from methane.

All of the above studies have looked at flat surfaces. However, Li/MgO surfaces are never perfectly flat; they can possess defects such as steps and corners with low-coordinated ions¹⁷⁻¹⁹ which can perhaps serve as distinct catalytic sites with separate reaction and activation energies. In particular, Trionfetti et al.¹⁹ have shown that Li/MgO catalysts prepared via the sol-gel method possess surface steps and that the Lidopant atoms preferably substitute Mg atoms at lowcoordination step sites. Furthermore, the sol-gel prepared Li/MgO catalysts show twice as much catalytic activity for hydrogen abstraction from propane than did sol-gel prepared MgO. Li/MgO catalysts prepared using the wet impregnation method however showed five times less catalytic activity than the sol-gel Li/MgO and also possessed lower amounts of morphological defects such as edges and a lower incorporation of Li ions. These experimental findings indicate that [Li⁺O⁻] defects at step edges could account for the increased catalytic activity observed in Li/MgO catalysts. Theoretical calculations of reaction and activation energies of hydrogen abstraction via [Li⁺O⁻] defects located on surface step edges are important to further explore the possibility that these sites could account for the catalytic properties of Li/MgO.

In a recent paper²⁰ the transition state energy barrier for hydrogen abstraction from methane at a step corner in Li/MgO was calculated using DFT-B3LYP.²¹ Depending on the position of the Li impurity, the barrier was found to be either slightly higher (0.44 eV) or lower (0.23 eV) than on the flat Li/MgO surface (0.28 eV). The barrier was lower than the experimental values mentioned above, but DFT-B3LYP is known to underestimate transition barrier energies.²² Reference 20 did not address the issue of the reaction products: neither the reaction energy nor the reaction product channels.

In this paper we continue the study of this important reaction and show that the abstraction of hydrogen from methane via a surface Li⁺O⁻ defect is more energetically favorable on a step-edge, and that the reaction energies are significantly more exothermic than for a flat surface. Note that we do not attempt here to calculate a more accurate reaction energy than the previous studies quoted in Table 1, rather we show that a significant energetic advantage is obtained when the reaction occurs at a step-edge. Additionally we examined the energetics of binding the methyl radical to the catalyst surface, either by itself or in conjunction with the binding of the hydrogen atom. We show that the binding of both the hydrogen atom and the methyl radical to step-edge oxygen atoms adjacent to the Li defect leads to an even greater energetic advantage. We also calculate the transition state energy barrier and describe the reaction path for the abstraction of hydrogen from methane at a step-edge Li⁺O⁻ surface defect site. We observe and describe two possible subsequent reaction paths. In both paths, hydrogen is first abstracted from methane at the step-edge oxygen atom to which it binds, producing a methyl radical. In the first path the methyl radical returns to the gas phase, while in the second it binds to an additional stepedge oxygen atom adjacent to the Li defect.

II. METHODS

We consider here three reactions for the hydrogen abstraction from methane on Li/MgO surfaces. The first reaction results in the binding of the hydrogen to the surface while the methyl radical departs to the gas phase:

$$CH_4 + [MgO]Li^+O^- \rightarrow CH_3^{\bullet} + [MgO]Li^+(OH)^-$$
(1)

In the second reaction it is the methyl radical that bonds to the surface and hydrogen goes to the gas phase:

$$CH_4 + [MgO]Li^+O^- \rightarrow H + [MgO]Li^+(OCH_3)^-$$
(2)

In the third reaction both hydrogen and the methyl radical attach to the surface:

		CH ₃	
		0	
		1	
$CH_4 + [MgO] Li^+O^-$	\rightarrow	[MgO] Li – O – H	(3)

We calculated the reaction energy by separating the reaction into two distinct stages:

- 1. The dissociation of methane into a hydrogen atom and methyl radical: $CH_4 \rightarrow CH_3^{\bullet} + H$. Here the dissociation energy is given by $E(CH_3^{\bullet}) + E(H) - E(CH_4)$, where *E* is the energy of the isolated relaxed species. Note that spin-polarized calculations were performed for all species with unpaired electrons (i.e., an odd number of valence electrons), in this case for the isolated hydrogen atom and the isolated methyl radical.
- 2. The binding energy gained when the hydrogen atom and/or methyl radical bind to the catalyst surface. In order to calculate the binding energies full ionic

relaxations are performed on the isolated binding species, the Li/MgO slab and the Li/MgO slab with the binding species bound to the surface. The binding energy is given by the energy of the relaxed Li/MgO slab plus the energy of the relaxed isolated binding species minus the energy of the relaxed Li/MgO slab:binding-species complex.

Hence for reaction 1 the binding energy is given by

$$E([MgO]Li^+O^-) + E(H) - E([MgO]Li^+(OH)^-)$$

For reaction 2 the binding energy is given by

$$E([MgO]Li^+O^-) + E(CH_3^\bullet) - E([MgO]Li^+(OCH_3)^-)$$

For reaction 3 the binding energy is given by

$$E([MgO]Li^+O^-) + E(CH_3^\bullet) + E(H) - E([MgO]Li^-O - H)$$

The reaction energy is given by the dissociation energy minus the binding energy. We confirmed that the reaction energy calculated by this method is the same as the reaction energy obtained when viewing the reaction as one step i.e. the energy of the relaxed isolated final unbound species plus the energy of the relaxed Li/MgO slab:binding-species complex minus the energy of the relaxed Li/MgO slab minus the energy of relaxed isolated methane.

Hence for reaction 1 the reaction energy is given by

$$E([MgO]Li^{+}(OH)^{-}) + E(CH_{3}^{\bullet}) - E([MgO]Li^{+}O^{-})$$
$$- E(CH_{4})$$

For reaction 2 the reaction energy is given by

$$E([MgO]Li^{+}(OCH_{3})^{-}) + E(H) - E([MgO]Li^{+}O^{-})$$

- $E(CH_{4})$

For reaction 3 the reaction energy is given by

We calculated the binding energies of the hydrogen atom and/or methyl radical to various catalytic surfaces, namely the flat pure MgO (100) surface, the flat Li/MgO (100) surface, and the stepped MgO and Li/MgO surfaces. We also studied which location in both the flat and stepped catalyst structure is energetically preferable for the Li substitutional defect.

All our calculations were carried out using plane-wave density functional theory with the Quantum-ESPRESSO package.²³ We first performed full ionic relaxations (see footnote 24 for details) before calculating the final energy and geometry. All energetic calculations were converged to an accuracy of 0.01 eV for wave function kinetic energy cutoff, k-point grid density and vacuum length.

To calculate the energies of the isolated methane molecule, methyl radical, and hydrogen atom, we placed the single atom/ molecule in the center of a periodically repeated large cubic supercell and performed the calculations using Γ -point sampling. Spin-polarized calculations were carried out for the hydrogen atom and methyl radical. Supercells with edge length of $15a_0$ and wave function kinetic energy cut-offs of 100 Ry were sufficient to obtain the desired accuracy in total energy of 0.01 eV. C–H bond lengths of 1.081 and 1.090 Å were obtained for the methyl radical and methane molecule respectively in good agreement with the respective experimental values²⁵ of 1.08 and 1.087 Å.

We described the Li/MgO (100) low index surface, within the framework of periodic plane-wave DFT, by studying a finite-thickness slab of Li/MgO. The periodic slabs are separated by a vacuum gap of 15.87a₀ in order to remove spurious slab-slab interactions. Additionally, all calculations were converged for slab thickness and we found that increasing the slab thickness from four atomic layers to five atomic layers only changed the binding energies by 0.002 eV. We used a supercell of dimensions 15.87a0 by 15.87a0 parallel to the MgO(100) surface corresponding to the DFT lattice parameter for bulk MgO of 4.20 Å, which compares well with the experimental value of 4.21 Å.25 Full ionic relaxations were performed for each structure in order to obtain the equilibrium geometries and energies. Wave function kinetic energy cut-offs of 60 Ry were sufficient to obtain the desired accuracy in total energy of 0.01 eV. We performed the slab calculations by smearing the electron occupancies and by performing spinpolarized calculations for systems with unpaired electrons (i.e., systems with an odd number of valence electrons). We converged results for k-point grid density, and found that a 2 \times 2×1 k-point mesh generated using the Monkhorst Pack²⁶ scheme was sufficient to obtain the desired accuracy (typically a change of several meV in binding energies was observed when increasing the k-point mesh density from $1 \times 1 \times 1$ to $2 \times 2 \times 2$ 1).

In order to calculate the reaction energies using DFT an exchange-correlation functional must be chosen which can give accurate dissociation and binding energies. We used plane-wave DFT with the Perdew-Burke-Ernzerhof PBE²⁷ GGA exchange correlation functional, which is known to give a good description of methane dissociation energies and the structural and cohesive properties of bulk MgO.²⁸ It is known that this functional sometimes overdelocalizes orbitals due to spurious electron self-interaction.²⁹ Despite this, the PBE results can still determine whether abstracting hydrogen at a surface step has significant advantages over abstraction on a flat surface. We verified this by performing additional calculations on smaller periodic structures using the BNL³⁰ functional (a range-separated hybrid functional), which corrects for selfinteraction^{31,32} but is more computer intensive than the nonhybrid PBE functional. For these calculations we used the range-separation parameter, γ , which gives the correct band gap for bulk MgO ($\gamma = 0.1$).³² It should be noted that while $\gamma = 0.1$ correctly models bulk MgO, it is not the ideal range-parameter for the dissociation of methane, for which a larger value should be used. However, as we are only using the BNL functional to verify the difference in the binding energy of hydrogen to flat Li/MgO or a stepped Li/MgO surface, the dissociation energy of methane calculated using BNL is not important.

We evaluated dispersion corrections for the most significant reactions using the nonlocal van der Waals density functional (vdW-DF).³³ Revised-PBE³⁴ was used as the gradient correction on the exchange part of the exchange-correlation functional.

Table 2. Relaxed Geometry and Energy Obtained Using PBE when Li Is Placed in Different Positions with Respect to the Step^a



Table 2. continued



"The Li atom is shown in pink, the Mg atoms are shown in beige, and the O atoms are shown in red. Note these structures are repeated periodically in the plane parallel to the (100) surface. For clarity atoms representing the continuation of the periodic structure in the step direction are shown faintly so that the periodic step structure will be easier to visualize. Li–O bonds of less than 2 Å are shown as colored lines.

III. RESULTS

A. Dissociation Energy of Methane. We calculated the dissociation energy of methane into an isolated hydrogen atom and an isolated methyl radical. We made sure all our calculations were converged for kinetic energy cutoff and vacuum length. When using the PBE GGA functional we obtained a dissociation energy of 4.70 eV. This is similar to the value of 4.85 eV obtained by Dash and Gillan¹¹ and compares well with the experimental value³⁵ of 4.5 eV. The difference of 0.2 eV between the experimental results and our result is very close to the typical zero-point energy of the CH bond.

B. Lithium Positions on the Surface and the Steps. In order to analyze the binding energies to the Li-doped MgO surface, we first checked the energy of different slab configurations in order to determine which position is more energetically favorable for the Li substitutional defect. We found that for a flat surface it is preferable for Li to be in the surface layer rather than in the subsurface layer by 0.04 eV. This is a small difference, not much larger than the degree of accuracy of our calculations. For the step configuration we tried placing Li in 5 different positions as shown in Table 2. It must be remembered that these are periodic structures in the horizontal direction (parallel to the (100) slab surface) and

therefore the periodically repeated unit cell is shown in the figure. We repeated all the calculations for thicker slabs in order to check that we were converged for slab thickness.

On the step the differences in energy are significant, with position A being the least favorable and position C being the most favorable. When Li is in position C (a low-coordination site at the edge of the step) Li and the surrounding atoms are less constrained than when they are in the bulk of the step. In other words, they have more geometrical freedom to move to energetically favorable positions which leads to a lower energy. Additionally as the Li atom is on the surface of the step it will not need to diffuse to a subsurface layer to substitute Mg. The experimental results given by Trionfetti et al.¹⁹ support our findings: they observe the incorporated Li⁺ ions preferably occupying low-coordination-number surface sites, such as step-edge sites.

C. Binding Energies of Hydrogen to Various Surfaces. The first and most fundamental reaction to be considered when studying hydrogen abstraction from methane is that given by reaction 1 in which hydrogen binds to the catalytic surface and the resulting methyl radical departs from the catalytic surface:

$$CH_4 + [MgO]Li^+O^- \rightarrow CH_3^{\bullet} + [MgO]Li^+(OH)^-$$
(1)

The binding energies of hydrogen to various surfaces as well as the overall reaction energies are shown in Table 3. As discussed

Table 3. Binding Energies of a Hydrogen Atom to Slabs of Different Compositions and the Corresponding Reaction $Energies^a$

slab composition	binding energy (eV)	reaction energy (eV)
flat (100) MgO slab (no Li)	0.82	3.88
MgO step (no Li)	1.73	2.97
flat (100) Li/MgO slab, Li in subsurface layer	4.42	0.28
flat (100) Li/MgO slab, Li on the surface	4.27	0.43
Li/MgO step, Li in position A at the bottom of the step-edge	4.77	-0.07
Li/MgO step, Li in energetically preferable position C at the top of the step-edge	4.95	-0.25
a _T ,,	. DDE 6	4: 1

"These calculations were performed using the PBE functional.

in section II, the binding energy is given by the energy of the relaxed (Li/)MgO slab plus the energy of the isolated hydrogen atom minus the energy of the relaxed (Li/)MgO:H complex. The reaction energies are given by subtracting the binding energy from the dissociation energy of methane into an isolated hydrogen atom and methyl radical.

From this table it is clear, as also noted by other groups previously (see e.g. ref.11), that the presence of Li dopant atoms makes it much more energetically favorable to bind hydrogen. The Li atom replaces a Mg atom leading to a creation of a $[Li^+O^-]$ center with a hole localized on one or more of the neighboring oxygen atoms. It has been speculated that the $[Li^+O^-]$ defect stabilizes the surface O^- species which binds with the hydrogen atom.⁶ Without the presence of the Li doping atom the reaction energy is strongly endothermic both for a flat and a stepped surface. Indeed it is known that the pristine flat MgO (100) surface is chemically inert.⁶

For Li-doped MgO surfaces, the overall reaction energy when the slab is flat is mildly endothermic and is slightly less endothermic when the Li is in the subsurface layer (the less energetically favorable position), as was also seen by references11 and 12. Here we show that while the overall reaction energy is **mildly endothermic on a flat surface**, it is **mildly exothermic when the Li atom is situated on a step**. Furthermore, it is most exothermic when the Li atom is situated in the most energetically favorable position, on the top corner of the step. The difference in reaction energy between the flat surface and the step surface is 0.53 eV which is a significant difference.

In Table 4 we show how hydrogen binds to the flat surface and the stepped surface. The difference in binding energies can be understood by comparing the images in Table 4 of the Li/ MgO surface with and without bound hydrogen. When hydrogen binds to the flat surface the Li/MgO lattice becomes greatly distorted. The bond between Li and the surface oxygen increases from 2.30 to 2.87 Å upon hydrogen bonding, greatly straining the lattice. When the surface has a stepped structure the atoms on the step are less constrained than on the flat surface and have much more freedom to move in space to the most energetically favorable position. Therefore, when the stepped lattice structures (with Li on the top step-edge) are compared, with and without bonded hydrogen, it is clear that the distortion of the lattice upon binding hydrogen is much smaller than for the flat surface. A measure of this is given by the relatively small increase in the length of the long Li–O bond from 2.59 to 2.75 Å upon hydrogen bonding. The reduction in the distortion of the Li/MgO lattice when hydrogen binds to a step edge rather than a flat surface corresponds to a lowering in lattice strain and thus more favorable binding energies. The gain in binding energy at the step may also be due to the higher reactivity (less stable electronic configuration) of the step structure. When Li is on the bottom of the step corner, energy is gained by the hydrogen atom approaching an additional oxygen atom.

It should be noted that the length of the O-H bond stays the same irrespective of the surface to which hydrogen binds. Additionally when Li is in the surface layer the H atom moves toward the Li atom, both in the flat and stepped surfaces.

1. Dispersion Corrections. We evaluated dispersion corrections for the most significant reactions using the nonlocal van der Waals density functional (vdW-DF).³³ Revised-PBE³⁴ was used as the gradient correction on the exchange part of the exchange-correlation functional. We chose to calculate the binding energies of the most energetically favorable reactions (Table 5).

The binding energies given in the table show that dispersion corrections make it more favorable to bind hydrogen to the catalyst surface. However, they do not significantly alter our principal finding that it is preferable by around 0.6 eV to bind to the step-edge rather than the flat catalytic surface.

2. Correction of Spurious Self-Interaction. In order to determine whether the spurious self-interaction present in local and semilocal exchange-correlation functionals affects the energetic advantage of hydrogen binding to a stepped rather than a flat surface, we also performed the calculations using the BNL³⁰ range-separated hybrid functional which corrects for self-interaction. We used the range parameter $\gamma = 0.1$ which correctly models bulk MgO, and in particular gives correct band-gaps.³² As the BNL functional is much more computer intensive we performed our calculations on smaller step structures and on flat surfaces with a smaller supercell (see Figure 1).

In all stepped structures we placed Li at the top edge of the step and for all flat surfaces we placed Li in the subsurface layer as these are the most energetically favorable positions for the binding of hydrogen. It should be noted that the BNL functional was implemented in conjunction with the local LDA functional. Therefore, we performed additional calculations using only LDA to differentiate between effects due to the choice of the local functional or due to the correction of selfinteraction.

As can be seen in Table 6 the choice of functional only slightly affects the amount of energy gained by binding hydrogen to a stepped rather than a flat surface; and correcting self-interaction does not have a significant effect on the relative binding energies. Note these calculations are only intended to provide an indication of the degree to which correcting for selfinteraction changes the energy gained by binding hydrogen to a stepped rather than a flat surface. Due to the insufficiently large structures that were necessary in order to perform computerintensive BNL calculations, the absolute values of energy gain are inaccurate, as can be seen when comparing the PBE results for the small and large structures. However, the principal qualitative observation that correcting self-interaction does not greatly alter the energy gained by binding to a stepped rather than a flat surface should remain valid.

Table 4. Relaxed Geometry Obtained Using PBE When Hydrogen Binds to the Li/MgO Surface^a

Hydrogen bound to a flat	0.001
	=0.97A
surface of Li/MgO (100) Li-O(1)	=2.87Å
laver. (c.f. dist	tances of ≈2.17Å
The binding oxygen atom	surface O atoms
O(1) is lifted significantly and sub-	surface Mg atoms)
away from the surface and the Li atom is pushed down	=1.92Å
from its sub-layer. (c.f. dist	tances of≈2.10Å
between	subsurface Mg
atoms a	nd subsubsurface
O atoms	5)
Mg-O(1)=2.25Å
(c.f Mg	-O≈2.10Å for
surface	atoms)
Li-0=2.	135Å within the
subsurfa	ace layer
(c.f Mg	-O ≈ 2.10Å in
subsurfa	ace layer)
Flat surface of Li/MgO	=2.30Å,
(100) without bound	=2.13Å
hydrogen.	
lifted out of the surface but	
to a much lesser extent than	
when hydrogen is bound.	

Table 4. continued



Table 4. continued

Description	Diagram	Bond lengths
Hydrogen bound to a flat surface where Li is in the surface layer. Note the hydrogen atom moves towards the Li ion.		
Hydrogen bound to a stepped surface where Li is in the subsurface layer at the bottom of the step-edge in energetically unfavorable position A. Here the hydrogen while bound to O(1) is also attracted to O(3)		H-O(1)=0.99Å H-O(3)=2.11Å Li-O(1)=2.57Å Li-O(6)=1.96Å

 a The H atom is shown in blue, the Li atom is shown in pink, the Mg atoms are shown in beige, and the O atoms are shown in red. Note these structures are repeated periodically in the plane parallel to the (100) surface. For clarity atoms representing the continuation of the periodic structure in the step direction are shown faintly so that the periodic step structure will be easier to visualize.

Table 5. Dispersion Corrections to the Binding Energy of Hydrogen to Li/MgO $\,$

		binding (e	binding energy (eV)	
binding species	slab composition	PBE	vdW- DF	
Н	Li/MgO-flat (100) surface (Li in subsurface layer)	4.42	4.61	
Н	Li/MgO step, Li in energetically preferable position C at the top of the step-edge	4.95	5.21	
ſ				



Figure 1. Left: Small step structure used for calculations performed with the BNL functional. Right: Small supercell used for calculations on flat surfaces performed with the BNL functional. Note these structures are repeated periodically in the directions parallel to the (100) surface. The Li atom is shown in pink, the Mg atoms are shown in beige, and the O atoms are shown in red.

Table 6. Effect of the Functional on the Binding Energies	of
Hydrogen to Flat and Stepped Li/MgO Surfaces	

	binding energy (eV)		
functional	flat (100) surface	stepped surface	energy gained by binding to stepped surface (eV)
PBE (large structure)	4.42	4.95	0.53
PBE (small structure)	4.00	4.95	0.95
LDA (small structure)	4.48	5.49	1.01
BNL (small structure)	4.61	5.52	0.91

D. Possibility of Binding the Methyl Radical to the Catalyst Surface. The previous subsection discussed the binding of hydrogen to the catalytic surface (reaction 1). Now we will consider whether it is favorable to bind the methyl radical to the surface instead of the hydrogen atom (reaction 2), or whether it would be favorable to bind both the methyl radical and the hydrogen atom (reaction 3). It is reasonable that both the hydrogen atom and the methyl radical could bond to two different oxygen atoms adjacent to the *same* Li defect, as the distance between these oxygen atoms is small and the products produced upon the dissociation of methane would be close enough to bind to the adjacent oxygen and the methyl radical could be not calculate the energy for bonding hydrogen and the methyl

radical to oxygen atoms adjacent to *different* Li defects as the distance would be too large.

1. Binding of the Methyl Radical Instead of Hydrogen to the Catalyst Surface (Reaction 2). As can be seen in Table 7

Table 7. Binding Energies of Hydrogen Atoms and Methyl Radicals to Slabs of Different Compositions, and the Corresponding Reaction $Energy^{a}$

binding species	slab composition	energy (eV)	reaction energy (eV)
Н	MgO-flat (100) surface	0.82	3.88
Н	MgO-step	1.73	2.97
Н	Li/MgO-flat (100) surface (Li in subsurface layer)	4.42	0.28
Н	Li/MgO-flat (100) surface (Li in surface layer)	4.27	0.43
Н	Li/MgO-step (Li at bottom edge of step in position A)	4.77	-0.07
Н	Li/MgO-step (Li at top step-edge in energetically favorable position C)	4.95	-0.25
CH_3	MgO-flat (100) surface	-1.06	5.76
CH_3	Li/MgO-flat (100) surface (Li in subsurface layer)	3.06	1.64
CH_3	Li/MgO-step (Li at the top step-edge in energetically favorable position C)	3.64	1.06
H+CH ₃	Li/MgO-flat (100) surface (Li in the subsurface layer)	3.51	1.19
H+CH ₃	Li/MgO-flat (100) surface (Li in the surface layer)	3.72	0.98
H+CH ₃	Li/MgO-step (Li at the top step-edge in energetically favorable position C, hydrogen binds to step-edge and the methyl radical binds to top of step terrace -see figure in Table 8)	4.63	0.07
H+CH ₃	Li/MgO-step (Li at the top step-edge in energetically favorable position C, hydrogen binds to step-edge and the methyl radical binds to step-edge -see figure in Table 8)	5.52	-0.82
^{<i>a</i>} These of	calculations were performed using the PBE	functiona	al.

the methyl radical does not bind to the flat pure MgO surface (binding energy = -1.06 eV). The methyl radical is distorted far away from its isolated planar shape when bound to the MgO surface (see Table 8, \angle HCH = 108° as compared to \angle HCH = 120° for the isolated methyl radical). When the methyl radical binds to the Li/MgO surface (flat or stepped) the binding energies are positive but smaller than the hydrogen binding energies by 1.3 eV, leading to significantly endothermic reaction energies. The distortion of the methyl radical also occurs when bound to the Li/MgO surface (see Table 8, where ∠HCH = $107^{\circ} - 108^{\circ}$ and \angle HCH = $105^{\circ} - 110^{\circ}$ for methyl bound to the flat and stepped surface respectively). Note the bond length between Li and the binding surface oxygen is 2.92 Å for the flat surface structure, which is comparable to the Li–O bond length when hydrogen bonds. This shows that the reduction in binding energy when the methyl radical bonds instead of hydrogen is not due to an increase in the distortion of the Li/ MgO substrate. Even when methyl is bound to the step-edge and so has more geometric freedom the reaction is still strongly endothermic.

It should be noted that the same energetic advantage of 0.6 eV to binding at the step-edge rather than the flat (100) surface is seen when either hydrogen or the methyl radical is the binding species. The similarity in the way the binding species bind to the Li/MgO step-edge can be seen by comparing the binding of the hydrogen atom with the binding of the methyl radical as shown in Tables 4 and 8: The methyl radical moves

toward the step-edge Li ion in the same way as can be seen for the bound H in Table 4. Additionally, the distortion of the step lattice upon methyl binding, as exemplified by the Li–O bond lengths, is very similar to when hydrogen binds. As mentioned above the distortion of the flat surface lattice was also very similar irrespective of whether hydrogen or methyl bonded to the surface O atom. This further strengthens our claim that the energetic gain, when the binding occurs on a stepped surface rather than a flat surface, arises in part due to the extra geometric freedom associated with the step structure and the corresponding reduction in distortion of the Li/MgO lattice.

The C–O bond length is only slightly affected by the substrate to which the methyl radical binds, as was also observed when hydrogen was the binding species.

We conclude that it is significantly less favorable to bind methyl instead of hydrogen to the catalyst surface.

2. Binding of Both Hydrogen and the Methyl Radical to the Catalyst Surface (Reaction 3). When both hydrogen and the methyl radical bind to the step-edge, the reaction energy is significantly exothermic (-0.82 eV). It should be noted (see Table 7) that when the methyl radical binds to the top of the step terrace the binding energy is much lower (by 0.89 eV), due to the much greater distortion of the Li/MgO lattice structure as seen in Table 9. When both hydrogen and the methyl radical bind to the flat Li/MgO surface the reaction energy is significantly endothermic irrespective of the position of the Li defect (see Table 7) and large distortion of the Li/MgO lattice is observed (see Table 9). These observations further strengthen our claim that the greater degree of freedom of the step-edge atoms and the subsequent reduction in lattice distortion give rise to the observed increase in binding energy and exothermic reaction energies. We also calculated the dispersion corrections, given by the vdW-DF nonlocal functional, for the binding of both hydrogen and the methyl radical to the step-edge. The reaction energy when corrected for dispersion is -0.63 eV, which is less favorable than the reaction energy of -0.82 eV obtained without correcting for dispersion. However, the qualitative conclusion remains that the reaction energy is significantly more exothermic when both hydrogen and the methyl radical bind to the step-edge than when only hydrogen binds.

We conclude that it is less favorable to bind both hydrogen and the methyl radical to the flat catalyst surface than only hydrogen. However, when **both hydrogen and the methyl radical bind to step-edge oxygen atoms the reaction energy is significantly more exothermic** (with a large exothermic reaction energy of -0.82 eV), than when only hydrogen binds (reaction energy of -0.25 eV).

E. Transition State Energy Barrier and Reaction Pathway. In the previous section we showed that the process in which hydrogen is abstracted from methane and attaches to the catalytic step-edge is an exothermic reaction. If subsequently the methyl radical also attaches to the stepedge, the reaction becomes even more exothermic. In this section we calculate the transition state energy barrier and describe the reaction path for both processes.

For the transition state calculations we studied a step where the Li atom was situated in the top edge position. This is an energetically favorable position for the Li dopant as described in section III.B. A problem emerged when the methane molecule approaches the step-edge along the "preferred direction", the vector of the hydroxyl (OH) bond within its final bound state (see vector in Figure 2). We noticed that for

Table 8. Relaxed Geometry Obtained Using PBE When Methyl Binds to the Li/MgO Surface^a



Table 8. continued



^{*a*}The H atoms are shown in blue, the Li atom is shown in pink, the Mg atoms are shown in beige, the O atoms are shown in red and the carbon atom is shown in yellow. Note these structures are repeated periodically in the direction parallel to the (100) surface. For clarity atoms representing the continuation of the periodic step structure in the step direction are shown faintly so that the periodic step structure will be easier to visualize.

the 3-atom-wide steps described in the previous sections, methane spuriously interacts also with the adjacent periodic image of the step. To alleviate this we decided to use a narrower step so as to increase the distance between adjacent step images (an alternative would be to increase the supercell size but this would incur a heavy computational cost). In both reaction paths the lower slab atoms were fixed while most of the step atoms were allowed to move freely (as demarcated using a black border in Figure 2). We found that these constraints together with the use of the narrower step did not significantly change the reaction energy (increased the reaction energy for the abstraction of H by +0.09 eV).

All reaction path searches were performed using the nudged elastic band (NEB)³⁶ method. We describe the method we used to find a good initial path for the NEB below. As there is an unpaired electron in the supercell (due to the odd number of valence electrons) we performed spin-polarized calculations, allowing for full relaxation of the ensemble spin state.

1. Abstraction of Hydrogen from Methane at the Catalytic Step-Edge. We now describe the first stage of the reaction, in

which hydrogen is abstracted from methane and bonds to the step-edge forming a hydroxyl group. In order to find a good initial path for the NEB calculations, we first explored the potential energy surface by

- Fix the C atom and binding H(1) atom positions along the "preferred direction", the vector of the hydroxyl (OH) bond within its final bound state (see vector in Figure 2).
- (2) Fully relax all other atoms (except for the fixed slab atoms described above).
- (3) Calculate the energy of the relaxed state.

Steps 1 to 3 were repeated for varying C and H(1) distances along the bonding vector and the 2D saddle point energy was found. This saddle point energy gives a very good estimate of the transition state energy. The initial path used in the NEB consisted of the initial state (the bare step and distant methane molecule), saddle-point state, and final state (hydrogen bound to step and distant methyl radical) together with evenly spaced intermediate states. The final NEB transition state is shown in

Table 9. Relaxed Geometry Obtained Using PBE when Methyl and Hydrogen Bind to the Li/MgO Surface^a



Table 9. continued



^aThe H atoms are shown in blue, the Li atom is shown in pink, the Mg atoms are shown in beige, the O atoms are shown in red, and the carbon atom is shown in yellow. Note these structures are repeated periodically in the direction parallel to the (100) surface. For clarity atoms representing the continuation of the periodic step structure in the step direction are shown faintly so that the periodic step structure will be easier to visualize.

Figure 2. The transition state energy barrier going from reactants (the bare step and distant methane molecule) to products (hydrogen bound to the step edge and distant methyl radical) was 0.21 eV. After the transition state is located we estimated the dispersion energy effect by performing vdW-DF single-point energy calculations at the initial and transition states. We found that the dispersion-corrected transition state energy barrier increases to 0.34 eV. It should be noted that all transition energies stated here have an accuracy of no better than 0.1 eV due to the narrow step and fixed lower slab atoms used for the transition state calculations.

The reaction path of hydrogen abstraction from methane at the step-edge is shown in Figure 3. The reactants (R_1 in Figure 3) are the relaxed Li/MgO step structure and the relaxed isolated methane molecule. The energy of R_1 is designated as the zero energy of the path. The reaction products (P_1 in Figure 3) are the relaxed configuration of the step with hydrogen fully

bonded to the edge and an isolated relaxed methyl radical. The calculated reaction energy is -0.16 eV. This value is slightly higher than -0.25 eV, calculated in section III.C, due to the narrower step and fixed lower slab atom positions used here.

During the reaction described in Figure 3, the methane molecule approaches the binding step-edge oxygen atom and the C-H methane bond elongates, until that bond is broken and an O-H bond is formed instead. The transition state with C-H = 1.28 Å and O-H=1.28 Å (TS₁ in Figure 3) has an energy of +0.21 eV. The minimum energy (-0.30 eV) along the reaction path occurs at point M in Figure 3 where the hydrogen is bonded to the step-edge (O-H distance is 0.97 Å) and the remaining methyl radical has not fully departed from the reaction site (C-H distance is 2.38 Å while it is 1.09 Å in methane and 1.28 Å in TS₁). That the minimum energy occurs when the methyl radical has not yet fully departed from the surface is probably due to the long-distance interaction of the



Figure 2. Narrower step structure used for the transition state and reaction path calculations. The carbon atom is shown in yellow, the hydrogen atoms in blue, the oxygen atoms in red, the magnesium atoms in beige, and the lithium atom in pink. The atoms with a bold black border are the slab atoms that are free to relax. The direction vector of the binding O–H bond is shown as a dashed arrow. The specific configuration shown in this figure is of the transition state for the abstraction of hydrogen from methane at the step-edge via the oxygen atom adjacent to a Li substitutional defect. The transition state bond lengths are the bonding O(1)–H(1) bond = 1.28 Å; the breaking C–H(1) bond = 1.28 Å; C–H(2) = 1.09 Å, C–H(3) = 1.09 Å, C–H(4) = 1.09 Å; O(1)–Mg(1) = 2.24 Å, O(1)–Mg(2) = 1.98 Å, O(1)–Mg(3) = 2.01 Å; Li–O(1) = 2.69 Å, Li–O(2) = 2.02 Å, Li–O(3) = 1.86 Å.

methyl radical with the hydroxyl group. During the entire reaction path the expectation value of the spin component S_z does not change significantly from 0.5 (the initial state has spin 0.485, the transition state has spin 0.47 and the final state has spin 0.5). We remind the reader that the expectation value of the spin component is an ensemble average. A value of 1/2 means that the highest occupied spin up eigenstate is fully occupied while that of the spin down is empty, and a value of spin zero means that in half of the Kohn–Sham particles the highest occupied spin up eigenstate is occupied while in the other half the spin down eigenstate is occupied. The spin contamination is small, as the occupied spin up and spin down orbital energies are all very similar, except for the singly occupied highest eigenstate.

After the formation of the O-H bond when the methyl radical has not yet fully detached from the surface (point M) there are several possibilities:

- (1) The methyl radical can fully detach from the surface and enter into the gas phase (Reaction 1). This requires an energy of 0.14 eV, which is readily available from the energy released by the formation of the O–H bond. There is experimental evidence^{4,5} that this channel can occur.
- (2) The system can dissipate its excess energy and the methyl radical will remain in proximity to the step-edge.
- (3) The methyl radical can leave the OH site and bond to an adjacent step-edge O atom. This process is described in detail in the next subsection.

2. Binding of the Methyl Radical to the Catalytic Step-Edge after Hydrogen Has Been Bound. We next studied the reaction pathway to bind the methyl radical to the step-edge oxygen atom O(3) when hydrogen is already bound to the



Figure 3. Reaction pathway of the abstraction of hydrogen from methane at the step-edge via an oxygen atom adjacent to a Li substitutional defect. The carbon atom is shown in yellow, the hydrogen atoms in blue, the oxygen atoms in red, the magnesium atoms in beige, and the lithium atom in pink. The zero energy is the energy of the reactants, R_1 : the energy of the relaxed Li/MgO step structure plus the energy of the relaxed isolated methane molecule. The dashed line showing -0.16 eV is the energy of the reaction products, P_1 : the energy of the relaxed [MgO] Li⁺ (OH)⁻ step structure plus the energy of the isolated relaxed methyl radical. TS₁ is the transition state and M is the energy minimum. The bold blue line is a guide to the eye based on the NEB path results.

other step-edge oxygen atom O(1) as shown in Figure 4. We did not explore binding to the other surface oxygen atom O(4)



Figure 4. Methyl radical bonding to the step-edge oxygen atom O(3) when hydrogen is already bound to the other step-edge oxygen atom O(1) adjacent to the substitutional Li atom. The carbon atom is shown in yellow, the hydrogen atoms in blue, the oxygen atoms in red, the magnesium atoms in beige, and the lithium atom in pink. The direction vector of the binding C–O bond is shown as a dashed arrow. The specific configuration shown in this figure is of the state for which the energies of the spin = 1/3 states and spin = 1/2 states cross. The spin = 1/2 configuration is shown here. The spin-crossing configuration bond lengths are the bonding C–O(3) bond distance = 2.38 Å; the bound O(1)–H(1) bond distance = 0.96 Å; C–H(2) = 1.08 Å, C–H(3) = 1.08 Å, C–H(4) = 1.09 Å; O(3)–Mg(1) = 2.01 Å, O(3)-Li = 1.84 Å, O(1)-Li = 2.74 Å; O(2)-Li = 2.03 Å.

adjacent to the Li defect as for the wider step this atom is on the step terrace surface and the reaction was much less energetically favorable.

While studying the reaction pathway we noticed a sensitivity to the way we chose the initial positions of the **free** atoms, i.e. when a full ionic relaxation was performed with fixed lower slab atoms and fixed carbon atom position, the energy obtained depended on the initial positions of the atoms which were free to relax. This is surprising as one would expect that the result of an ionic relaxation should be independent of the initial positions of the free atoms, and indicates the existence of a metastable state decoupled from the global minimum. We set the initial positions of the free atoms and performed the ionic relaxations in the following two ways:

Method A ("Product $P_2 \rightarrow Reactant R_2$ ", Black Curve in Figure 5, Top Panel). The reaction path starts at the product P_2 (see Figure 5) given by the fully relaxed state when the methyl radical is bonded to O(3) and the hydrogen atom to O(1), and the lower slab atoms are fixed, as described above. The methyl radical is then adiabtically shifted a small distance away from the step along the bonded C-O(3) direction vector (as shown in Figure 4) and then all the atoms except for the carbon and fixed slab atoms are relaxed, and the energy obtained is plotted in Figure 5 (top panel). The relaxed atomic positions now comprise the initial atomic step positions for the next calculation where the methyl radical is shifted further away from the step along the bonded C-O(3) direction vector. Once again all the atoms except for the carbon and fixed slab atoms are relaxed and the new relaxed energy and atomic positions are calculated. This process is repeated to obtain the reaction path.

Method B ("Reactant $R_2 \rightarrow$ Product P_2 ", Red Curve in Figure 5, Top Panel). The reaction path starts from the relaxed state where the methyl radical is far from the hydrogen-bonded step (C-O(3) = 3.67Å), and the positions of the lower slab atoms and the carbon atom are fixed (configuration R_2 in Figure 5). The methyl radical is then adiabatically shifted toward the step-edge along the bonded C-O(3) direction vector while relaxing all the atoms except for the carbon and fixed slab atoms at each stage.

The red and black diabatic curves in the top panel of Figure 5 cross at a configuration designated C which is shown in Figure 4. In configuration C the C–O(3) bond length is 2.38 Å and the energy of configuration C is 0.64 eV larger than that of the methyl-O(3) bonded configuration P_2 . It should be noted that the energy of C is 0.38 eV higher than the minimum energy along the H-abstraction reaction path at configuration M and 0.08 eV larger than that of the relative energies of R_1 , M, R_2 , and P_2 are shown in Figure 6 in the next section which summarizes the entire reaction pathway.

The adiabatic procedure described above did not allow for a smooth transition between the two curves, indicating zero diabatic coupling. Looking at the expectation value of the spin component S_z along these two diabatic curves in Figure 5 we see that the red curve has spin 1/2 while the black curve has a reduced value of about 1/3 at the crossing point C. This rather large difference in spin explains why there is no way to move adiabatically between these two diabats. We remind the reader that the expectation value of the spin component is an ensemble average: A value of 1/2 means that the highest occupied spin up eigenstate is fully occupied while that of the spin down is empty, and a value of 1/3 means that in 83% of the Kohn–Sham particles the highest occupied spin up eigenstate is occupied.

The path discussed above does not allow for the methyl binding to occur because of the zero diabatic coupling due to the two different spin states. We therefore carried out a more systematic search using NEB. Here, we fixed the initial state (the methyl radical sufficiently far away from the step (C-O(3))=3 Å) and therefore in a spin = 1/2 state) and final state (methyl fully bonded) and we did not specify an initial path in order to allow the system to reach a path where the spin states could cross smoothly. Such a path was found but involved a significantly larger reaction barrier and is shown in the bottom panel of Figure 5. The energy of the transition state (labeled TS_2 in Figure 5) is 1.08 eV larger than that of the methyl-O(3) bonded configuration P_2 . It should be noted that the energy of TS_2 is 0.81 eV higher in energy than the minimum energy along the H-abstraction reaction path at configuration M and 0.51 eV larger than that of the reactants at R₁. The entire reaction path showing these relative energies is presented in Figure 6 in the next section. We estimated the dispersion energy effect by performing vdW-DF single-point energy calculations at the initial (R_1) and transition (TS_2) states. We found that the dispersion-corrected transition state energy barrier increases from 0.51 to 0.52 eV. The transition state TS₂ and its bond lengths are shown in the inset in the bottom panel of Figure 5.

Article



Figure 5. Reaction path for the methyl radical to bond to the step-edge oxygen atom O(3) when hydrogen is already bound to the other step-edge oxygen atom O(1) adjacent to the Li defect. All energies are in relation to the state where the methyl is fully bonded, labeled P_2 in the figure. A C-O(3) bond length of 1.43 Å is obtained for the fully bonded state as represented by the vertical dashed line. The zero energy is shown as a horizontal dashed line for the reader's convenience. The reactants R_2 consist of the fully relaxed step with hydrogen bonded to O(1) and the methyl radical at a distance C-O(3) = 3.67 Å. All calculations are spin-polarized. The small numbers on the graph show the spin S_z expectation value. Top: Energy obtained from an ionic relaxation. The position of the carbon atom and lower slab atoms are kept fixed as described in the text and the remaining atoms are free to relax. The black squares represent the energy obtained from a full ionic relaxation where the initial free slab atom positions are given by the fully relaxed state when the initial free slab atom positions are given by the fully relaxed state when the initial free slab atom positions are given by the fully relaxed state when the methyl radical is sufficiently far from the step (method B, see text). The crossing point of the two diabatic curves is labeled C. Bottom: Results from the NEB calculation. The initial configuration used in the NEB calculation corresponds to the point in the figure with C-O(3) = 3 Å, and the final point was the fully bonded state P_2 . R_2 is also shown connected to the initial NEB state by a dashed blue line. The transition state, TS_2 , is shown as an inset. The transition state bond lengths are the bonding C-O(3) bond distance = 1.91 Å; the bound O(1)-H(1) bond distance = 0.96 Å; C-H(2) = 1.09 Å, C-H(3) = 1.09 Å, C-H(4) = 1.09 Å; O(3)-Mg(1) = 2.17 Å, O(3)-Li = 1.93 Å, O(1)-Li = 2.59 Å; O(2)-Li = 1.94 Å.



Figure 6. Reaction pathway for hydrogen abstraction from methane at a step-edge Li^+O^- defect. In the first reaction pathway corresponding to reaction 1, the methyl radical product leaves the Li/MgO surface and enters the gas phase (the final state is labeled P₁). In the second reaction pathway, corresponding to reaction 3, the methyl radical bonds to the adjacent step-edge oxygen atom, (the final state is labeled P₂). All energies are in relation to the reactants, R₁, which consist of the fully relaxed Li/MgO step and the relaxed isolated methane molecule. The transition energies for hydrogen abstraction and methyl bonding are labeled TS₁ and TS₂ respectively. The minimum energy of the hydrogen abstraction stage is labeled M. The reactants for the methyl bonding stage are labeled R₂ and consist of the hydrogen-bonded Li/MgO step and the methyl radical 3.67 Å away from the adjacent step-edge oxygen atom. (a) The transition state energies when corrected for dispersion are TS₁ = 0.34 eV and TS₂ = 0.52 eV. (b) The product energies when the calculations are performed on the wide step and all slab atoms are free to move are P₁ = -0.25 eV and P₂ = -0.82 eV.

IV. CONCLUSIONS AND DISCUSSION

In this paper we have used first-principle DFT-calculations to study the abstraction of hydrogen from methane via a surface Li⁺O⁻ defect on a Li-doped MgO catalyst. Li/MgO surfaces are not perfectly flat but possess steps and corners with low-coordinated ions.^{17–19} In particular, it was observed¹⁹ that sol– gel prepared Li/MgO catalysts exhibited both increased catalytic performance and preferred substitution of Li ions at low-coordinate step sites. The nonflat, stepped surface is a different catalytic material from the flat surface and so it is necessary to study the reaction energy and pathway for hydrogen abstraction at [Li⁺O⁻] defects on this surface too. When hydrogen is abstracted from methane a hydrogen atom and methyl radical are produced. We looked at three possible reaction outcomes: Reaction 1 where hydrogen binds to a surface oxygen-atom adjacent to a Li defect and the methyl radical departs from the surface and enters the gas phase. There is experimental evidence^{4,5} that the methyl radicals do bond in the gas phase to create a C-C bond and form ethane. Reaction 2 where the methyl radical binds to a surface oxygen-atom adjacent to a Li defect and hydrogen enters the gas phase. Reaction 3 where both the methyl radical and hydrogen bind to surface oxygen atoms adjacent to a Li defect. We summarize and discuss the reaction energies, mechanisms and activation energies.

A. Reaction Energies. As a first stage in studying the step defect in Li/MgO we determined the most energetically favorable position for the Li substitutional defect and found it to be at the top of the step-edge. We next studied the hydrogen abstraction reaction and found that Li^+O^- defects are essential. This was already established for a flat surface (see, e.g., ref 11)

and we confirmed that it also holds for a stepped surface: without this defect the abstraction reaction is extremely endothermic (>3 eV).

We found that there was a significant increase in reactivity when the reactions studied occurred via a Li⁺O⁻ defect located at the step-edge rather than on a flat surface. This resulted from the increase in binding energy at the step-edge. For H abstraction from methane (Reaction 1) the reaction at the step edge via a Li^+O^- defect is exothermic by -0.25 eV, whereas it is endothermic by +0.28 eV at the flat surface. Thus, there is a 0.53 eV (0.6 eV with dispersion corrections) energetic advantage to performing the reaction at a surface step. While there is uncertainty in the literature as to whether the reaction on the flat surface is endothermic or exothermic our results show that the reaction on the stepped surface is very likely to be exothermic because even if we subtract 0.6 eV from the most endothermic reported flat surface result (as given in Table 1) we still obtain an exothermic reaction energy at the step-edge. This result is of importance because if this reaction is the essential first step of the entire catalytic process it must be exothermic.

The increase in reactivity at the stepped rather than flat surface occurs not only when hydrogen binds to a step-edge oxygen atom (reaction 1) but also for methyl binding (reaction 2). However, the energy released upon binding methyl to the surface is not of sufficient magnitude to compensate for the energy needed to break the CH bond in methane. Thus, the reaction energy when only methyl binds to the Li/MgO surface (reaction 2) is endothermic for both the flat (+1.6 eV) and stepped (+1 eV) surface, and the methyl radical will not bind instead of hydrogen.

When *both* hydrogen and methyl bind to adjacent step-edge oxygen atoms (reaction 3) the energetic advantage to binding at a step is even higher (an advantage of 1.8 eV is obtained). The reaction energy, in this case, is exothermic at the step, by -0.82 eV (-0.63 eV when corrected for dispersion) while highly endothermic (~ 1 eV) on a flat surface.

The gain in binding energy at the step is due to the higher reactivity (less stable electronic configuration) of the step structure and also to the enhanced geometric freedom of the atoms at the step-edge relative to the flat surface. This freedom leads to a reduction in lattice distortion and strain upon hydrogen and/or methyl binding. We note that the same trend of an increase in the relative binding energy when binding to a step-edge rather than a flat surface was also observed when we used a range-separated hybrid functional which corrects for the self-interaction of the electrons.

B. Reaction Pathways and Transition State Barrier Energies. The reaction pathway for hydrogen abstraction from methane at a step-edge Li^+O^- defect is shown in Figure 6. In the first reaction pathway corresponding to reaction 1, the methyl radical product leaves the Li/MgO surface and enters the gas phase, P₁. In the second reaction pathway, corresponding to reaction 3, the methyl radical bonds to the adjacent step-edge oxygen atom, P₂.

Both reactions 1 and 3 have the same first step of abstraction of hydrogen from methane at a step-edge oxygen atom adjacent to a step-edge Li defect. The barrier for this step is 0.21 eV (the energy difference between TS₁ and the reactants R₁ in Figure 6), which increased to 0.34 eV with dispersion corrections. This value compares reasonably well with the value of 0.44 eV for the activation energy reported in ref 20 for H abstraction at the corner of an island (as opposed to at the edge of a step in our case). These activation energies are significantly lower than the experimental values of 0.88 eV^{14} to 2.4 eV^2 for the consumption of methane and formation of gas phase methyl radicals or C2 hydrocarbons over Li-doped MgO. The discrepancy between the theoretical and experimental results does not necessarily mean that the step/island mechanism is wrong since it could also be explained by the tendency of PBE and B3LYP to underestimate activation energy barriers.²

After the common first stage, reaction 1 then goes through to completion with the methyl radical departing the surface and entering the gas phase. There is no additional barrier for this process, as the required energy (0.14 eV) to go from the energy minimum state M to the reaction products P_1 is readily available from the energy released by the formation of the O– H bond. There is experimental evidence^{4,5} that this channel can occur.

Reaction 3 on the other hand goes through a second stage, involving a larger barrier, in which the methyl radical approaches an adjacent step-edge oxygen atom and binds to it. We wondered whether instead of two steps one can achieve reaction 3 in one concerted step. However, we could not find such a mechanism using NEB. This may be due to the relatively large distance (4.5 Å) between these two oxygen binding sites (see footnote 37). Hence we conclude that reaction 3 indeed involves two stages, the hydrogen atom is first abstracted from methane and binds to step-edge oxygen atom O(1) and subsequently the methyl radical binds to the adjacent step-edge oxygen atom O(3). The second stage, where the methyl radical approaches the step-edge and binds to it, involves crossing a barrier of 0.5 eV (the energy difference between the reactants R_1 and transition state TS₂ in Figure 6). There are two limits to

consider for reaction 3: If both substages occur as a single dynamical step then the reaction barrier for this reaction will be 0.5 eV. This is still smaller than the experimental activation energy but is significantly closer to it. The second limit is that both stages occur as separate dynamical steps and the total rate is the kinetic combination of the rates of the two processes. In this case the reaction barrier of the second stage is measured with respect to the point M and gives a value of is 0.8 eV (the energy difference between state M and TS₂ in Figure 6), which is very close to the reported experimental activation energy. The catalytic function of the Li/MgO surface must involve a step of releasing the bonded CH₃ radical. Such a process could perhaps occur by the heterogeneous interaction $(CH_3)_{gas}$ + $(CH_3)_{surf} \rightarrow C_2H_6$ which is highly exothermic as the energy of the LiO-CH₃ bond is only 0.4 eV, which is much smaller than the 3.9 eV C-C bond energy of ethane.²⁵

In summary, we have clearly shown that when hydrogen is abstracted from methane via a surface Li⁺O⁻ defect, there is a significant energetic advantage to binding hydrogen to a stepedge oxygen atom rather than on a flat surface. Furthermore, we have shown that the reaction energy for abstracting hydrogen from methane is exothermic when it occurs at stepedge. We have shown that there are two possible reaction pathways following the abstraction of hydrogen from methane and its bonding to the step-edge: the first in which the methyl radical immediately departs from the surface and enters the gas phase, and a second in which the methyl radical bonds to an adjacent step-edge oxygen atom. The reaction energy is more exothermic and the transition state barrier is larger in the second pathway. These findings suggest that surface steps which include lithium defects could be responsible for the catalytic behavior of Li/MgO.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Lunsford, J. H. The Catalytic Conversion of Methane to Higher Hydrocarbons. *Catal. Today* **1990**, *6*, 235–259.

(2) Ito, T.; Wang, J.; Lin, C. H.; Lunsford, J. H. Oxidative Dimerization of Methane over a Lithium-Promoted Magnesium Oxide Catalyst. *J. Am. Chem. Soc.* **1985**, *107*, 5062–5068.

(3) Driscoll, D. J.; Lunsford, J. H. Gas-Phase Radical Formation during the Reactions of Methane, Ethane, Ethylene, and Propylene over Selected Oxide Catalysts. *J. Phys. Chem.* **1985**, *89*, 4415–4418.

(4) Lunsford, J. H. *Methane Conversion by Oxidative Processes*; Van Nostrand Reinhold Catalysis Series: New York, 1992; pp 3–29.

(5) Driscoll, D. J.; Martir, W.; Wang, J. X.; Lunsford, J. H. Formation of Gas-Phase Methyl Radicals over Magnesium Oxide. *J. Am. Chem. Soc.* **1985**, *107*, 58–63.

(6) Arndt, S.; Laugel, G.; Levchenko, S.; Horn, R.; Baerns, M.; Scheffler, M.; Schlögl, R.; Schomäcker, R. A Critical Assessment of Li/ MgO-based Catalysts for the Oxidative Coupling of Methane. *Catal. Rev. Sci. Eng.* **2011**, *53*, 424–514. (7) Børve, K. J.; Pettersson, L. G. M. Hydrogen Abstraction from Methane on an MgO(001) Surface. *J. Phys. Chem.* **1991**, *95*, 7401–7405.

(8) Ackermann, L.; Gale, J. D.; Catlow, C. R. A. Interaction of Methane with a [Li] 0 center on MgO (100): HF, Post-HF, and DFT Cluster Model Studies. *J. Phys. Chem. B* **1997**, *101*, 10028–10034.

(9) Catlow, C. R. A.; French, S. A.; Sokol, A. A.; Thomas, J. M. Computational Approaches to the Determination of Active Site Structures and Reaction Mechanisms in Heterogeneous Catalysts. *Philos. Trans. R. Soc. A* **2005**, *363*, 913–936.

(10) Orlando, R.; Cora, F.; Millini, R.; Perego, G.; Dovesi, R. Hydrogen Abstraction from Methane by Li Doped MgO: A Periodic Quantum Mechanical Study. *J. Chem. Phys.* **1996**, *105*, 8937–8943.

(11) Dash, L. K.; Gillan, M. J. Assessment of Competing Mechanisms of the Abstraction of Hydrogen from CH_4 on Li/MgO (001). *Surf. Sci.* **2004**, *549*, 217–226 (2004).

(12) Nolan, M.; Watson, G. W. The Electronic Structure of Alkali Doped Alkaline Earth Metal Oxides: Li Doping of MgO Studied with DFT-GGA and GGA+*U. Surf. Sci.* **2005**, *586*, 25–37.

(13) Scanlon, D. O.; Walsh, A.; Morgan, B. J.; Watson, G. W. Competing Defect Mechanisms and Hydrogen Adsorption on Li-Doped MgO Low Index Surfaces: A DFT+ U Study. *e-J. Surf. Sci. Nanotechnol.* **2009**, *7*, 395–404.

(14) Muzykantov, V. S.; Shestov, A. A.; Ehwald, H. Mechanisms of Catalytic Activation of Methane and Ethylene on Magnesia Surface Elucidated by Isotopic Kinetics. *Catal. Today* **1995**, *24*, 243–244.

(15) Wu, M.-C.; Truong, C. M.; Coulter, K.; Goodman, D. W. Investigations of Active Sites for Methane Activation in the Oxidative Coupling Reaction over Pure and Li-Promoted MgO Catalysts. *J. Catal.* **1993**, *140*, 344–352. Wu, M.-C.; Truong, C. M.; Coulter, K.; Goodman, D. W. Nature of Active Sites in the Oxidative Coupling of Methane to Ethane over Li/MgO catalysts. *J. Vac. Sci. Technol. A* **1993**, *11*, 2174–2178.

(16) Orlando, R.; Millini, R.; Perego, G.; Dovesi, R. Catalytic Properties of F-centres at the Magnesium Oxide Surface: Hydrogen Abstraction from Methane. *J. Mol. Catal. A: Chem.* **1997**, *119*, 253– 262.

(17) Myrach, P.; Nilius, N.; Levchenko, S. V.; Gonchar, A.; Risse, T.; Dinse, K.-P.; Boatner, L. A.; Frandsen, W.; Horn, R.; Freund, H.-J.; et al. Temperature-Dependent Morphology, Magnetic and Optical Properties of Li-Doped MgO. *ChemCatChem* **2010**, *2*, 854–862.

(18) Zavyalova, U.; Geske, M.; Horn, R.; Weinberg, G.; Frandsen, W.; Schuster, M.; Schlögl, R. Morphology and Microstructure of Li/ MgO Catalysts for the Oxidative Coupling of Methane. *ChemCatChem* **2011**, *3*, 949–959.

(19) Trionfetti, C.; Babich, I. V.; Seshan, K.; Lefferts, L. Presence of Lithium ions in MgO Lattice: Surface Characterization by Infrared Spectroscopy and Reactivity towards Oxidative Conversion of Propane. *Langmuir* **2008**, *24*, 8220–8228.

(20) Kwapien, K.; Paier, J.; Sauer, J.; Geske, M.; Zavyalova, U.; Horn, R.; Schwach, P.; Trunschke, A.; Schlögl, R. Sites for Methane Activation on Lithium-Doped Magnesium Oxide Surfaces. *Angew. Chem., Int. Ed.* **2014**, *53*, 8774–8778.

(21) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652. Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785–789.

(22) Zheng, J.; Zhao, Y.; Truhlar, D. G. Representative Benchmark Suites for Barrier Heights of Diverse Reaction Types and Assessment of Electronic Structure Methods for Thermochemical Kinetics. J. Chem. Theory Comput. 2007, 3, 569–582. Vydrov, O. A.; Scuseria, G. E. Assessment of a Long-Range Corrected Hybrid Functional. J. Chem. Phys. 2006, 125, 234109.

(23) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; et al. QUANTUM ESPRESSO: a Modular and Open-Source Software Project for Quantum Simulations of Materials. *J. Phys.: Condens. Matter* **2009**, *21*, 395502. (24) For the ionic relaxation calculations the convergence threshold on the total energy and forces were 0.0001 Ry and 0.001 Ry/a_0 respectively.

(25) Haynes, W. M., Ed.; CRC Handbook of Chemistry and Physics, 95th ed. (Internet Version); CRC Press/Taylor and Francis: Boca Raton, FL, 2015.

(26) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* **1976**, *13*, 5188–5192.

(27) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(28) Bredow, T.; Gerson, A. R. Effect of Exchange and Correlation on Bulk Properties of MgO, NiO, and CoO. *Phys. Rev. B* 2000, *61*, 5194–5201.

(29) Cohen, A. J.; Mori-Sánchez, P.; Yang, W. Insights into Current Limitations of Density Functional Theory. *Science* 2008, 321, 792– 794. Zhang, Y.; Yang, W. A Challenge for Density Functionals: Self-Interaction Error Increases for Systems with a Noninteger Number of Electrons. J. Chem. Phys. 1998, 109, 2604–2608. Champagne, B.; Perpete, E. A.; van Gisbergen, S. J.; Baerends, E. J.; Snijders, J. G.; Soubra-Ghaoui, C.; Robins, K. A.; Kirtman, B. Assessment of Conventional Density Functional Schemes for Computing the Polarizabilities and Hyperpolarizabilities of Conjugated Oligomers: An Ab Initio Investigation of Polyacetylene Chains. J. Chem. Phys. 1998, 109, 10489–10498. Kümmel, S.; Kronik, L. Orbital-Dependent Density Functionals: Theory and Applications. Rev. Mod. Phys. 2008, 80, 3–60. Baer, R.; Livshits, E.; Salzner, U. Tuned Range-Separated Hybrids in Density Functional Theory. Annu. Rev. Phys. Chem. 2010, 61, 85–109.

(30) Baer, R.; Neuhauser, D. Density Functional Theory with Correct Long-Range Asymptotic Behavior. *Phys. Rev. Lett.* **2005**, *94*, 043002.

(31) Stein, T.; Eisenberg, H.; Kronik, L.; Baer, R. Fundamental Gaps in Finite Systems from Eigenvalues of a Generalized Kohn-Sham Method. *Phys. Rev. Lett.* **2010**, *105*, 266802.

(32) Eisenberg, H. R.; Baer, R. A New Generalized Kohn-Sham Method for Fundamental Band-Gaps in Solids. *Phys. Chem. Chem. Phys.* 2009, 11, 4674–4680.

(33) Dion, M.; Rydberg, H.; Schröder, E.; Langreth, D. C.; Lundqvist, B. I. Van der Waals Density Functional for General Geometries. *Phys. Rev. Lett.* 2004, 92, 246401. Thonhauser, T.; Cooper, V. R.; Li, S.; Puzder, A.; Hyldgaard, P.; Langreth, D. C. Van der Waals Density Functional: Self-Consistent Potential and the Nature of the Van der Waals Bond. *Phys. Rev. B* 2007, 76, 125112. Román-Pérez, G.; Soler, J. M. Efficient Implementation of a Van der Waals Density Functional: Application to Double-Wall Carbon Nanotubes. *Phys. Rev. Lett.* 2009, 103, 096102.

(34) Zhang, Y.; Yang, W. Comment on Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1998**, *80*, 890.

(35) Chase, M. W., Jr; Davies, C. A.; Downey, J. R., Jr; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. JANAF Thermochemical Tables. J. Phys. Chem. Ref. Data **1985**, 14 (Suppl. 1), 571.

(36) Mills, G.; Jónsson, H. Quantum and Thermal Effects in H_2 Dissociative Adsorption: Evaluation of Free Energy Barriers in Multidimensional Quantum Systems. *Phys. Rev. Lett.* **1994**, *72*, 1124–1127. Mills, G.; Jónsson, H.; Schenter, G. K. Reversible Work Transition State Theory: Application to Dissociative Adsorption of Hydrogen. *Surf. Sci.* **1995**, *324*, 305–337.

(37) Note that when the system is in the minimum energy configuration M, following hydrogen abstraction, the methyl carbon atom is 3.35 Å from the O(1) oxygen atom to which H is bound, 2.38 Å from the binding hydrogen atom, and 4.35 Å away from the adjacent O(3) atom to which it will bind.

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